A Mechanistic Study into the Reaction Between Carbon Dioxide and Amines

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Signature: ................................................................. Date: ..............................................
To

My Family and Dale for all your love, support, encouragement and understanding.
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<th>Full Form</th>
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<tr>
<td>$^1$H NMR</td>
<td>Hydrogen NMR</td>
</tr>
<tr>
<td>1-HP</td>
<td>$N$-Hydroxypiperidine</td>
</tr>
<tr>
<td>1-MP</td>
<td>$N$-Methylpiperidine</td>
</tr>
<tr>
<td>1-PE</td>
<td>$N$-Hydroxyethylpiperidine</td>
</tr>
<tr>
<td>2, 5-DMPZ</td>
<td>2, 5-Dimethylpiperazine</td>
</tr>
<tr>
<td>2, 6-DMPZ</td>
<td>2, 6-Dimethylpiperazine</td>
</tr>
<tr>
<td>2-MP</td>
<td>2-Methylpiperidine</td>
</tr>
<tr>
<td>2-PE</td>
<td>2-(2-hydroxyethyl)piperidine</td>
</tr>
<tr>
<td>2-PM</td>
<td>2-(hydroxymethyl)piperidine</td>
</tr>
<tr>
<td>3-HP</td>
<td>3-Hydroxypiperidine</td>
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<tr>
<td>3-MP</td>
<td>3- Methylpiperidine</td>
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<td>3-PM</td>
<td>3-(hydroxymethyl)piperidine</td>
</tr>
<tr>
<td>4-HP</td>
<td>4-Hydroxypiperidine</td>
</tr>
<tr>
<td>4-MP</td>
<td>4- Methylpiperidine</td>
</tr>
<tr>
<td>4-PE</td>
<td>4-(2-hydroxyethyl)piperidine</td>
</tr>
<tr>
<td>4-PM</td>
<td>4-(hydroxymethyl)piperidine</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>Carbon NMR</td>
</tr>
<tr>
<td>AMP</td>
<td>2-Amino-2-methyl-1-propanol</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>B3LYP</td>
<td>DFT hybrid functional</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$C_A$</td>
<td>CO$_2$ absorption capacity (mol CO$_2$ / mol amine)</td>
</tr>
<tr>
<td>$Ca$</td>
<td>Alpha carbon</td>
</tr>
<tr>
<td>CID</td>
<td>Collision-induced dissociation</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>COO$^-$</td>
<td>Carboxylate functional group</td>
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<tr>
<td>DAP</td>
<td>1, 3-Diaminopropane</td>
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<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMHHPY</td>
<td>2, 2-Dimethylhexahydropyrimidine</td>
</tr>
<tr>
<td>ESI</td>
<td>Electro-spray ionization</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic Potential</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>H$^+$</td>
<td>Protonated</td>
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<td>Water</td>
</tr>
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<td>Bicarbonate ion</td>
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<tr>
<td>HHPY</td>
<td>Hexahydopyrimidine</td>
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<tr>
<td>HHPZ</td>
<td>Hexahydropyridazine</td>
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<tr>
<td>K$_2$CO$_3$</td>
<td>Potassium Carbonate</td>
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<tr>
<td>$K_g$</td>
<td>Overall mass transfer coefficient (mol/s cm$^2$ Pa), measured using WWC</td>
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<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
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<tr>
<td>MDEA</td>
<td>Methyldiethanolamine</td>
</tr>
<tr>
<td>MHHPY</td>
<td>2-Methylhexahydropyrimidine</td>
</tr>
<tr>
<td>MP2</td>
<td>Moller-Plesset second-order</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>Sodium bicarbonate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>PCC</td>
<td>Post Combustion Capture</td>
</tr>
<tr>
<td>PZ</td>
<td>Piperazine</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxide ion</td>
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<tr>
<td>$R_{IA}$</td>
<td>Initial absorption rate (mol CO$_2$ / mol amine, min$^{-1}$), measured using TGA</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>$\nu_{asCOO^-}$</td>
<td>Infrared vibrational mode - asymmetric COO$^-$ stretch</td>
</tr>
<tr>
<td>$\nu_{C-N-C}$</td>
<td>Infrared vibrational mode - C-N-C stretching vibration</td>
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<td>$\nu_{N-COO^-}$</td>
<td>Infrared vibrational mode - N-COO$^-$ stretching vibration</td>
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<tr>
<td>$\nu_{sCOO^-}$</td>
<td>Infrared vibrational mode - Symmetric COO$^-$ stretch</td>
</tr>
<tr>
<td>$\nu_{sC-O^-}$</td>
<td>Infrared vibrational mode - Symmetric C-O$^-$ stretch</td>
</tr>
<tr>
<td>WWC</td>
<td>Wetted wall column</td>
</tr>
</tbody>
</table>
Abstract

The increasing level of atmospheric CO$_2$ has been attributed to anthropogenic emissions from fossil fuel combustion and industrial processes. At present, post combustion CO$_2$ capture (PCC) from coal-fired power stations, using aqueous amine-based absorbents, is considered the most mature technology for reducing CO$_2$ emissions in the short term.

The economics and feasibility of this technology is highly dependent on several factors, in particularly the absorbents capacity to absorb CO$_2$, the rate of absorption and the energy required for absorbent regeneration. To reduce the high energy requirements and cost of the process most research and development efforts have focused on the development of more cost effective and superior performing amines.

While the CO$_2$ absorption rate and capacity of absorbents are important performance indicators in determining absorbent efficiency, another important aspect of CO$_2$/amine capture chemistry is the lability of the carbamate species formed and its susceptibility to hydrolysis and subsequent bicarbonate formation. Increased bicarbonate formation is associated with increased absorption capacities and a lower heat of regeneration. Amine structure will determine carbamate lability and thus susceptibility to hydrolysis. The molecular properties that give rise to enhanced CO$_2$ absorption characteristics are still not yet fully understood.

In this study the amine and carbamate properties that confer enhanced CO$_2$ absorption capacities, rates and carbamate lability has been investigated. This has been achieved using Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) spectroscopy to follow in situ the chemical reactions occurring between CO$_2$ and a series of heterocyclic monoamines and novel diamines.

The monoamines investigated included piperidine and a series of commercially available functionalised piperidine derivatives, e.g. those with methyl-, hydroxyl- and hydroxyalkyl-substituents. The diamines investigated included novel hexahydropyrimidine (HHPY), methyl
hexahydropyrimidines (MHHPY and DMHHPY) and hexahydropridazine (HHPZ); piperazine (PZ), and 2,6- and 2,5- dimethyl piperazines (2,6-DMPZ and 2,5-DMPZ).

The effect of structure on CO₂ / amine reactivity was assessed according to a correlation between the infrared active ionic reaction products (carbamate, bicarbonate and protonated amine) and cumulative CO₂ absorption; CO₂ absorption capacity; initial rate of CO₂ absorption; and a correlation between the atomic properties of the amine and carbamate derivative with the infrared spectral data, CO₂ absorption capacity and initial absorption rate. Calculations using B3LYP / 6-31+G** and MP2 / 6-31+G** were performed to investigate the atomic properties of the amines and carbamate derivative. The N-COO⁻ carbamate bond and resonance structure of the carboxylate moiety were analysed.

Knowledge of carbamate / bicarbonate speciation during the absorption process enabled the observation of reaction mechanisms as well as the determination of carbamate lability in the studied amine / CO₂ / H₂O systems. We report on the first real-time observation of carbamate hydrolysis in secondary amine absorbent systems.

For the monoamines analysed the formation of the carbamate derivatives of the 3- and 4- hydroxy, 3- and 4- hydroxymethyl, and 4-hydroxyethyl substituted piperidines were found to be kinetically less favourable than the carbamate derivatives of piperidine and the 3- and 4- methyl substituted piperidines. As the CO₂ loading of piperidine and the 3- and 4- methyl and hydroxyalkyl substituted piperidines exceeded 0.5 mol CO₂ / mol amine, the hydrolysis of the carbamate derivative of these amines was observed. Piperidine and its 3- and 4- alkyl and hydroxyalkyl substituted analogues were found to display enhanced CO₂ absorption capacities and rates compared to that of their acyclic counterpart’s monoethanolamine (MEA) and diethanolamine (DEA). These amines were also found to form a more hydrolytically labile carbamate derivative at high CO₂ loadings (≥ 0.5 mol CO₂ / mol amine).

The 2- alkyl and hydroxyalkyl substituted piperidines were found to favour bicarbonate formation in the reaction with CO₂. For the first time, the ability of these amines to form a carbamate on absorption of CO₂, one that is inherently susceptible to hydrolysis in an aqueous environment was observed. Theoretical analysis for the 2- alkyl and hydroxyalkyl substituted piperidines suggest that a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area on the nitrogen atom both play a role in destabilising the carbamate derivative and increasing its susceptibility to hydrolysis. The contribution of each is dependent on the type and size of the substituent present. The structure of the carbamate derivatives of these amines revealed shorter N-COO⁻ bond lengths and a less delocalised electron distribution in the carboxylate moiety.
For the diamines analysed PZ was found to form a hydrolysis resistant carbamate derivative, while HHPY formed a more labile carbamate species with an increased susceptibility to hydrolysis particularly at higher CO$_2$ loadings (>0.5 moles of CO$_2$ per mole of amine). HHPY exhibited similar reactivity toward CO$_2$ as PZ, but with improved aqueous solubility. The α-methyl substituted MHHPY favoured bicarbonate formation, but MHHPY exhibited a comparable CO$_2$ absorption rate compared with conventional amines MEA and DEA. MHHPY showed improved reactivity compared to the conventional α-methyl substituted primary amine 2-amino-2-methyl-1-propanol (AMP). HHPZ was relatively non-reactive towards CO$_2$.

DMHHPY was representative of a blended amine system and its reactivity highlighted the advantages of such a system. 1, 3-dimainopropane (DAP) is the starting material in the synthesis of DMHHPY and was carried through to the final product resulting in a DMHHPY / DAP blended amine system. PZ / AMP and piperidine / AMP blended amine systems were also investigated. The results highlighted the superior performance of PZ as an absorption accelerator in blended amine systems, as opposed to a sole CO$_2$ capture absorbent. The diamine nature of PZ and its hydrolysis resistant carbamate derivative both contribute to this enhanced performance. The B3LYP / 6-31+G** and MP2 / 6-31+G** calculations showed the positions of the heterocyclic diamines affected carbamate stability, which influenced hydrolysis rates.
1 Introduction

1.1 Post Combustion CO₂ Capture

Post Combustion Capture (PCC) of carbon dioxide (CO₂) generated from coal-fired power stations has been identified as a crucial part of the global solution to climate change. Carbon dioxide capture has become a major target for emission reduction strategies due to the rapidly increasing levels of atmospheric CO₂. The dominant driving force is anthropogenic CO₂ emissions from fossil fuel combustion and industrial processes.\textsuperscript{[1, 2]}

Coal-fired power stations play a vital role in meeting Australia’s energy demand, however they are the largest point source emitters of CO₂ in Australia and worldwide.\textsuperscript{[3]} While it is clear that any significant reduction in Australia’s long-term greenhouse gas emissions must involve changing our approach to energy production and consumption, technologies such as PCC are required to reduce CO₂ levels in the short term. The prospect of integrating PCC in both existing and new coal-fired power stations offers the potential to lower CO₂ emissions in the face of existing and predicted growth in the number of coal-fired power stations.\textsuperscript{[4]}

There are a number of prospective PCC technologies being investigated for the separation of CO₂ from flue gas streams. These include:\textsuperscript{[5]}

i. Adsorption of CO₂ onto solid surfaces such as activated carbon, alumina, metallic oxides and zeolites.

ii. Physical absorption of CO₂ into a solvent such as ionic liquids, methanol and Selexol (dimethyl ethers of polyethylene glycol).

iii. Chemical absorption of CO₂ into an absorbent such as aqueous amines and aqueous potassium carbonate.

iv. Membrane-based separation.
Adsorption, physical absorption and membrane-based separation offer a much lower selectivity for CO₂ compared to chemical absorption. This reduces their economic feasibility and applicability to flue gas streams from coal-fired power stations, which have a low CO₂ concentration (typical partial pressures of 12-15 %[6]). These technologies are more suited to processes that generate flue gas with a much higher CO₂ partial pressure, such as oxyfuel and integrated gasification combined cycle (IGCC) processes.[5] The most effective method to remove CO₂ from the flue gas of a coal-fired power station is by chemical reaction with a liquid absorbent.

At present, aqueous amine-based PCC systems are viewed as the most promising available technology for reducing CO₂ emissions from coal-fired power stations, despite the fact that there has been no full scale proof-of-concept demonstration to date.[7] The PCC process involves separating CO₂ from other gases by reactive chemical absorption and re-releasing CO₂ from the absorbent by heating in a two-step process. The end product is a relatively pure CO₂ gas stream that is suitable for compression and storage or industrial use.[8, 9] This method is industrially proven for absorbents such as aqueous monoethanolamine (MEA) and has been used for decades to remove CO₂ from gas streams in small-scale commercial processes such as natural gas processing and in the production of ammonia, hydrogen and ethanol.[6, 10]

Over the past few years there has been significant progress in the design and operation of CO₂ capture pilot plants, with numerous research groups (Mitsubishi Heavy Industries (MHI), CSIRO, International Test Centre (ITC) for CO₂ capture, University of Texas, CASTOR) establishing power station based pilot plants across Australia and worldwide.[5, 11] ITC has established a fully operating semi-commercial demonstration plant that is at present capturing 4 tonnes of CO₂ per day from the flue gas stream of one unit (139 MW) of the Boundary Dam power station (875 MW) in Canada.[5, 12]

The major challenge leading up to the deployment of aqueous amine-based PCC on a large scale is adapting the existing technology to suit conditions matching that of a flue gas stream from a coal-fired power plant. As mentioned previously, CO₂ is present in flue gas at dilute concentrations and low partial pressures (±1 bar), which dictates that a high volume of gas be treated.[7] Australian coal-fired power plants do not have flue gas desulphurisation or selective catalytic reduction for the removal of oxides of sulphur (SOₓ) or nitrogen (NOₓ) respectively. The presence of these acid gases causes the formation of heat stable salts and degradation of the amine-based absorbent.[13] The NOₓ and SOₓ levels experienced in an Australian flue gas are typically around 190 ppm and 200 ppm respectively.[14] A typical flue gas composition for a black and brown coal combustion power plant is provided in Table 1-1.
Table 1-1. Typical flue gas composition for a black and brown coal combustion plant.\cite{3, 14}

<table>
<thead>
<tr>
<th>Flue Gas Component</th>
<th>Black Coal (% vol)</th>
<th>Brown Coal (% vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>71%</td>
<td>61%</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>12.6%</td>
<td>12%</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>11.1%</td>
<td>24%</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>3-5%</td>
<td>3-5%</td>
</tr>
</tbody>
</table>

Under these conditions and at high volume gas flows, there are a number of practical problems associated with the use of conventional absorbents, such as MEA, to capture CO\textsubscript{2}. These problems include:\cite{15}

i. A high energy input required for regeneration of the amine at high temperatures (> 100 °C);

ii. A high rate of corrosion of the process equipment;

iii. A high volatility causing absorbent loss;

iv. A high rate of amine degradation in the presence of oxygen;

v. Precipitation of heat stable salts.

All of the above factors have the potential to reduce the efficiency of the separation process and translate into a high energy and cost penalty for large-scale application of PCC.\cite{8, 15}

Research and development programs are underway worldwide to reduce the cost and energy requirements of the PCC process.\cite{5, 6} One approach to reducing the energy requirements and cost of the process is through the development of more cost effective and superior performing amines. There is considerable scope to develop absorbents that demonstrate a higher reactivity for CO\textsubscript{2}, lower energy requirements for regeneration and a greater chemical stability, particularly in the face of an increasing move towards demonstration scale PCC plants.
1. Introduction

1.2  Aqueous Amine-Based Post Combustion Capture

1.2.1  The Cyclic Absorption / Desorption Process

The principle process governing amine-based PCC is the cyclic absorption / desorption of CO\textsubscript{2} by an aqueous amine solution, as shown in Figure 1-1.

![Flow diagram of the principle process governing the removal of CO\textsubscript{2} from flue gas by an aqueous amine solution.](image)

The two main components of the process design are two columns, an absorber and a stripper. Since flue gas is ejected post-boiler at a temperature of $\geq 120$ °C, it is first cooled to a temperature range of 40-55 °C. The flue gas is then fed into the absorber column, which is operated at around 40 °C, where the CO\textsubscript{2} is counter-currently contacted with an aqueous amine solution and absorbed via a fast chemical reaction. The CO\textsubscript{2}-free flue gas exits the top of the absorber, while the amine solution is pumped to the stripper column through a cross-heat exchanger, where it is pre-heated by the hot lean solution from the stripper bottom.$^{[16]}$ The
stripper column is operated at a temperature of 100-120°C to reverse the absorption reaction and liberate the CO$_2$, regenerating the amine absorbent. The liberation of CO$_2$ is an endothermic reaction that consumes energy, so sufficient energy (or heat) must be provided to reverse the chemical reaction and break up the CO$_2$-amine complex formed during absorption. The gas stream containing the liberated CO$_2$ exits the top of the stripper, where any volatilised absorbent is condensed and returned as reflux to the top stage of the stripper. The hot lean amine solution exiting the bottom of the stripper is pumped through the cross-heat exchanger and cooled, before being returned to the absorber for re-absorption.$^{[16]}$

Because Australian coal-fired power plants do not remove SO$_x$ and NO$_x$ from flue gas, it can be incorporated in the absorption / stripping process, so that prior to the removal of CO$_2$, SO$_x$ and NO$_x$ are removed from the flue gas stream.

Deployment of current industry standard technology (30 wt % aqueous MEA) on a large scale applies a considerable efficiency penalty to the power generation process. Because PCC absorbent regeneration is energy intensive,$^{[5]}$ it will result in a 25-30 % reduction in the net efficiency of a coal-fired power plant.$^{[17, 18]}$ For instance, the Boundary Dam PCC plant (Canada) is reported to reduce the power stations generating capacity for one unit from 139 MW to 100 MW,$^{[12]}$ using a proprietary absorbent system (Fluor’s Econamine FG$^{SM}$ Technology)$^{[5]}$.

Clearly, the economics and feasibility of the technology is largely dependent on the absorbent system, in particularly its capacity to absorb CO$_2$, how fast it can absorb CO$_2$ (rate) and the energy required (heat supplied) to re-release the CO$_2$ and regenerate the absorbent. Lower capital and operational costs are associated with higher capacities and absorption rates and smaller energy requirements. The key to better process economics lies within solvent development and finding highly efficient absorbents, tailored for post-combustion capture.$^{[9]}$

1.2.2 Conventional Amine-Based Absorbents

Conventional amines used in the absorption / desorption of CO$_2$ from flue gas streams fall within three classes: primary ($R'\text{NH}_2$), secondary ($R'R''\text{NH}$) and tertiary amines ($R'R'R''\text{N}$), classified according to the number of organic substituent’s attached to the nitrogen atom.$^{[19]}$ Some industrially important amines$^{[20]}$ are presented in Figure 1-2.
1. Introduction

Primary Amines

\[
\text{H}_2\text{N} - \text{OH} \quad \text{H}_2\text{N} - \text{OH} \quad \text{H}_2\text{N} - \text{O} - \text{OH}
\]

monoethanolamine (MEA) \hspace{1cm} 2-amino-2-methyl-1-propanol (AMP) \hspace{1cm} diglycolamine (DGA)

Secondary Amines

\[
\begin{align*}
\text{HO} & - \text{N} - \text{OH} \\
\text{HO} & - \text{N} - \text{OH}
\end{align*}
\]

diethanolamine (DEA) \hspace{1cm} diisopropanolamine (DIPA)

\[
\begin{align*}
\text{HN} & - \text{N} - \text{NH} \\
\text{HN} & - \text{N} - \text{NH}
\end{align*}
\]

piperidine \hspace{1cm} piperazine (PZ) \hspace{1cm} 2-piperidinethanol (2-PE)

Tertiary Amines

\[
\begin{align*}
\text{HO} & - \text{N} - \text{OH} \\
\text{HO} & - \text{N} - \text{OH}
\end{align*}
\]

triethanolamine (TEA) \hspace{1cm} methyldiethanolamine (MDEA)

Figure 1-2. The structure of primary, secondary and tertiary amines. AMP and 2-PE are examples of a “sterically-hindered” primary and secondary amine respectively.

1.2.2.1 Primary, Secondary and Tertiary Amines

Generally, primary and secondary amines react with CO\(_2\) to form carbamates. They exhibit faster reaction rates in the absorption of CO\(_2\), compared to tertiary amines. However, a higher heat of reaction is also associated with carbamate formation, meaning a larger input of energy is required for regeneration. The opposite trend is observed for tertiary amines, which exhibit slow
reaction rates, but are much more easily regenerated, requiring a smaller input of energy.\textsuperscript{[9]} \(\text{CO}_2\) absorption by tertiary amines occurs via bicarbonate formation. The reaction mechanism by which primary, secondary and tertiary amines react with \(\text{CO}_2\) is further discussed below in Section 1.4.

### 1.2.2.2 Sterically-Hindered Amines

Another class of amines that have evolved as potential absorbents for the capture of \(\text{CO}_2\) and have received considerable attention are known as the “sterically-hindered” amines. The common structural feature of the amines that fall within this class is the presence of one or more alkyl substituents on the carbon alpha (C\(\alpha\)) to the amine group. These amines have been found to form mostly bicarbonate on absorption of \(\text{CO}_2\) and exhibit higher \(\text{CO}_2\) loading capacities and comparable absorption rates\textsuperscript{[21]} to their unhindered primary or secondary counterparts, as well as a lower regeneration cost.\textsuperscript{[20]} The examples of sterically-hindered amines provided in Figure 1-2 include the primary amine 2-amino-2-methyl-1-propanol (AMP), which has two methyl substituents on C\(\alpha\) and whose un-substituted primary counterpart is MEA; and the secondary heterocyclic amine 2-piperidinethanol (2-PE), which has a hydroxyethyl substituent on C\(\alpha\) and whose un-substituted secondary counterpart is piperidine.\textsuperscript{[8, 16, 20, 22]} Another cyclic amine that has received considerable attention is the secondary diamine piperazine (PZ), which can be used as an additive for tertiary amines to form amine blends. The piperazine functions to enhance the rate of absorption of \(\text{CO}_2\), whilst maintaining the low heat of regeneration and higher absorption capacity of the tertiary amine.\textsuperscript{[20]}

### 1.3 Monoethanolamine

MEA being a conventional absorbent is widely used and offers a number of advantages over other commercial amines. Also as the most extensively studied amine it is relatively well characterised with respect to its interaction with \(\text{CO}_2\). For these reasons MEA has become a benchmark against which novel amines are compared. Currently only a select few proprietary formulations are available from international commercial suppliers such as Fluor\textsuperscript{[23]}, BASF\textsuperscript{[24]} and MHI\textsuperscript{[25]}, for which they claim improved PCC performance characteristics compared to MEA.

MEA is a relatively cheap absorbent and has a high reactivity for \(\text{CO}_2\), with a fast reaction rate and low molecular weight, providing for a high absorbing capacity on a mass basis. Other
advantages of MEA include a reasonable thermal stability and slow thermal degradation rate.\textsuperscript{[26]} Despite these favourable absorption characteristics there are a number of disadvantages associated with MEA and considerable scope for improvement.

Associated with MEA’s rapid reaction with CO\textsubscript{2} is a high heat of reaction and the formation of a very stable carbamate. Both of these characteristics contribute to a high energy requirement for absorbent regeneration.\textsuperscript{[26]}

In the absorption of CO\textsubscript{2} two molecules of MEA reacts with one molecule of CO\textsubscript{2} limiting the loading capacity of MEA to a hypothetical upper limit of 0.5 mol CO\textsubscript{2} / mol amine (Section 1.4.2).\textsuperscript{[26]}

In the presence of oxygen-bearing flue gas MEA undergoes oxidative degradation, contributing to amine loss during the cyclic absorption / desorption process; and at the high temperatures used in the stripper, there is also some amine loss due to the volatility of MEA and a high corrosive potential.\textsuperscript{[26]}

For an absorbent to prevail as an ideal energy efficient commercial absorbent for the removal of CO\textsubscript{2}, several performance criteria must be satisfied. These include:\textsuperscript{[15, 26]}

\begin{enumerate}
\item High absorption capacity
\item High reaction rate for CO\textsubscript{2}
\item Low regeneration energy
\item High resistance to degradation (oxidative and thermal)
\item Low vapour pressure
\item Low corrosiveness.
\end{enumerate}

The general trend with the amines that have been previously or are currently being studied is that they show favourable characteristics with respect to one criterion but are deficient in another. For instance, an absorbent that has superior absorption properties, which may be characterised by a high forward reaction rate or high absorption capacity, may not have similar stripping characteristics. Because CO\textsubscript{2} absorption by amines involves mass transfer with chemical reaction, the higher the reaction rate, the greater the mass transfer coefficient. This reduces the required contacting surface area, which leads to a smaller absorber and reduced capital costs. However, also associated with this higher reactivity for CO\textsubscript{2} is a higher heat of reaction, meaning a larger input of energy is required for regeneration of the absorbent. The reverse is also true, with the more easily regenerated absorbents tending to exhibit slower
reaction rates and requiring a larger contacting surface area in the absorber. Similarly, an absorbent possessing a higher loading capacity may have inferior mass transfer properties. \textsuperscript{[15, 26]}

The design of the ideal absorbent involves the development of each distinct property contributing to the absorption / desorption process and formulating it into a single absorbent, which may consist of a single superior amine or a blend of amines, each contributing a desired characteristic.

In addressing the issues of corrosion and solvent degradation (thermal and oxidative degradation), significant efforts are being made worldwide in the development of inhibitors and new process configurations to reduce the impact of the flue gas contaminants O\textsubscript{2}, SO\textsubscript{x} and NO\textsubscript{x}, such as:\textsuperscript{[27-30]}

i. Development of additives that minimise corrosion;

ii. Development of free radical scavengers to reduce oxidative degradation;

iii. The inclusion of an upstream alkaline scrubber to remove SO\textsubscript{x} from the fed flue gas prior to entering the absorber column;

iv. Operating the stripper column at temperatures ≤ 100 °C to minimise thermal degradation; and

v. Inclusion of a water wash section at the top of the absorber column to minimise volatile amine emissions in the scrubbed flue gas.

1.4 The Reaction between Carbon Dioxide and Aqueous Amines

1.4.1 General Overview

When CO\textsubscript{2} reacts with amines in aqueous solution carbamate, bicarbonate and protonated amine (R'R"NH\textsuperscript{+}) are generated. A small concentration of free CO\textsubscript{2} will also be present in solution.\textsuperscript{[31]} The degree of carbamate versus bicarbonate formation will impact on the CO\textsubscript{2} absorption capacity, absorption rate and regeneration energy of the amine-based absorbent. Amines that form a stable carbamate tend to exhibit faster reaction rates, however their absorption capacity is limited by the extent to which carbamate formation is kinetically favoured and a larger input of energy is required for regeneration. On the other hand, amines
that form more bicarbonate than carbamate exhibit higher absorption capacities and require less energy for regeneration.

1.4.2 Reaction Mechanism of Primary and Secondary Amines

As mentioned previously, primary and secondary amines typically react rapidly with CO$_2$ in an aqueous environment to form a carbamate (R'R"N-COO$^-$), as shown in Scheme 1-1. This is a two-step mechanism that proceeds by the formation of the intermediate carboxamic acid (1) (a carboxylic acid derivative) followed by rapid deprotonation to the carbamate species (2) (a carboxylate moiety).\[32\] The deprotonation requires a Lewis base ‘B’, which is typically a molecule of amine, though water can also accept the proton. This means that two molecules of amine react with one molecule of CO$_2$, limiting the absorption capacity of a primary and secondary amines to a hypothetical upper limit of 0.5 mole of CO$_2$ per mole of amine (mol CO$_2$ / mol amine).\[20\]

\[
\begin{align*}
R'\text{NH} + \text{CO}_2 + B & \rightleftharpoons R'\text{N} \text{COOH} \rightleftharpoons R'\text{NCOO}^- + \text{BH}^+ \\
& \rightleftharpoons R'\text{NH} + \text{HO}_2\text{COO}^-
\end{align*}
\]

Scheme 1-1. Reaction mechanism leading to carbamate formation (2) for the reaction of CO$_2$ with primary and secondary amines. Base ‘B’ is typically a second amine molecule.

The carbamate species (2) has been reported to undergo hydrolysis to produce bicarbonate (HCO$_3^-$) (3) and regenerate a free amine\[20, 33-35\] as shown in Scheme 1-1. However it has yet to be directly observed. The observation of improved absorption capacities, beyond the theoretical
upper limit of 0.5 mol CO$_2$ / mol amine, and bicarbonate formation can be attributed to carbamate hydrolysis. Given the stability of the carbamate formed from primary and secondary amines hydrolysis does not occur at a readily appreciable rate.$^{[33]}$ A certain amount of carbamate hydrolysis, as well as CO$_2$ hydrolysis, is anticipated to occur with most amines, so that even with MEA and diethanolamine (DEA), two amines known to form stable carbamates, the loading will always exceed 0.5 mol CO$_2$ / mol amine. The degree of carbamate hydrolysis is determined by parameters such as pH, alkanolamine concentration and the chemical stability of the carbamate.$^{[36]}$

An alternate mechanism for carbamate formation that is widely cited in the scientific literature is the “zwitterion mechanism”.$^{[20, 32, 37-42]}$ The concept, first suggested by Caplow$^{[43]}$ and latter reintroduced by Danckwerts,$^{[44]}$ postulates a two-step reaction mechanism that proceeds by the formation of an ion pair intermediate $R_1R_2\text{-NH}_2^+$COO$^-$. The ion pair undergoes a base ($R_1R_2\text{-NH}_2$ or $H_2O$) catalysed deprotonation to form the carbamate derivative. While it is a widely cited reaction mechanism there is neither theoretical$^{[45]}$ nor experimental$^{[46]}$ studies to date that can support the formation of a zwitterionic species. The proton transfer that occurs is virtually instantaneous in aqueous solutions.$^{[20]}$ Such a zwitterion intermediate would most likely be unstable and have an extremely short lifetime, or not exist at all.$^{[45, 47]}$

### 1.4.3 Reaction Mechanism of Tertiary Amines

Tertiary amines, such as triethanolamine (TEA) and methyldiethanolamine (MDEA) (Figure 1-2), do not react directly with CO$_2$ to form the carbamate species, as in the case of primary and secondary amines. The lack of a free proton on the nitrogen atom of these amines inhibits the carbamate formation and generally results in a low reactivity with CO$_2$.$^{[20, 38, 48]}$ Instead, tertiary amines are thought to behave as a catalyst, facilitating the CO$_2$ hydrolysis reaction to form bicarbonate.$^{[20, 38, 49]}$ The bicarbonate pathway permits for higher CO$_2$ absorption capacities, with the stoichiometry of the reaction being 1 mol CO$_2$ / mol amine.

Donaldson and Nguyen$^{[49]}$ proposed a reaction mechanism whereby free amine forms hydrogen bonds with water, as shown in Scheme 1-2. This interaction involves the lone-pair of electrons on the nitrogen atom enhancing the reactivity between H$_2$O and CO$_2$.$^{[50]}$ In the case of MDEA, previous studies have reported that in the absence of water there is no reaction with CO$_2$.}$^{[51]}$
Scheme 1-2. The base-catalysed reaction mechanism, governing the interaction between tertiary alkanolamines and CO$_2$, to form bicarbonate.$^{[49, 52]}$

Since the heat of reaction associated with bicarbonate formation is lower than that associated with carbamate formation, tertiary amines are much more easily regenerated compared to primary and secondary amines.$^{[20, 38]}$ Tertiary amines have also been shown to lose less of their absorption capacity after regeneration than the primary amines,$^{[38]}$ providing for lower absorbent costs. Despite the advantages of higher loading capacities and relative ease of solvent regeneration associated with tertiary amines, the low reaction rate for CO$_2$ absorption limits their use.$^{[21]}$

### 1.5 The Relationship between Reactivity and Structure

The scientific literature on CO$_2$ absorption by aqueous amines clearly establishes that a definite relationship exists between the structure of amines and their reactivity towards CO$_2$.$^{[21, 36, 38, 48, 53]}$ The molecular structure of conventional absorbents, such as the primary and secondary amines MEA and DEA respectively, allow for the formation of stable carbamate derivatives. With the formation of a stable carbamate there is an underlying assumption that the forward rate of reaction increases proportionally with increasing stability of the carbamate species.$^{[52]}$ However a larger input of energy is required for regeneration given the kinetic stability of the carbamate formed, and thus higher regeneration costs.$^{[20]}$ The stability of the carbamate can be accounted for by a number of factors, including.$^{[52]}$

i. Stability through bonds by electron donation and withdrawal effects;

ii. Steric effects;

iii. Intramolecular hydrogen bonding; and

iv. Solvent stabilisation.
1.5.1 Amines with Substitution at the Alpha Carbon

Amines with one or more alkyl substituents at the α-carbon (Cα) (termed “sterically-hindered” amines in industry parlance), such as the dimethyl substituted AMP, are characterised as forming carbamates of low stability with bicarbonate being the sole product of CO₂ absorption.⁴¹ Based on ¹³C NMR data, Chakraborty et al.⁵⁴ first reported that the carbamate of AMP is formed to a much lesser extent than the carbamate of its non-substituted counterpart MEA, with bicarbonate being the sole reaction product. The aforementioned carbamate stability has been and remains to be largely assessed in relation to speciation and the degree of carbamate formation versus bicarbonate formation.⁴¹, ³⁵, ³⁶, ⁵⁴, ⁵⁷, ⁵⁸

The increase in bicarbonate formation exhibited by Cα-substituted amines allow for higher CO₂ loadings than that attainable with their non-substituted counterparts.⁴⁰, ⁴¹, ⁵⁴ An additional advantage of these amines, is that the heat of reaction associated with bicarbonate formation is lower than that of carbamate formation, thus reducing absorbent regeneration energies.⁴⁰

There is an inconsistency in the literature on whether or not Cα-substituted amines do form a carbamate species, one that is inherently susceptible to hydrolysis and subsequent bicarbonate formation.⁵⁴, ⁵⁹, ⁶⁰

Recently, Ismael et al.⁶⁰ examined the mechanism of carbamate formation by the absorption of CO₂ in AMP using DFT calculations. Ismael et al.⁶⁰ suggested that it was kinetically unfavourable for AMP to form a carbamate in the reaction with CO₂, suggesting that the reaction proceeds directly to bicarbonate formation via an OH⁻ catalysis mechanism, similar to that observed in the case of tertiary amines. Tertiary amines are considered the ultimate sterically-hindered amine.

Until recently, there has been no direct observation of the carbamate species of “sterically-hindered” amines. Jackson et al.,⁵⁴ is the first study to observe these allusive anions. The direct observation of the carbamate derivatives of the Cα-substituted amines AMP and tris(hydroxymethyl)amino methane (THAM) were reported. Negative-ion electrospray ionization mass spectrometry (ESI-MS) was used to analyse for the carbamate derivatives of these amines, which were formed as result of the reaction with sodium bicarbonate (NaHCO₃) in aqueous solution. The results obtained provided evidence of the existence of Cα-substituted carbamate anions. However, it has still not been established whether they form directly via the reaction with CO₂ or bicarbonate during the absorption process.

The effect of Cα-substituents, such as that in AMP, on carbamate stability can manifest itself through either steric constraints on the amino nitrogen and / or by inducing a change in the
electronic environment of the amino nitrogen. However, current explanations for the variation in reactivity towards CO$_2$ between structurally different amines tend to focus solely on the concept of steric constraints.$^{[20, 21, 36, 48, 52-54, 56]}$ With increasing steric crowding around the amino nitrogen there is a subsequent increase in bicarbonate formation and hence decrease in carbamate stability. Both electronic and steric modifications will affect amine reactivity towards CO$_2$. This will be either by inducing a kinetic constraint along the carbamate reaction pathway, similar to that of tertiary amines, or by reducing the nucleophilicity of the amino nitrogen towards CO$_2$ and subsequently increasing the susceptibility of the resultant carbamate derivative to hydrolysis.

Based on molecular orbital arguments and computational calculations, Chakroborty et al.$^{[19]}$ reported that the dimethyl C$\alpha$-substituent in AMP reduced the negative charge at the nitrogen donor site by 3.4%, compared to its non-hindered counterpart MEA. Furthermore, Chakroborty et al.$^{[19]}$ proposed that this change in the electronic environment of the amino nitrogen reduced the amine’s basic strength, weakening the bonding interaction with CO$_2$ and thus generating an unstable carbamate derivative, inherently more susceptible to hydrolysis. There have been no further studies expanding on these findings, particularly with respect to the steric / electronic effect of substituents larger than a methyl group.

1.5.2 Heterocyclic Amines

Recently heterocyclic amines such as piperazine (PZ) and piperidine (Figure 1-2) have attracted considerable attention due to their increased reactivity for CO$_2$ absorption.$^{[48, 52, 61, 62]}$ Piperazine in particular, has been found to exhibit significantly enhanced CO$_2$ absorption rates (53 000 m$^3$ / kmol s), along with an increased absorption capacity compared to other primary and secondary amines such as MEA (7 000 m$^3$ / kmol s) and DEA (1 200 m$^3$ / kmol s) respectively.$^{[61]}$ This increased reactivity towards CO$_2$ has simply been attributed to the cyclic and diamine structure of PZ.$^{[61]}$ No further investigation into the influence of structural characteristics such as the electronic properties of the amino nitrogen and / or carbamate structure on CO$_2$ absorption have been reported. Within PZ the second amine moiety offers potential for enhanced CO$_2$ absorption capacity either in the form of a second reactive site for carbamate formation or proton acceptance, in the catalysis of bicarbonate formation or in modifying / enhancing the reactivity of the first amine site.

The low aqueous solubility of piperazine (1.7 mol L$^{-1}$ (146 g L$^{-1}$) at 20 °C)$^{[21]}$ and piperazine carbamate (1.3 mol L$^{-1}$ (170 g L$^{-1}$) before precipitation)$^{[22]}$ limits its use as a sole CO$_2$ capture absorbent.$^{[22]}$ Rather, piperazine is commonly used in catalytic quantities as an absorption
accelerator in aqueous solutions of sterically-hindered or tertiary amines.\textsuperscript{22-26} Only recently has Freeman et al.\textsuperscript{62} investigated the use of a concentrated aqueous PZ (8 mol L\textsuperscript{-1}) process as a novel CO\textsubscript{2} capture technology. To reach 8 mol L\textsuperscript{-1} the PZ concentration is gradually increased while CO\textsubscript{2} is added to maintain a CO\textsubscript{2} loading of 0.25 mol CO\textsubscript{2} / mol amine. At this CO\textsubscript{2} loading 8 mol L\textsuperscript{-1} PZ is reported to maintain a liquid solution with no precipitation at room temperature.

Theoretically one molecule of PZ can react with two molecules of CO\textsubscript{2}, given that both amine nitrogens are reactive. However this is not always the case with diamines in a CO\textsubscript{2} / H\textsubscript{2}O system. Typically it is reported that one amino group acts as the reactive centre and binds with CO\textsubscript{2}, while the second amino group becomes protonated, rendering it inactive and unable to bind a second CO\textsubscript{2} molecule. However, speciation data obtained by Bishnoi and Rochelle\textsuperscript{61} suggests otherwise leading to the proposal that the second amine nitrogen of PZ is in fact reactive. In this study \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded and analysed for a series of PZ solutions at different CO\textsubscript{2} loadings (0, 0.38, 0.57 and 0.91 mol CO\textsubscript{2} / mol amine) to identify the dominant reaction products present. From the data obtained five piperazine species were identified, including piperazine dicarbamate, and are shown in Figure 1-3. In the initial stages of CO\textsubscript{2} absorption or at low loading, piperazine carbamate and protonated piperazine were found to be the most prevalent reaction products. With increasing levels of CO\textsubscript{2} absorbed PZ was found to be predominantly in the form of protonated piperazine carbamate. Although piperazine dicarbamate was found to be present it was never the dominant reaction product, though its detection does indicate that the second nitrogen is in fact reactive and able to bind a second CO\textsubscript{2} molecule.\textsuperscript{61}

Da Silva and Svendsen\textsuperscript{48} also commented on the strong tendency of heterocyclic amines to form carbamates. Based on molecular modelling they suggested that it was the outcome of solvent effects, primarily the high solvation energy of the carbamate derivative and the low solvation energy of the neutral amine. The combination of these two solvent effects was said to favour carbamate formation. Furthermore, the high solvation energies of the heterocyclic carbamate derivatives were suggested to arise from the increased accessibility of a carbamate group on a cyclic molecule. Da Silva and Svendsen\textsuperscript{48} concluded that carbamate stability could not be explained in terms of a single molecular characteristic.
1. Introduction

Solvent stabilisation\textsuperscript{[48, 52]} and hydrogen bonding\textsuperscript{[63]} will play a crucial role in stabilizing the carbamate species, however both of these contributions are strongly influenced by the structure of the amine. Clearly, our understandings of the amine and carbamate properties that give rise to enhanced CO\textsubscript{2} absorption characteristics are still only rudimentary. As such, a thorough understanding of the factors influencing carbamate and bicarbonate formation, as well as carbamate hydrolysis, is essential for the development of new amine absorbent systems.

Figure 1-3. Piperazine species identified by Bishnoi and Rochelle\textsuperscript{[61]} based \textsuperscript{13}C and \textsuperscript{1}H NMR data obtained for piperazine solutions at different CO\textsubscript{2} loadings.
1.6 Amine Blends

Recently, blends of amines have received considerable attention as potentially superior absorbents for the removal of CO$_2$ from flue gas streams. These amine systems typically consist of an aqueous solution of a primary/secondary amine and a tertiary amine in varying compositions. The resulting absorbent is thought to take advantage of the primary/secondary amines fast reaction rate with CO$_2$ whilst retaining the higher absorption capacity and lower heat of reaction of the tertiary amine.$^{[64, 65]}$ By combining the specific advantages of each amine component it is believed that a considerable improvement in CO$_2$ absorption rates can be realised as well as easier regeneration of amine blends, compared to the conventional single amine absorbents.$^{[66, 67]}$ Furthermore the selectivity of the amine blend toward CO$_2$ can be set by varying the concentration of each amine. This provides an additional degree of optimisation for achieving precisely the desired separation for a given process.$^{[64, 68, 69]}$

Chakravarty et al.$^{[64]}$ was the first to suggest the potential of blended amine systems in terms of combining the specific advantages of each amine. This group investigated aqueous blends of the primary amine MEA and the tertiary amine MDEA. The results showed that a small amount of primary amine added to a tertiary amine can increase the initial CO$_2$ absorption rate by an order of magnitude without appreciably changing the stripping characteristics.

The BASF corporation has patented and commercialised an activated MDEA process in which MDEA is mixed with small amounts of PZ (0.05-0.8 mol L$^{-1}$)$^{[70]}$. These absorbents have successfully been used for high capacity CO$_2$ removal from synthesis gas in ammonia plants and hydrogen/carbon monoxide plants.$^{[68]}$

There is a large body of research in the scientific literature reporting on CO$_2$ absorption into mixed amine systems. Most current research focuses on experimentally measuring and modelling the absorption kinetics and vapour-liquid equilibria (VLE) of these blended amine systems. Some of the different blends that have been investigated and modelled are provided in Table 1-2. However, the synergistic (or otherwise) relationship between the two different amine constituents is not yet fully understood.
Table 1-2. The different amine blends that have been investigated in the literature. Studies of these systems have focused on modelling of the absorption kinetics and vapour-liquid equilibria.

<table>
<thead>
<tr>
<th>Amine Blend</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA + PZ</td>
<td>[66, 68, 70-79]</td>
</tr>
<tr>
<td>MDEA + MEA</td>
<td>[64, 66, 68, 69, 80-88]</td>
</tr>
<tr>
<td>MDEA + DEA</td>
<td>[68, 80, 82, 86, 89-92]</td>
</tr>
<tr>
<td>MDEA + DGA (Diglycolamine)</td>
<td>[86]</td>
</tr>
<tr>
<td>MDEA + MMEA</td>
<td>[86, 93]</td>
</tr>
<tr>
<td>MDEA + DIPA (Diisopropylamine)</td>
<td>[86, 93]</td>
</tr>
<tr>
<td>MDEA + TETA (triethylene tetramine)</td>
<td>[94, 95]</td>
</tr>
<tr>
<td>MDEA + HMDA (Hexamethylenediamine)</td>
<td>[96]</td>
</tr>
<tr>
<td>MDEA + 2-(1-piperazinyl)-ethylamine</td>
<td>[97]</td>
</tr>
<tr>
<td>MEA + PZ</td>
<td>[98]</td>
</tr>
<tr>
<td>DEA + PZ</td>
<td>[67]</td>
</tr>
<tr>
<td>AMP + PZ</td>
<td>[99, 100]</td>
</tr>
<tr>
<td>AMP + MEA</td>
<td>[65, 83, 101-103]</td>
</tr>
<tr>
<td>AMP + DEA</td>
<td>[102, 104, 105]</td>
</tr>
<tr>
<td>AMP + MDEA</td>
<td>[86, 106]</td>
</tr>
<tr>
<td>TIPA (Triisopropanolamine) + MEA</td>
<td>[107]</td>
</tr>
<tr>
<td>TIPA + PZ</td>
<td>[107]</td>
</tr>
<tr>
<td>AHPD (2-amino-2-hydroxymethyl-1,3-propanediol) + PZ</td>
<td>[108]</td>
</tr>
</tbody>
</table>

### 1.6.1 Heterocyclic Amines as Promoters

The use of heterocyclic amines, such as piperazine, as additives in tertiary and Cα-substituted amine absorbents, as well as inorganic systems such as potassium carbonate, has
been found to result in significantly enhanced CO\textsubscript{2} absorption characteristics compared to that of other blended amines.

As mentioned previously, the rate constant for CO\textsubscript{2} absorption by PZ is reported to be much higher than that of conventional amines such as MEA or DEA, as well as other amines with similar pK\textsubscript{a} values.\textsuperscript{[61]} Bishnoi and Rochelle\textsuperscript{[68]} investigated the kinetics of a PZ / MDEA blend compared to MEA / MDEA and DEA / MDEA. The PZ / MDEA system was found to absorb CO\textsubscript{2} much faster than the MEA or DEA blends at similar concentrations. The predicted rate constant of PZ / CO\textsubscript{2} was also found to double in the presence of MDEA. This increase was attributed to the participation of MDEA in the reaction of PZ with CO\textsubscript{2}.\textsuperscript{[68]} From \textsuperscript{1}H and \textsuperscript{13}C NMR data obtained for a PZ / MDEA system at high loading, the piperazine dicarbamate species has also been reported to be present in higher concentrations compared to that of a simple PZ / H\textsubscript{2}O / CO\textsubscript{2} system.\textsuperscript{[77]} The presence of MDEA, at significantly higher concentrations than PZ, appears to catalyse the carbamate forming reaction between CO\textsubscript{2} and PZ. This has also been reported for PZ activated AMP\textsuperscript{[99]} and suggests that an amine / amine interaction contributes to the enhanced CO\textsubscript{2} absorption of the blended systems, rather than the two amines simply acting as separate entities in solution. The interaction of the two amines could catalyse carbamate formation and subsequently the rapid hydrolysis of the carbamate species to bicarbonate. The physical properties of blends, such as reduced surface tension\textsuperscript{[109-111]} and viscosity,\textsuperscript{[109, 112, 113]} may also contribute to the enhancement of CO\textsubscript{2} absorption. However the exact mechanism of interaction is not yet fully understood.

The increased efficiency of heterocyclic amines, PZ activated tertiary and Cα-substituted amines, as well as other amine blends, has marked these systems as potential superior absorbents for the removal of CO\textsubscript{2} from flue gas streams. For this reason it is important to have a more in-depth understanding of how mechanistically they function at a molecular level, if further progress is to be made towards the development of superior CO\textsubscript{2} capture absorbents. Further characterisation of the structure-activity relationship between CO\textsubscript{2} and heterocyclic amines will aid in elucidating the internal workings of amine blends.

\subsection{1.7 Project Overview}

The chemical reactions involved in CO\textsubscript{2} absorption / desorption by aqueous amine-based absorbents for PCC are continually being investigated to identify potential for and make improvements in efficiency. From review of the PCC literature a relationship was identified between amine structure and CO\textsubscript{2} / amine reactivity, with heterocyclic amines emerging as a
potentially superior CO₂ capture absorbents.\cite{48,52,61,62} As mentioned, this class of amine has been found to exhibit significantly enhanced CO₂ absorption rates and capacities compared to acyclic amines. However, much of the work in this area has focused on the heterocyclic amine piperazine, but the molecular properties that give rise to enhanced CO₂ absorption characteristics are not yet fully understood.

The objective of this work is to determine the effect molecular structure has on the CO₂ absorption capacity, initial absorption rate and carbamate lability of heterocyclic amines. This will be achieved through an in-depth structure-activity relationship analysis.

The aim is to investigate the structure-activity relationship over a much broader class of heterocyclic amines, including monoamines, such as piperidine and functionalised piperidine derivatives; and diamines, such as PZ and hexahydroprazidines, to provide an insight into the effect molecular structure has on CO₂ / amine reactivity and the enhanced reactivity of cyclic amines compared to acyclic amines. To address the primary research aims of this thesis, two subsets of heterocyclic amines have been investigated, including:

i. Monoamines- piperidine and a series of commercially available functionalised piperidine derivatives, e.g. those with methyl-, hydroxyl- and hydroxyalkyl-substituents.

ii. Diamines- PZ, methyl substituted PZ’s and a series of in-house synthesised novel heterocyclic diamines, including hexahydroprazidine (HHPY), 2-methylhexahydroprazidine (MHHPY), 2,2-dimethylhexahydroprazidine (DMHHPY) and hexahydroprazidine (HHPZ).

The diamine analogues proposed for evaluation retain PZ’s two ring nitrogens varying in their relative positions and ring substituents. This approach will allow for rapid determination of the effect of the position of the nitrogen atoms within the six member ring and the outcome on CO₂ / amine reactivity. It will also provide for a series of potential novel CO₂ capture absorbents that possess enhanced CO₂ capture characteristics, but with improved aqueous solubility compared to PZ. The novel HHPY, MHHPY, DMHHPY and HHPZ will be synthesised.

The chemical reactions between CO₂ and the heterocyclic amines will be followed in-situ using Attenuated Total Reflectance (ATR) FT-IR spectroscopy. Currently, there is no literature available on the in-situ infrared analysis of amine / CO₂ / H₂O systems or the infrared spectrum of secondary amine carbamate derivatives, such as piperidine-1-carboxylate or 1-piperazinium-
4-carboxylate (protonated PZ carbamate). This work is thus the first such study on these amines.

The effect of structure on CO$_2$/amine reactivity will be investigated as follows:

i. The infrared active reaction products including, carbamate versus bicarbonate formation with cumulative CO$_2$ absorption. Cumulative CO$_2$ absorption data will be collected simultaneously with the infrared spectral data.

ii. CO$_2$ absorption capacity. This parameter will be calculated from the cumulative CO$_2$ absorption data.

iii. Initial rate of CO$_2$ absorption. For the monoamines this parameter will be measured using a wetted wall column (WWC) and for the diamines a thermal gravimetric analysis (TGA) method will be used.

iv. Correlation between the atomic properties of the amine and carbamate derivative with the infrared spectral data, CO$_2$ absorption capacity and initial absorption rate.

While the CO$_2$ absorption rate and capacity of an amine-based absorbent are important performance indicators in determining absorbent efficiency, another important aspect of CO$_2$/amine capture chemistry is the lability of the carbamate species formed and its susceptibility to hydrolysis and subsequent bicarbonate formation. Increased bicarbonate formation is associated with increased absorption capacities and a lower heat of regeneration. Amine structure will determine carbamate lability and thus susceptibility to hydrolysis. A correlation between the CO$_2$ absorption data and infrared peak absorbance, those assigned to carbamate and bicarbonate formation, will enable the determination and comparison of reaction mechanisms and carbamate lability between the structurally different amines.

The atomic properties of the amines and carbamate derivatives will be investigated using B3LYP / 6-31+G** and MP2 / 6-31+G** (Spartan 08[114]) calculations. The N-COO$^-$ bond, which is formed in the carbamate derivatives of the heterocyclic amines, as well as the resonance structure (charge delocalisation) of the carboxylate moiety will be analysed. Gas-phase harmonic frequency and intensity calculations will also be performed to verify the assigned experimental carbamate infrared stretching frequencies.

Lastly, once the CO$_2$ absorption characteristics and carbamate properties of the individual heterocyclic amines have been established, the role of these amines and the effect of structure in a blended system will be characterised using the in-situ FT-IR technique and WWC. The formulations that will be investigated and compared include PZ / AMP and piperidine / AMP.
2. Experimental Design

2.1 Carbon Dioxide Absorption Capacity / *In-situ* FT-IR Measurements

2.1.1 Background

As mentioned previously (Section 1.4), when CO$_2$ reacts with amines in an aqueous environment, carbamate, bicarbonate and protonated amine are generated. Amines and their reaction products absorb radiation in the mid-infrared frequency range ($4000$-$400$ cm$^{-1}$). FT-IR spectroscopy is therefore capable of detecting these absorbing species\cite{115-118} if they are present in a high enough concentration and/or their absorbance is not masked by other more intense absorbance. Recent advances in ATR FT-IR spectroscopy have allowed for the convenient and rapid analysis of these chemical species to be carried out *in-situ* during the CO$_2$ absorption process. This is a particular valuable tool, as it can provide an insight into the reaction mechanism and pathway that is difficult to otherwise observe. Measurements can also be achieved on a continuous basis without disturbing the system.

In this study, knowledge of carbamate/bicarbonate speciation during the absorption process will enable the determination of the effect molecular structure has on reaction mechanisms and carbamate lability.

To quantify the effect molecular structure has on the reactivity of the amino nitrogen, the CO$_2$ absorption capacity and initial absorption rate was measured and calculated for each individual amine investigated. The CO$_2$ absorption capacity was measured simultaneously with the infrared spectral data during a typical CO$_2$ absorption / FT-IR experiment. This section describes the apparatus and experimental procedure used. Determination of initial CO$_2$ absorption rates is discussed in Section 2.2.
2. Experimental Design

2.1.2 Apparatus

A schematic representation of the absorption reactor apparatus used in these experiments is shown in Figure 2-1. The system consists of a pair of factory calibrated mass flow controllers for the delivery of a 13% CO\textsubscript{2} (v / v) in N\textsubscript{2} gas stream at a flow rate of 1.8 L min\textsuperscript{-1} and ambient pressure. All mass flow controllers referred to in this thesis were Bronkhurst EL-Flow controllers.

The gas is first fed into a mixing chamber and pre-saturated with a water humidifier. The CO\textsubscript{2} / N\textsubscript{2} gas stream is pre-saturated with water, to reduce evaporation of the aqueous amine solution on entry of the feed gas into the absorption reactor. The humidified CO\textsubscript{2} / N\textsubscript{2} gas stream is then bubbled through the amine solution in a glass reactor vessel. The reactor consists of a three neck 100 ml round bottom flask fitted with an open-ended Dreschel bottle head for gas dispersion. Both the humidifier and absorption reactor were maintained at 40°C by a temperature controlled water bath. The reactor gas outlet was passed through a condenser for cooling and to remove moisture and any volatised solvent before being sent to a CO\textsubscript{2} gas analyser. The temperature of the coolant passing through the condenser was set at approximately 5-10 °C.

The CO\textsubscript{2} content of both the reactor gas inlet and outlet was measured using a Horiba VS-3001 General Purpose Gas Sampling Unit in line with a Horiba VA-3000 Multi-gas Analyser Unit. The gas sampling unit dehumidified and split the gas stream between the analyser and exhaust. The analyser unit made use of non-dispersive infrared (NDIR) detection to directly determine the CO\textsubscript{2} concentration in the sample gas mixture. The difference between the CO\textsubscript{2} concentration of the reactor gas inlet and outlet was used to determine the amount of CO\textsubscript{2} absorbed by the amine solution (Section 2.1.3.4).

The data from the gas analyser unit was collected using a National Instruments NI SCXI 1000 series data logger and a computer running LabVIEW 10.0 software. The ATR FT-IR spectrometer (Mettler-Toledo ReactIR iC10-K6) was also interfaced with the computer, so that both the absorption reactor system and the FT-IR spectrometer were run simultaneously.

The FT-IR spectrometer, with a Mercury Cadmium Telluride (MCT) detector, was equipped with a diamond tipped ATR probe (36 cm). The probe was coupled to the spectrometer by a K6 conduit, as shown in Figure 2-2.
Figure 2-1. Schematic of the CO\(_2\) absorption reactor / FT-IR system. The sections highlighted in red represent the ‘System Bypass’ and ‘Reactor Bypass’ used in the calibration of the CO\(_2\) gas analyser prior to an experimental run (Section 2.1.3.3).
2. Experimental Design

Figure 2-2. Mettler-Toledo ReactIR iC10-K6 FT-IR spectrometer coupled to a mirror based K6 conduit with an attenuated total reflectance (ATR) diamond tipped probed, used to collect in-situ infrared spectral data during a typical CO\textsubscript{2} absorption / FT-IR experiment with an aqueous amine solution.\textsuperscript{[119]}

The ATR probe allowed for the real time measurement of infrared spectra inside the absorption reactor. The diamond sensor has two optical ranges of 4000-2250 cm\textsuperscript{-1} and 1950-650 cm\textsuperscript{-1}. The spectral region of 2250-1950 cm\textsuperscript{-1} was a ‘blind spot’ were the diamond absorbs infrared energy. The species of interest in this work did not absorb in this region.

The spectrometer was continually purged with 100\% N\textsubscript{2} to prevent any water vapour from collecting in the optics, which may have obscured the spectral data.

2.1.3 Experimental Procedure

2.1.3.1 System Calibration

Prior to conducting an experiment the reactor system was first purged with 100 \% N\textsubscript{2} to remove any residual CO\textsubscript{2}. Once purged the zero measurement of the analyser was set to correct for any drift using the instruments internal span control. Using the ‘System Bypass’, shown in Figure 2-1 (highlighted in red), the span of the analyser was then calibrated with a flow of 21 \% CO\textsubscript{2} in N\textsubscript{2} calibration gas and the analyser adjusted for any drift.

Following the calibration of the analyser the mass flow controllers were adjusted for a 13\%
CO₂ in N₂ gas mixture at a flow rate of 1.8 L min⁻¹. Using the ‘Reactor Bypass’ as shown in Figure 2-1 (highlighted in red) the gas mixture was first passed through the humidifier, bypassing the absorption reactor, and passing directly to the CO₂ analyser. The system was allowed to reach equilibrium, which was achieved when the analyser reported a value of 13% CO₂. The gas flow was then switched to pass through the absorption reactor, containing the aqueous amine solution, for commencement of the experiment.

The diamond tipped probe was cleaned with distilled water and acetone before commencement, and on completion, of all experiments. Before each experiment the probe was aligned to maximise the peak height and contrast. Alignment was achieved by adjusting the mirrors of the optical conduit and MCT detector.

2.1.3.2 Sample Preparation

For a typical experiment the amine was prepared and analysed at 3 mol L⁻¹ concentration, unless otherwise stated. For all experiments a 30 mL reaction volume was used. The required weight of each amine was calculated based on their individual molecular weight and weighed into a 100 mL round bottom flask. The solution was made up to 30 mL with Milli-Que water and stirred until fully dissolved. Less soluble amines required some heating to attain complete dissolution.

The amines investigated were purchased from Sigma Aldrich, Acros Organics and Tokyo Chemical Industry, with a purity of ≥ 95% and used without further purification (Table 2-1), unless otherwise stated. All gases used in this work were purchased from BOC, with a purity of > 99.9% purity.
### Table 2-1. List of chemicals, their respective purity and source.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous Piperazine</td>
<td>≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methydiethanolamine (MDEA)</td>
<td>≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Piperidine</td>
<td>≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>1-hydroxypiperidine</td>
<td>≥ 96.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>1-methylpiperidine</td>
<td>99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>1-(2-hydroxethyl)piperidine</td>
<td>99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>95.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2-(hydroxymethyl)piperidine</td>
<td>&gt; 98.0 %</td>
<td>Tokyo Chemical Industry</td>
</tr>
<tr>
<td>2-methylpiperidine</td>
<td>98.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2-(2-hydroxyethyl)piperidine</td>
<td>&gt; 96.0 %</td>
<td>Tokyo Chemical Industry</td>
</tr>
<tr>
<td>2,5-Dimethylpiperazine</td>
<td>98.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2,6-Dimethylpiperazine</td>
<td>99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>3-(hydroxymethyl)piperidine</td>
<td>96.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>3-hydroxypiperidine</td>
<td>≥ 98.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>3-methylpiperidine</td>
<td>99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
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<td>97.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
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<td>98.0 %</td>
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<tr>
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<td>96.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>4-(2-hydroxyethyl)piperidine</td>
<td>97.0 %</td>
<td>Acros Organic</td>
</tr>
<tr>
<td></td>
<td>97.0 %</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
2. Experimental Design

2.1.3.3 Experimental Procedure

The reaction vessel containing the sample amine was placed in the water bath and connected to the gas delivery system. Experiments were run by initially allowing the humidifier and absorption reactor, to thermally equilibrate at 40°C. During this period the system was purged and calibrated, as per Section 2.1.3.1.

The ATR probe was then inserted into the aqueous amine solution through a side neck on the multi-necked round bottom flask as shown in Figure 2-3. Once the reactor was fully sealed, the pre-saturated CO$_2$ / N$_2$ gas stream was then introduced into the reactor and the experiment commenced. Each experiment was run until chemical equilibrium had been reached and the CO$_2$ concentration at the reactor gas outlet returned to its original value of 13%. The time to return to equilibrium was amine dependent, but a run typically lasted between 45-90 mins.

Figure 2-3. Photograph of the experimental setup used during a typical CO$_2$ absorption / FT-IR experiment showing the reactor vessel, FT-IR probe, gas in and gas out connections, pre-saturator and water bath.

In-situ infrared measurements were obtained simultaneously with the CO$_2$ absorption measurements. The FT-IR spectrometer was set to continuously collect spectra for the duration of the absorption experiment over the spectral range of 4000-650 cm$^{-1}$. Each spectrum was recorded as the average of 256 scans over a sampling interval of fifteen seconds with a
resolution of 4 cm\(^{-1}\). Prior to analysis of the amine / CO\(_2\) / H\(_2\)O spectra the baseline was adjusted to zero.

2. Experimental Design

2.1.3.4 Calculation of Absorption Capacity

The CO\(_2\) absorption capacity of each amine was calculated as follows:

The percentage CO\(_2\) at the gas inlet ‘%CO\(_{2in}\)’ was calculated from the CO\(_2\) inlet flow rate ‘\(F_{CO_2in}\)’ (mL min\(^{-1}\)) and the total CO\(_2\) / N\(_2\) inlet flow rate ‘\(F_{flow}\)’ (mL min\(^{-1}\)) (Equation 2.1):

\[
\%CO_{2in} = \frac{F_{CO_2in}}{F_{flow}} \times 100\% \tag{2.1}
\]

The volume of CO\(_2\) at the gas inlet ‘\(V_{CO_2in}\)’ (mL) was calculated from ‘\(F_{CO_2in}\)’ (\(\Delta t = \) change in time) (Equation 2.2):

\[
V_{CO_2in} = F_{CO_2in} \times \Delta t \tag{2.2}
\]

The volume of CO\(_2\) at the gas outlet ‘\(V_{CO_2out}\)’ (mL) was calculated from the total CO\(_2\) / N\(_2\) outlet flow rate ‘\(F_{out}\)’ (mL min\(^{-1}\)), the N\(_2\) flow rate ‘\(F_{N_2}\)’ (mL min\(^{-1}\)) and the change in time (Equation 2.3):

\[
V_{CO_2out} = (F_{out} - F_{N_2}) \times \Delta t \tag{2.3}
\]

‘\(F_{out}\)’ was calculated from ‘\(F_{N_2}\)’ and the percentage concentration of CO\(_2\) at the gas outlet, ‘%CO\(_{2out}\)’ (Equation 2.4):

\[
F_{out} = \frac{F_{N_2}}{100 - \%CO_{2out}} \times 100 \tag{2.4}
\]
2.2 Initial Carbon Dioxide Absorption Rate

Substitution of Equation 2.4 into Equation 2.3 gives Equation 2.5:

\[
V_{\text{CO}_2,\text{out}} = \left( \frac{F_{N_2}}{1 - \frac{\% \text{CO}_2,\text{out}}{100}} - F_{N_2} \right) \times \Delta t
\]

The volume of CO\(_2\) consumed \(V_{\text{CO}_2,\text{Consumed}}\) (mL) is calculated using Equation 2.6:

\[
V_{\text{CO}_2,\text{ Consumed}} = V_{\text{CO}_2,\text{in}} - V_{\text{CO}_2,\text{out}}
\]

The absorption capacity \(AC_{\text{mol/mol}}\) of an amine is then calculated using Equation 2.7:

\[
AC_{\text{mol/mol}} = \frac{V_{\text{CO}_2,\text{Consumed}}}{22414 \times \left( \frac{T}{T_0} \right) \times MW_{\text{A}}_{\text{min}} e / \text{Masa}_{\text{min}} e}
\]

The cumulative absorption capacity with time was determined by progressively adding together the incremental results from Equation 2.7, to provide the CO\(_2\) loading for an amine (mol CO\(_2\)/mol amine) at any time during the absorption experiment.

2.2 Initial Carbon Dioxide Absorption Rate

2.2.1 Background

The initial CO\(_2\) absorption rate was measured using two different methods in this study. For the monoamines a wetted-wall column (WWC) apparatus was used to measure the mass transfer coefficient \(K_G\) at zero loading. The WWC apparatus mimics the gas–liquid contacting that occurs in packed columns, where a gas stream enters at the bottom and a liquid stream at the top, such as the absorber column in a PCC plant.\(^{[20]}\) Briefly, the WWC counter-currently contacts a falling thin liquid film of aqueous amine with a saturated N\(_2\) / CO\(_2\) gas stream. This occurs at different CO\(_2\) partial pressures and on the surface of a stainless rod of a known surface
area. The amine CO₂ absorption flux and mass transfer coefficient (mol.s⁻¹.cm⁻².Pa⁻¹) at zero loading can be calculated from the amount of CO₂ absorbed and the known experimental parameters including gas flow rate and contact surface area of the liquid film with the gas.

For the diamines analysed a thermal gravimetric analyser (TGA) was used to analyse the initial rate of CO₂ absorption. The reason this method was chosen was because of the smaller sample sizes available for analysis, keeping in mind the quantity required for repeat absorption / FT-IR experiments (detailed in Section 2.1). With the first subset of amines being commercially available, larger quantities of the amines were obtainable for analysis on the WCC apparatus. Briefly, the TGA instrument measures the increase in mass of an aqueous amine solution when exposed to a gas stream of 15% CO₂ (v/v) in N₂. An absorption curve can then be calculated for each amine. Initial absorption rates (mol CO₂ / mol amine. min⁻¹) are calculated using linear regression to determine the slope of the absorption curve.

This section describes the WWC and TGA methods used for determining initial CO₂ absorption rates.

2.2.2 Wetted-Wall Column

2.2.2.1 Apparatus

A simplified schematic of the WWC apparatus is shown in Figure 2-4.

The WWC consists of a stainless steel rod (or column) (effective height 8.21 cm and diameter 1.27 cm), over which a thin film of amine solution flows under gravity (Figure 2-5a). The amine solution is pumped, using a Micropump GA-V21, from the reservoir at a flow rate of 170 mL min⁻¹ up the inside of the column. It flows out the top and down the outer surface of the column as an evenly distributed thin film, before being returned to the reservoir to form a closed loop. The reservoir (600 mL) is situated in a water bath controlled at 40 °C. The column is contained within a jacketed glass cover (internal diameter of 2.54 cm), through which water from the water bath is circulated to maintain the temperature of the column at 40°C and establish isothermal conditions (Figure 2-5b). A T-type thermocouple (± 1 °C) is used to measure the temperature of the test solution inside the column (Figure 2-5b).
Figure 2-4. Schematic of the wetted wall column (WWC) and associated apparatus used to analyse the initial CO₂ absorption rates of the functionalised piperidines analysed in this study.
2. Experimental Design

Figure 2-5. A schematic representation of the WWC apparatus showing a) the thin liquid film, gas flow into the column and position of the thermocouple; b) the WWC with the jacketed glass cover and gas flow out of the column, and c) a photograph of the actual WWC experimental setup.
A pair of factory calibrated mass flow controllers are used to deliver a CO$_2$ in N$_2$ gas stream, at different CO$_2$ partial pressures (0 - 20 kPa) and with a flow rate of 5 L min$^{-1}$, to the wetted wall column. The CO$_2$ / N$_2$ gas stream is first passed through a 1/8” stainless steel coil (approximately 550 cm in length) and saturator for heating and pre-humidification of the gas stream. Both the coil and saturator were immersed in the water bath. The purpose of this was to minimise any evaporative amine / water losses from contacting a hot dry gas stream with the thin liquid film. From the saturator the humidified CO$_2$ / N$_2$ gas stream was then fed into the WWC. It entered at the base of the column and counter-currently contacted the falling thin film as it moved upwards and passed over the outer column surface. The gas stream then exited at the top of the column (Figure 2-5a and b) and was passed through a condenser for cooling and to remove moisture and any volatised solvent, before being sent to a CO$_2$ gas analyser.

The CO$_2$ content of both the WWC’s gas inlet and outlet was measured using a Horiba VS-3001 gas sampling unit and VA-3000 gas analyser unit (specifications for which have been discussed previously in Section 2.1.2.). The difference between the CO$_2$ concentration of the gas inlet and outlet was used to determine the amount of CO$_2$ absorbed into the liquid film. This, in conjunction with the known experimental parameters including gas flow rate and contact area for reaction (the column gave a known surface area between the liquid and gas flow), was used to determine the CO$_2$ absorption flux and resultant kinetics (overall mass transfer coefficient, $K_{G}$) (Section 2.2.2.4).

The data from the gas analyser unit was collected using a National Instruments NI SCXI 1000 series data logger and a computer running LabVIEW SignalExpress 2010 software.

2.2.2.2 Sample Preparation

For a typical experiment the amine was prepared and analysed at 1 mol L$^{-1}$ concentration, unless otherwise stated. For all experiments a 1 L reaction volume was used. The required weight of each amine to be analysed was calculated based on their individual molecular weight and weighed into a 1 L volumetric flask. The solution was made up to 1 L with Milli-Que water and stirred until fully dissolved. Less soluble amines required some heating to attain complete dissolution. The amine solution, 600 mL, was placed in a sample bottle (sample reservoir, Figure 2-4) in the water bath which was set at 40 °C. A further 250 mL of the amine solution was also placed in a sample bottle (250 mL) (rinse solution) and used to pre-rinse the WWC prior to the start of an experiment. The remaining amine solution was placed in a syringe and used to manually adjust the solution level inside the WWC during the experiment.
2.2.2.3 Experimental Procedure

Experiments were run by initially flushing the WWC with the rinse solution for several minutes. This was performed whilst the sample reservoir in the water bath was let reach thermal equilibrium at 40 °C. The sample reservoir was then attached to the WWC system and the filled syringe attached to the needle valve as shown in Figure 2-4.

The amine solution was introduced into the WWC by slowly increasing the pump speed and adjusting the solution volume with the filled syringe until the desired liquid flow rate of 170 mL min\(^{-1}\) achieved. This liquid flow rate was chosen to ensure continuous and ripple free film formation. The presence of ripples in the thin film will enhance the CO\(_2\) absorption rate and thus lead to erroneous results.\(^{[121]}\)

Using the ‘Reactor Bypass, shown in Figure 2-4 (highlighted in red), the desired gas flow rate and CO\(_2\) partial pressure was set. The gas flow was then switched to pass through the column. The system was allowed to reach a steady state which was achieved when the CO\(_2\) concentration at the column gas outlet was constant. This CO\(_2\) concentration was recorded. The gas flow was then switched back to the ‘Reactor Bypass’ and the CO\(_2\) / N\(_2\) flow rates varied to deliver a different CO\(_2\) partial pressure. The gas flow was then switched back to the column, allowed to reach a steady state, and the CO\(_2\) concentration at the column gas outlet recorded. This was repeated until measurements at CO\(_2\) partial pressures of 0, 4, 8, 12, 16 and 20 kPa had been completed. The system was operated at atmospheric pressure.

The large solution volume (600 mL), relative to the gas-liquid contact area, was used in the operation of the WCC to ensure the continuous replenishment of the film. This ensured that during experiments the total CO\(_2\) loading of the solution (zero loading) did not change significantly during the course of the experiment.

Calibration of the analyser was achieved during the experiment by bypassing the WWC and adjusting the CO\(_2\) partial pressure to give a known concentration.

2.2.2.4 Calculation of CO\(_2\) Absorption Flux and Overall Mass-Transfer Coefficient

The reactive chemical absorption of CO\(_2\) into a thin liquid film of aqueous amine can be described as a combination of diffusion and chemical reaction processes. The CO\(_2\) diffused from the gas phase across the gas-liquid interface into the liquid phase where it underwent a chemical reaction,\(^{[120]}\) as illustrated in Figure 2-6.
2. Experimental Design

Figure 2-6. Illustration showing the gas and liquid mass transfer processes occurring in a segment of the wetted-wall column.\textsuperscript{[120]}

The mass transfer rate of CO\textsubscript{2} across the gas-liquid interface into the liquid phase is influenced by the concentration gradient of CO\textsubscript{2} in the direction of mass transfer within each phase.\textsuperscript{[122]} The concentration of CO\textsubscript{2} in the gas phase falls from its bulk gas partial pressure ‘P\textsubscript{CO2}’ (kPa) to its partial pressure at the gas-liquid interface ‘P\textsubscript{CO2,i}’ (kPa) according to the gas-side mass transfer coefficient ‘k_g’. The mass flux of CO\textsubscript{2} ‘N\textsubscript{CO2}’ across the gas-liquid interface at a steady state can therefore be represented in terms of ‘k_g’ and driving force (concentration gradient, (P\textsubscript{CO2} – P\textsubscript{CO2,i})), as per Equation 2-8: \textsuperscript{[120, 122]}

\[
N_{\text{CO2}} = k_g (P_{\text{CO2}} - P_{\text{CO2,i}})
\]  \hspace{1cm} 2-8

On the liquid side of the gas-liquid interface the mass flux of CO\textsubscript{2} was driven by diffusion and chemical reactions that occur in the liquid film and act to consume CO\textsubscript{2}. The concentration of dissolved CO\textsubscript{2} at the gas-liquid interface ‘x\textsubscript{CO2,i}’ falls by diffusion and chemical reaction to the bulk dissolved CO\textsubscript{2} concentration ‘x\textsubscript{CO2}’ according to the liquid side mass transfer
2. Experimental Design

coefficient ‘$k_l$’ (Equation 2-9),\footnote{120,123}

\[
N_{CO_2} = k_l (x_{CO_2,i} - x_{CO_2})
\]

2-9

Since the mass transfer driving force takes place over extremely small distances, determination of the CO$_2$ concentration at the gas-liquid interface ($P_{CO_2,i}$ and $x_{CO_2,i}$) is very difficult. Therefore, the mass flux of CO$_2$ into and out of the amine solution was calculated and characterised by the overall mass transfer coefficient ‘$K_G$’ and the CO$_2$ partial pressure driving force ($P_{CO_2} - P^{*}_{CO_2}$), as per Equation 2-10: \footnote{120,122,123}

\[
N_{CO_2} = K_G (P_{CO_2} - P^{*}_{CO_2})
\]

2-10

where $P_{CO_2}$ is the partial pressure in the WWC reactor and $P^{*}_{CO_2}$ is the equilibrium CO$_2$ partial pressure. $P^{*}_{CO_2}$ is assumed to be constant for a particular CO$_2$ solution loading as the rate of CO$_2$ absorption is small relative to the total CO$_2$ concentration of the liquid.\footnote{120,122}

The overall mass transfer coefficient is related to the liquid and gas phase mass transfer coefficients as per Equation 2-11:\footnote{62}

\[
\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_l}
\]

2-11

Therefore, according to Equation 2-10, by plotting $N_{CO_2}$ versus applied CO$_2$ partial pressure (‘$P_{CO_2}$’) ‘$K_G$’ can be determined by linear regression according to Equation 2-12:\footnote{120,123}

\[
N_{CO_2} = K_G \times P_{CO_2} + b
\]

2-12

During each WWC experiment (Section 2.2.2.3), the CO$_2$ concentration of the column gas outlet was recorded at several bulk gas CO$_2$ partial pressures (0 – 20 kPa). Using Equation 2.1 to 2.6 (Section 2.1.2.4) the amount of CO$_2$ consumed at each of these bulk CO$_2$ partial pressures was calculated. The amount of CO$_2$ consumed and the known experimental parameters (gas-liquid contact area and gas flow rate) were then used to calculate the CO$_2$ absorption flux ($N_{CO_2}$)
at each different bulk CO$_2$ partial pressure. The CO$_2$ absorption flux was the number of moles of CO$_2$ absorbed per second per unit area of contact between the liquid and gas (mol.s$^{-1}$cm$^{-2}$).

The applied CO$_2$ partial pressure (‘P$_{CO2}$’) in the WWC was then calculated as the logarithmic mean of the inlet and outlet CO$_2$ partial pressures (Equation 2-13) (it was assumed CO$_2$ has a log mean distribution over the column height).\cite{120,123}

\[
P_{CO2} = \frac{P_{CO2, in} - P_{CO2, out}}{\ln(P_{CO2, in}/P_{CO2, out})}
\]

The CO$_2$ absorption flux was then plotted against the applied CO$_2$ partial pressure ‘P$_{CO2}$’, yielding a straight line with a slope equal to the overall mass transfer coefficient ‘K$_G$’ (mol.s$^{-1}$cm$^{-2}$Pa$^{-1}$).\cite{120} An example is provided in Figure 2-7 for an aqueous piperidine solution.

![Figure 2-7. Calculated CO$_2$ absorption flux (N$_{CO2}$) versus applied CO$_2$ partial pressure (P$_{CO2}$) for an aqueous piperidine solution (1 mol L$^{-1}$) at 40 °C and zero loading.](image-url)
2.2.3 Isothermal Gravimetric Analysis

2.2.3.1 Apparatus

Initial CO₂ absorption rates were also measured using a Setaram Labsys TG-DTA / DSC thermal gravimetric analyser (TGA). This instrument consists of a micro balance housed within a metal element heated furnace. It was setup with two gas stream inputs, one providing a 100 % N₂ and the other a 15% CO₂ in N₂ mix. A pair of factory calibrated mass flow controllers are used to deliver the gas stream at a flow rate of 30 mL min⁻¹ to the amine solution.

The amine solution is placed in a 100 µL alumina crucible, situated on the micro balance. The gas stream enters the furnace and sweeps over the top of the amine solution. The change in mass of the crucible was used to determine the amount of CO₂ absorbed by the amine solution as a function of time.

The data from the TGA unit was collected using a computer running SETSOFT 2000.

2.2.3.2 Sample Preparation

For a typical experiment the amine was prepared and analysed at 1.5 mol L⁻¹ concentration, unless otherwise stated. For all experiments a 1 mL reaction volume was used. The required weight of each amine to be analysed was calculated based on their individual molecular weight and weighed into a 10 mL sample vial. The solution was made up to 1 mL with Milli-Que water and stirred till dissolved. Less soluble amines required some heating to attain complete dissolution.

An empty 100 µL alumina crucible was first used to zero the TGA’s micro balance. A 100 (± 5) mg of the amine solution was then placed in the same crucible, put back on the TGA balance and the furnace closed ready for commencement of the experiment.

The commercially available amines investigated were purchased from Sigma Aldrich with a purity of ≥ 95% (Table 2-1) and used without further purification. Those not commercially available were synthesised according to the procedures outlined in Section 6.

2.2.3.3 Experimental Procedure

Two separate TGA experiments were performed for each amine. The first experiment determined the mass loss due to evaporation when the amine solution was exposed to a 100%
N$_2$ gas stream. The second experiment determined the mass increase of the amine solution when exposed to a 15% CO$_2$ in N$_2$ gas stream over the same length of time.

Each experiment was performed using a fresh 100 µL aliquot of the amine solution. Table 2-2 provides a summary of the pre-programmed temperature and gas stream cycles used for the evaporation and absorption run by the TGA method. The instrument was operated in isothermal mode at 40°C and ambient pressure.

<table>
<thead>
<tr>
<th>Initial Temperature (°C)</th>
<th>Final Temperature (°C)</th>
<th>Cycle Duration (min)</th>
<th>Gas Stream (evaporation run)</th>
<th>Gas Stream (absorption run)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>40</td>
<td>4 (heating)</td>
<td>100% N$_2$</td>
<td>100% N$_2$</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>16</td>
<td>100% N$_2$</td>
<td>100% N$_2$</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>360</td>
<td>100% N$_2$</td>
<td>15% CO$_2$, 85% N$_2$</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>20 (cooling)</td>
<td>100% N$_2$</td>
<td>100% N$_2$</td>
</tr>
</tbody>
</table>

2.2.3.4 Calculation of Initial CO$_2$ Absorption Rates

A CO$_2$ absorption curve was calculated for each amine by subtracting the mass at time $t$ of the evaporation run from the mass at time $t$ of the absorption run. An example is provided in Figure 2-8 for an aqueous solution of PZ. It can be seen from Figure 2-8 that the initial mass increase of the amine solution (between $t = 180$ and $t = 678$ secs (3 to 11.3 mins)) follows a linear trend with a correlation coefficient ($R^2$ value) $\geq 0.995$. The slope of the absorption curve in this linear region was used to estimate the initial CO$_2$ absorption rate (mol / mol.s$^{-1}$) of the amine solution.
2. Experimental Design

![Graph showing the absorption curve obtained using the TGA method.](image1)

**Figure 2-8.**

**a)** The absorption curve obtained using the TGA method, showing moles of CO$_2$ absorbed per mole of amine ($n_{\text{CO}_2} / n_{\text{amine}}$) as function of time $t$ for an aqueous piperazine (1.5 mol L$^{-1}$) solution. The red dashed line, between $t = 180$ and $t = 678$ secs (3 to 11.3 mins), is the linear region used to calculate the initial CO$_2$ absorption rate; and **b)** Shows the linear relationship of the curve in this region, with the slope of the curve (4.53 mol / mol.min$^{-1}$ (x $10^{2}$)) taken as the initial CO$_2$ absorption rate.

$$y = 4.53E-02x + 3.83E-02$$

$R^2 = 9.95E-01$
Due to the lack of mixing, this method is influenced by the liquid properties of the amine solution such as viscosity and surface tension, so the calculated rate does not necessarily represent the intrinsic reaction kinetics.\cite{124} However this method did allow a relative comparison of the initial CO$_2$ absorption rates for the subset of amines tested as 1.5 mol L$^{-1}$ solutions.

The advantage of using the TGA method is that it requires only milligrams of material allowing testing of amines difficult to obtain, such as those synthesised in small quantities. The WWC technique on the other hand required between 80 - 130 g of amine (1 mol L$^{-1}$) for a single experiment.

The apparatuses and experimental procedures described in this chapter have been designed in-house by CSIRO’s staff specifically for the testing and characterisation of amine absorbents for the PCC process.
3 Conventional Amines

3.1 Introduction

This chapter focuses on developing and validating in-situ ATR FT-IR spectroscopy as a viable method for monitoring carbamate / bicarbonate speciation in an amine / CO\(_2\) / H\(_2\)O system. To achieve this, amines that are well established in the gas scrubbing industry (‘conventional amines’) were selected for analysis. The amines investigated include primary amine MEA, secondary amine DEA, tertiary amine MDEA and C\(_\alpha\)-substituted amine AMP. MEA is considered the industry standard.

As mentioned previously in Section 1.4.2, it is well established in the literature that primary and secondary amines typically react with CO\(_2\) in an aqueous environment to form a carbamate. Whereas, tertiary amines cannot react directly with CO\(_2\) to form a carbamate due to the absence of hydrogen atoms bonded directly to the nitrogen atom (Section 1.4.3). Instead tertiary amines form bicarbonate via a base-catalysed reaction pathway.\(^{[20, 38, 49]}\) Primary amines with one or more substituents at C\(_\alpha\) are an exception to the generalised reaction pathway identified above for primary amines. The dominant reaction product for these amines is bicarbonate (Section 1.5.1).\(^{[21, 36, 48, 54-56]}\)

The amines investigated in this chapter were analysed using the CO\(_2\) absorption / FT-IR apparatus described in Section 2.1. The chemical species formed during the absorption process (carbamate, bicarbonate and protonated amine) were identified using the infrared absorbance of characteristic functional groups such as carboxylates and amino compounds. There are few examples of infrared analysis of carbamate species in the literature, and this is the first report of in-situ infrared monitoring of aqueous amine / CO\(_2\) / H\(_2\)O system. The results are detailed below.
3. Conventional Amines

3.2 Primary and Secondary Amines

3.2.1 MEA / CO₂ / H₂O System

Although the spectra was scanned from 4000-650 cm⁻¹, the infrared spectral window 1750-950 cm⁻¹ was focused on for monitoring the chemical species evolving in solution as CO₂ was being absorbed by the amine. This spectral region contained well-defined peaks and the most relevant information. The region above 1750 cm⁻¹ contains a ‘blind spot’ were the diamond of the ATR probe absorbs (2250-1950 cm⁻¹) and the broad O-H stretch of water is situated and of significant intensity. The region below 950 cm⁻¹ is the superimposition of multiple absorbing species in the amine / CO₂ / H₂O system. All spectra presented in this thesis are in the 1750-950 cm⁻¹ spectral window.

Figure 3-1 shows the infrared spectral changes that occur in the 1750-950 cm⁻¹ region as CO₂ is absorbed by an aqueous MEA solution. The most striking feature in the original aqueous MEA spectra and subsequent spectra is the broad absorbance band arising at 1643 cm⁻¹. This band is present in the spectrum of pure water and has been assigned to the O-H bending mode of water.⁴¹²⁵,⁴¹²⁶

![Infrared Spectral Profile for MEA (3 mol L⁻¹) from no CO₂ loading to a maximum loading of 0.56 mol CO₂ / mol amine in the region of interest.](image-url)
MEA is a primary amine and will typically react with CO$_2$ to form a carbamate and protonated amine. Figure 3-1 shows four major infrared absorbance bands to evolve with CO$_2$ absorption. These bands are therefore assigned to the formation of 2-hydroxyethylcarbamate (MEA-carbamate) and/or protonated MEA (MEA-H$^+$). Specific assignment of these bands is detailed below.

Three of the four major absorbance bands were assigned to the vibrational modes of 2-hydroxyethylcarbamate, as shown in Figure 3-1. The N-COO$^-$ stretching vibration ($\nu_{N-COO^-}$) at 1322 cm$^{-1}$ and the asymmetric and symmetric COO$^-$ stretching vibrations ($\nu_{asCOO^-}$ and $\nu_{sCOO^-}$) of the carboxylate moiety at 1567 cm$^{-1}$ (strong) and 1386 cm$^{-1}$ (weaker) respectively. The $\nu_{asCOO^-}$ signal was more intense than $\nu_{sCOO^-}$. This is consistent with the literature on the infrared absorbance of carboxylates, with the asymmetric stretch of carboxylates reported to be the more intense of these two bands.$^{[126]}$ Further confirmation of these assignments was provided in subsequent studies in which examined the carbamate derivatives of heterocyclic amines (Sections 4.1 and 5.1). The main purpose of this preliminary study was to establish that carbamate and bicarbonate formed as result of the reaction between CO$_2$ and aqueous amines could be identified and monitored using in-situ FT-IR spectroscopy. This is evident in Figure 3-1.

The absorbance bands at 1075 and 1026 cm$^{-1}$ in Figure 3-1 and 0 mol CO$_2$/ mol amine were assigned to the N-C(H$_2$) and C-O(H) stretch of MEA$^{[116, 127]}$ respectively. The intermolecular interactions between the amine moiety and CO$_2$ during the absorption process results in a shift in the N-C(H$_2$) stretch to 1069 cm$^{-1}$. The C-O stretch undergoes a similar shift in frequency to 1016 cm$^{-1}$.

The absorbance band that evolves at 1492 cm$^{-1}$ was assigned to MEA-H$^+$. This assignment was based on the R-NH$_3^+$ stretching frequency of $\alpha$-amino acids, which have been reported to absorb in the 1530-1490 cm$^{-1}$ region of the spectrum.$^{[128, 129]}$ The positions of the N-H stretching bands are sensitive to the degree of hydrogen bonding, both intermolecular and intramolecular, in a sample.$^{[126]}$

The shoulder that emerges in the 1360-1350 cm$^{-1}$ region at higher CO$_2$ loadings (> 0.5 mol CO$_2$ / mol amine) was tentatively assigned to the corresponding formation of bicarbonate. As can be seen in Figure 3-1 this band was partially obscured by the more intense neighbouring $\nu_{N-COO^-}$ and $\nu_{sCOO^-}$ absorbance bands of 2-hydroxyethylcarbamate at 1322 cm$^{-1}$ and 1386 cm$^{-1}$ respectively.

There are two possible reaction pathways that can lead to the formation of bicarbonate in an
aqueous amine environment. The first pathway is via the hydrolysis of the carbamate species (Equation 1 and 2, [34, 36, 41, 130] Scheme 3-1). The second pathway is via the direct nucleophilic attack of OH⁻ on dissolved CO₂ (Equation 3 and 4,[20, 34, 41, 130, 131] Scheme 3-1). The second pathway is the base-catalysed reaction mechanism of tertiary amines (Section 1.4.3). In aqueous amine solutions the contribution of the un-catalysed hydration of CO₂ is reported to be negligible.[131, 132] A degree of carbamate hydrolysis was anticipated with most primary and secondary amines.[36] This would account for the CO₂ loading of MEA exceeding 0.5 mol CO₂/mol amine and the observation of bicarbonate absorbance in the MEA / CO₂ / H₂O spectra at CO₂ loadings above this (Figure 3-1). However, as mentioned previously in Section 1.4.2 it has yet to be directly observed.

\[
\begin{align*}
R'R''NH + CO₂ + B & \rightleftharpoons R'R''NC(=O)O' + BH^+ & (1) \\
R'R''NC(=O)O' + H₂O & \rightleftharpoons R'R''NH + HCO₃^- & (2) \\
R'R''R'''N + H₂O & \rightleftharpoons R'R''R'''NH + OH^- & (3) \\
OH^- + CO₂ & \rightleftharpoons HCO₃^- & (4)
\end{align*}
\]

Scheme 3-1. A set of equilibria equations for the reaction between amines and CO₂ in an aqueous environment. Equation (1) is the reaction of a primary / secondary amine with CO₂ to form a carbamate. Base ‘B’ in Equation (1) is typically a second amine molecule, though it can also be a molecule of water or OH⁻; Equation (2) is the hydrolysis of the carbamate to generate bicarbonate and a free amine; Equations (3) and (4) shows the reported base-catalysed reaction pathway observed with tertiary amines.

For the spectral peaks assigned to the vibrational modes of 2-hydroxyethylcarbamate (1567 cm⁻¹, 1386 cm⁻¹ and 1322 cm⁻¹) and MEA-H⁺ (1492 cm⁻¹) Figure 3-2 shows that a near linear relationship existed between the intensity of infrared peak absorbance and cumulative CO₂ absorption at low CO₂ loadings (< 0.5 mol CO₂/mol amine). As the CO₂ loading exceeds 0.5 mol CO₂/mol amine, there was a slight change in the absorbance curves of the four peaks. This may be attributed to a decrease in the amount of free amine available to react with CO₂ or the onset of a new reaction pathway such as the hydrolysis of carbamate to bicarbonate.
3. Conventional Amines

For the primary and secondary amines carbamate formation was expected to be rapid upon introduction of CO₂ to the amine solution. The intensity of the infrared shoulder emerging between 1360 and 1350 cm⁻¹ in Figure 3-2 increased more slowly with time, with quite a significant increase above a CO₂ loading of 0.5 mol CO₂ / mol amine. Given the frequency of this peak and the apparent increase in growth rate at loadings > 0.5 mol CO₂ / mol amine, this was assigned as indicative of bicarbonate formation. The frequency of the bicarbonate absorbance band in an amine / CO₂ / H₂O system was confirmed by separate experiments that are detailed below (Section 3.3 and 3.4).

3.2.2 DEA / CO₂ / H₂O System

The sequential infrared spectra for a DEA / CO₂ / H₂O system recorded in the 1750-950 cm⁻¹ region is shown in Figure 3-3. The infrared spectra presented is somewhat similar to that of the MEA / CO₂ / H₂O system (Figure 3-1), with the exception that five major FT-IR peaks are shown to evolve with CO₂ absorption. Only four major peaks were seen to evolve in the MEA / CO₂ / H₂O system. There are also slight shifts in key infrared stretching frequencies.
3. Conventional Amines

![Infrared spectral profile for DEA (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.60 mol CO\(_2\) / mol amine in the region of interest.](image)

Of the five major FT-IR peaks, three were assigned to the vibrational modes of the carbamate species bis(hydroxyethyl)carbamate (DEA-carbamate) including \(\nu_{\text{N-COO}^-}\) at 1302 cm\(^{-1}\) and the \(\nu_{\text{asCOO}^-}\) and \(\nu_{\text{COO}^-}\) of the carboxylate moiety at 1533 and 1414 cm\(^{-1}\) respectively. Both the \(\nu_{\text{N-COO}^-}\) and the \(\nu_{\text{asCOO}^-}\) of bis(hydroxyethyl)carbamate are detected at a lower frequency than that observed for the corresponding 2-hydroxyethylcarbamate (1326 and 1567 cm\(^{-1}\) respectively). The \(\nu_{\text{asCOO}^-}\) band was found to shift to a higher frequency. This trend in \(\nu_{\text{asCOO}^-}\) and \(\nu_{\text{COO}^-}\) was consistent with results reported by Cabaniss and McVey\(^{[133]}\), who investigated the ATR FT-IR spectra of a series of aliphatic monocarboxylates (formate through to hexanoate). They found the \(\nu_{\text{asCOO}^-}\) frequency to decrease as the number of carbon atoms N increased from 2 to 6 and \(\nu_{\text{COO}^-}\) mirrored this trend, increasing in frequency as N increased.\(^{[133]}\)

The absorbance band that evolves at 1481 cm\(^{-1}\) was assigned to protonated DEA (DEA-H\(^+\)). Further confirmation of this assignment is provided in succeeding chapters with regards to protonated secondary cyclic amines including piperidine and piperazine (Section 4.1.1.2 and 5.1.1 respectively).

For the spectral peaks assigned to the vibrational modes of bis(hydroxyethyl)carbamate
(1533, 1414 and 1302 cm\(^{-1}\)) and DEA-H\(^+\) (1481 cm\(^{-1}\)) a near linear relationship was found to exist between infrared peak absorbance and cumulative CO\(_2\) absorption at low CO\(_2\) loadings (Figure 3-4), similar to that observed for the MEA / CO\(_2\) / H\(_2\)O system (c.f. Figure 3-2). Peak absorbance is observed to increase at the rate of carbamate formation at the reaction onset and slowly decline as the CO\(_2\) loading exceeds 0.5 mol CO\(_2\) / mol amine. Again, this is most likely due to the hydrolysis of the carbamate derivative to bicarbonate.

The broad absorbance band that emerges at around 1360 cm\(^{-1}\) in Figure 3-3, and assigned as indicative of bicarbonate formation, is far more prominent than that observed for the MEA / CO\(_2\) / H\(_2\)O system (c.f. Figure 3-1). This is reflected in the slightly higher absorption capacity obtained for DEA (0.6 mol CO\(_2\) / mol amine) compared to MEA (0.56 mol CO\(_2\) / mol amine).

The following chapters describe a structure-activity relationship study for a series of heterocyclic monoamines and diamines to shed more light on the chemistry of carbamate hydrolysis.
3.3 Tertiary Amines

3.3.1 MDEA / CO$_2$ / H$_2$O System

MDEA is a tertiary amine, and as such bicarbonate formation was the preferred chemical reaction pathway for the absorption of CO$_2$. The infrared spectral data obtained for this amine has therefore been used as a baseline for bicarbonate formation in an amine / CO$_2$ / H$_2$O system.

The sequential infrared spectra for a MDEA / CO$_2$ / H$_2$O system recorded in the 1750-950 cm$^{-1}$ region is shown in Figure 3-5. The spectra presented shows the evolution of a broad absorbance band in the 1360-1350 cm$^{-1}$ region (peak maxima = 1358 cm$^{-1}$). This broad absorbance band is accompanied by a smaller absorbance band at 1304 cm$^{-1}$. The frequency of these two bands is in good agreement with published data.$^{[115]}$

![Infrared spectral profile for MDEA (3 mol L$^{-1}$) from no CO$_2$ loading to a loading of 0.27 mol CO$_2$ / mol amine in the region of interest.](image)

Figure 3-5.
Falk & Miller investigated the infrared spectrum of CO$_2$ in aqueous solution, reporting bicarbonate to give rise to multiple bands, including a main absorbance band at 1360 cm$^{-1}$ ($\nu_{\text{C-O}}$) and two smaller absorbance bands near 1300 and 1240 cm$^{-1}$.[115]

### 3.4 Sterically-Hindered Amines

#### 3.4.1 AMP / CO$_2$ / H$_2$O System

The sequential infrared spectra for an AMP / CO$_2$ / H$_2$O system recorded in the 1750-950 cm$^{-1}$ region is shown in Figure 3-6. The spectral data presented shows the evolution of a broad absorbance band in the 1360-1350 cm$^{-1}$ region (peak maxima at 1358 cm$^{-1}$), similar to that observed with the MDEA / CO$_2$ / H$_2$O system, though of increased intensity.

![Infrared spectral profile for AMP (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.84 mol CO$_2$/mol amine in the region of interest.](image)

Figure 3-6. Infrared spectral profile for AMP (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.84 mol CO$_2$/mol amine in the region of interest.

Figure 3-6 also shows the evolution of an additional absorbance band at 1540 cm$^{-1}$. The frequency of this band does correspond with the assigned $\nu_{\text{asCOO}^-}$ carbamate stretching
frequencies at 1567 and 1533 cm\(^{-1}\) in the un-substituted analogues MEA and DEA / CO\(_2\) / H\(_2\)O systems respectively (Figure 3-3 and 3-1 respectively). This band was not observed in the MDEA / CO\(_2\) / H\(_2\)O system (Figure 3-5). It is therefore tentatively assigned to carbamate formation in the AMP / CO\(_2\) / H\(_2\)O system. Further confirmation of this assignment and the ability of sterically-hindered amines to form a carbamate in an amine / CO\(_2\) / H\(_2\)O system is provided in Section 4.3.3.

The results presented in this chapter demonstrate that both carbamate and bicarbonate formation can be monitored in an amine / CO\(_2\) / H\(_2\)O system using \textit{in-situ} ATR FT-IR spectroscopy. This technique can be utilised in the structure-activity relationship analysis of heterocyclic amines.
4 Heterocyclic Amines I: Functionalised Piperidines

4.1 Introduction

In the previous chapter, it was demonstrated that ATR FT-IR spectroscopy could be used to monitor in-situ the reaction occurring between CO$_2$ and amines during the absorption process. This chapter will outline the application of this technique as part of a structure-activity relationship study on a series of heterocyclic monoamines.

The monoamines examined in this chapter include piperidine, as well as commercially available functionalised piperidine derivatives, such as alkyl, hydroxyl and hydroxyalkyl substituted analogues. Figure 4-1 provides the names and chemical structures of the amines analysed.

The effect of structure on CO$_2$ / amine reactivity has been investigated as follows:

i. The infrared active reaction products including, carbamate versus bicarbonate formation with cumulative CO$_2$ absorption.

ii. CO$_2$ absorption capacity. This parameter was measured simultaneously with the infrared spectral data, as described in Section 2.1.

iii. Initial rate of CO$_2$ absorption. This parameter was measured using the wetted wall column (WWC) technique described in Section 2.2.2.

iv. Correlation between the atomic properties of the amine and carbamate derivative with the infrared spectral data, CO$_2$ absorption capacity and initial absorption rate. The computational approach used to calculate atomic properties is described in Section 4.2.
4. Heterocyclic Amines I: Functionalised Piperidines

Figure 4-1. Structures for the subset of functionalised piperidines examined in this study

Alkyl Substitution

N-methylpiperidine (1-MP)
2-methylpiperidine (2-MP)
3-methylpiperidine (3-MP)
4-methylpiperidine (4-MP)

Hydroxy Substitution

N-hydroxypiperidine (1-HP)
3-hydroxy piperidine (3-HP)
4-hydroxypiperidine (4-HP)

Hydroxyalkyl Substitution

2-(hydroxymethyl)piperidine (2-PM)
3-(hydroxymethyl)piperidine (3-PM)
4-(hydroxymethyl)piperidine (4-PM)

N-(2-hydroxyethyl)piperidine (1-PE)
2-(2-hydroxyethyl)piperidine (2-PE)
4-(2-hydroxyethyl)piperidine (4-PE)
4.2 Computational Details

Calculations were carried out using density functional theory (DFT) and \textit{ab initio} Møller-Plesset second-order (MP2) perturbation theory. These were performed to calculate and compare optimised geometries (gas-phase) of the heterocyclic amines and their carbamate derivatives.

DFT calculations were employed as they are computationally economical and, thus, applicable to larger molecules such as the amines investigated. DFT have also been reported to yield accurate geometries and reasonable vibration frequencies.\cite{134, 135} DFT calculations were conducted at the B3LYP level of theory. MP2 calculations were performed for comparative purposes.

The initial geometries of the heterocyclic amines and carbamates were calculated using molecular mechanics approaches based on the MMFF94 force field and a Monte-Carlo search algorithm was used to obtain a set of low energy conformers for each species.

Each subset of low energy conformers were then optimised at the B3LYP / 6-31+G** and MP2 / 6-31+G** level of theory, to obtain an equilibrium geometry corresponding to an energy minima (characterised by a gradient < 0.001). The optimised structures were confirmed to be true minima by vibrational frequencies calculations. There were no imaginary frequencies.

The gas-phase harmonic frequency and intensity calculations were also used to guide in the assignment of the experimental carbamate vibrational modes. All calculations were performed with the ‘Spartan 08’\cite{114} computational software package, using the default parameters.

4.3 Infrared Spectral Data

4.3.1 Piperidine

The sequential infrared spectra collected for a piperidine / CO\textsubscript{2} / H\textsubscript{2}O system recorded in the 1750-950 cm\textsuperscript{-1} region is shown in Figure 4-2. The spectra were collected during a typical CO\textsubscript{2} absorption / FT-IR experiment (Section 2.1).
The infrared spectral profile presented in Figure 4-2 is similar to that of the DEA / CO\textsubscript{2} / H\textsubscript{2}O system discussed in the previous chapter. Five major FT-IR peaks can be seen to evolve with CO\textsubscript{2} absorption and are assigned to the vibrational modes of the potential reaction products including:

i. Piperidine-1-carboxylate (piperidine-carbamate);

ii. Protonated piperidine (piperidine-H\textsuperscript{+}); and

iii. Bicarbonate (HCO\textsubscript{3}\textsuperscript{-}).

Piperidine is a secondary amine, similar to DEA, and was expected to react with CO\textsubscript{2} in solution to form a carbamate derivative. Assignment of the spectral peaks that evolved is detailed below.

4.3.1.1 Vibrational Modes of Piperidine-1-carboxylate

Of the five main peaks observed, three were assigned to the stretching frequencies of
4. Heterocyclic Amines I: Functionalised Piperidines

4.1  Piperidine-1-carboxylate, as shown in Figure 4-2:

i. 1283 cm\(^{-1}\) - \(\nu_{N\text{-}COO}\) of the carboxylate moiety

ii. 1434 cm\(^{-1}\) - \(\nu_{s\text{-}COO}\) of the carboxylate moiety

iii. 1514 cm\(^{-1}\) - \(\nu_{as\text{-}COO}\) of the carboxylate moiety

Although the carbamate species is a carboxylic acid derivative (R'R''NC\(_{2}\)), it does not give rise to the typical strong carbonyl (C=O) absorbance band around 1700 cm\(^{-1}\). The electron distribution of the COO\(^{-}\) group of the deprotonated carboxylic acid diffuses across both C-O bonds equivalently to stabilise the carboxylate moiety. The two oxygen atoms become coupled, giving rise two absorbance bands, an asymmetric (\(\nu_{as\text{-}COO}\)) and symmetric (\(\nu_{s\text{-}COO}\)) COO\(^{-}\) stretch. These two bands occur at lower frequencies than the \(\nu_{C=O}\) of carboxylic acids.\[126]\n
Geometry optimisation of piperidine-1-carboxylate revealed both C-O bond lengths to be identical with \(r_{N\text{-}C} = 1.258 \, \text{Å} \) (B3LYP) and \(r_{N\text{-}C} = 1.264 \, \text{Å} \) (MP2). The partial negative charges on both oxygen atoms were also identical.

The frequency of the \(\nu_{as\text{-}COO}\) (1514 cm\(^{-1}\)) and \(\nu_{s\text{-}COO}\) (1434 cm\(^{-1}\)) of piperidine-1-carboxylate agree well with literature values for carboxylate \(\nu_{as\text{-}COO}\) and \(\nu_{s\text{-}COO}\) vibrations, which place the signals between 1650-1540 cm\(^{-1}\) and 1450-1360 cm\(^{-1}\) respectively, depending on the molecular constituents.\[126, 133\] The \(\nu_{as\text{-}COO}\) and \(\nu_{s\text{-}COO}\) of 2-hydroxyethylcarbamate (1567 cm\(^{-1}\) and 1386 cm\(^{-1}\) respectively) and bis(hydroxyethyl)carbamate (1533 cm\(^{-1}\) and 1414 cm\(^{-1}\) respectively), investigated in the previous chapter (Section 3.1) also agree well with the literature values.

The \(\nu_{as\text{-}COO}\) of piperidine-1-carboxylate occurs at a lower frequency than that of bis(hydroxyethyl)carbamate and 2-hydroxyethylcarbamate. The \(\nu_{s\text{-}COO}\) vibration occurs at a higher frequency. This is consistent with the results of Cabaniss and McVey\[133\] and the trend in \(\nu_{as\text{-}COO}\) and \(\nu_{s\text{-}COO}\) frequencies observed for bis(hydroxyethyl)carbamate and 2-hydroxyethylcarbamate in Section 3.2. The \(\nu_{as\text{-}COO}\) vibration shifts to a lower frequency as the carbon chain length increases from \(n= 2\) (MEA) to \(n= 5\) (piperidine) and the \(\nu_{s\text{-}COO}\) vibration shifts to a higher frequency.

As the infrared stretching frequencies of aqueous carbamates have not been previously reported, gas phase frequency and intensity calculations were used to aid in the assignment of key vibrational modes. See Section 4.2 for computational details.

The B3LYP calculations placed the \(\nu_{N\text{-}COO}\) of piperidine-1-carboxylate as a single intense
band at 1289 cm\(^{-1}\), similar in shape to that emerging at 1283 cm\(^{-1}\) in Figure 4-2. The MP2 calculations placed this band at 1287 cm\(^{-1}\). No frequency scaling factors were applied in the B3LYP and MP2 calculations. The calculated values agree well with the experimentally observed \(\nu_{N-COO}\) frequency of 1283 cm\(^{-1}\), despite the exclusion of anharmonic effects and solvent corrections in the calculations. A similar correlation between predicted and experimental values was also obtained for the \(\nu_{N-COO}\) band of 2-hydroxyethylcarbamate at 1322 cm\(^{-1}\) (Figure 3-1), 1311 cm\(^{-1}\) (B3LYP) and 1329 cm\(^{-1}\) (MP2); and bis(hydroxyethyl)carbamate at 1302 cm\(^{-1}\) (Figure 3-3), 1304 cm\(^{-1}\) (B3LYP) and 1313 cm\(^{-1}\) (MP2).

The B3LYP calculations also predicted a much smaller \(\nu_{N-COO}\) absorbance band at 1337 cm\(^{-1}\). The MP2 calculations placed this band at 1350 cm\(^{-1}\). In Figure 4-2, a small peak can be seen evolving at 1354 cm\(^{-1}\) in the initial stages of CO\(_2\) absorption. However, after a CO\(_2\) loading of about 0.5 mol CO\(_2\) / mol amine this peak becomes consumed by a much broader absorbance band. This broad peak has been attributed to the formation of bicarbonate via the carbamate hydrolysis pathway at high CO\(_2\) loadings (> 0.5 mol CO\(_2\) / mol amine) (Section 4.3.1.3). However, due to the superimposition of these two absorbance bands it is difficult to accurately assign. Further evidence with regards to these two assignments is discussed below in Section 4.3.1.3 and 4.3.3.1.

The \(\nu_{N-COO}\) absorbance band at 1283 cm\(^{-1}\) in Figure 4-2, was accompanied by a smaller band at 1261 cm\(^{-1}\). This band was assigned to the \((R')H_2C-N(CO_2)-CH_2(R')\) stretch (\(\nu_{C-N-C}\)) of piperidine-1-carboxylate. A similar absorbance band was also observed at the same frequency (1261 cm\(^{-1}\)) in the DEA / CO\(_2\) / H\(_2\)O shown in Figure 3-3, though broader in shape. This band was not observed in the spectra obtained for the MEA / CO\(_2\) / H\(_2\)O system (Figure 3-1). The B3LYP calculations placed the \(\nu_{C-N-C}\) absorbance of piperidine-1-carboxylate at 1289 cm\(^{-1}\). The MP2 calculations placed this band at 1299 cm\(^{-1}\). This coincides with the calculated \(\nu_{N-COO}\) frequency at 1289 cm\(^{-1}\) (B3LYP) and 1287 cm\(^{-1}\) (MP2). The \(\nu_{C-N-C}\) absorbance was predicted to be less intense then the \(\nu_{N-COO}\) absorbance.

The B3LYP calculations for the \(\nu_{asCOO}\) and \(\nu_{sCOO}\) of piperidine-1-carboxylate did not agree well with the experimental results. \(\nu_{asCOO}\) absorbance was placed as a single intense absorbance band at 1694 cm\(^{-1}\) (1704 cm\(^{-1}\) (MP2)). \(\nu_{sCOO}\) was placed as a very weak absorbance band at 1402 cm\(^{-1}\) (B3LYP) (1423 cm\(^{-1}\) (MP2)). Similar results were obtained for 2-hydroxyethylcarbamate and bis(hydroxyethyl)carbamate.

Both the symmetric and asymmetric COO\(^-\) stretching modes are appreciably affected by anharmonicity and solvation effects\(^{136}\) compared to the N-COO\(^-\) stretching mode. This would
account for the large differences between the experimental solution phase and calculated gas phase results obtained for $\nu_{s\text{COO}}^-$ and $\nu_{as\text{COO}}^-$. 

### 4.3.1.2 Vibrational modes of Piperidine-$H^+$

The absorbance band that appears at 1477 cm$^{-1}$, in Figure 4-2, has been assigned to the NH$_2^+$ bending mode of piperidine-$H^+$. To confirm this assignment spectral data was collected during the gradual acidification of the original piperidine solution using hydrochloric acid (HCl) (36 wt %, Sigma Aldrich) (Figure 4-3). Figure 4-3 shows a small peak evolving at around 1477 cm$^{-1}$ on protonation of the amine functionality.

![Infrared spectral profile for piperidine (3 mol L$^{-1}$) before and after acidification with hydrochloric acid in the region of interest.](image)

The B3LYP calculations predicted piperidine-$H^+$ to have two NH$_2^+$ bending modes, one at 1661 cm$^{-1}$ (scissoring) and another at 1437 cm$^{-1}$ (wagging). The MP2 calculations placed these two bands at 1675 cm$^{-1}$ and 1465 cm$^{-1}$ respectively. The wagging vibration was predicted to be the more intense of the two vibrations. The calculated values for the NH$_2^+$ wagging vibration are in reasonably good agreement with the experimental value of 1477 cm$^{-1}$. 

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An absorbance band in the 1700-1620 cm\(^{-1}\) region was expected to evolve in both the piperidine / CO\(_2\) / H\(_2\)O and piperidine / HCl / H\(_2\)O systems.\(^{[128]}\) However, this region is obscured by the dominant broad water absorbance band at 1643 cm\(^{-1}\), as can been seen in Figure 4-2 and 4-3. The 1643 cm\(^{-1}\) absorbance band did however increase in intensity with increasing CO\(_2\) absorption and HCl concentration respectively.

The calculated and experimental values obtained for piperidine-H\(^+\) are consistent with those obtained for DEA-H\(^+\). The B3LYP calculations predicted two NH\(_2\)\(^+\) bending modes for DEA-H\(^+\), one at 1674 cm\(^{-1}\) (scissoring) and another at 1453 cm\(^{-1}\) (wagging). These values were calculated to be 1696 cm\(^{-1}\) and 1467 cm\(^{-1}\) respectively, using the MP2 approach. The wagging vibration was predicted to be the more intense of the two vibrations. The calculated values obtained for the wagging vibration at 1453 cm\(^{-1}\) (B3LYP) and 1467 cm\(^{-1}\) (MP2) are in reasonable good agreement with the experimentally observed DEA-H\(^+\) frequency of 1481 cm\(^{-1}\) in Figure 3-3 (Section 3.2.2).

A similar correlation between theoretical and experimental vibrational frequencies was also obtained for MEA-H\(^+\). In the MEA / CO\(_2\) / H\(_2\)O system, shown in Figure 3-1 (Section 3.2.1), the absorbance band that evolved at 1492 cm\(^{-1}\) was assigned to the NH\(_3\)\(^+\) stretching frequency. The B3LYP calculations predicted MEA-H\(^+\) to have two NH\(_3\)\(^+\) bending modes, one at 1650 cm\(^{-1}\) (twisting) and another at 1512 cm\(^{-1}\) (scissoring). These values were calculated to be 1681 cm\(^{-1}\) and 1532 cm\(^{-1}\) respectively, using the MP2 approach.

### 4.3.1.3 Bicarbonate Formation

For the spectral peaks assigned to the vibrational modes of piperidine-1-carboxylate (1514, 1434 and 1283 cm\(^{-1}\)) and piperidine-H\(^+\) (1477 cm\(^{-1}\)) a near linear relationship was found to exist between the intensity of infrared peak absorbance and cumulative CO\(_2\) absorption at low CO\(_2\) loadings (< 0.5 mol CO\(_2\) / mol amine), as shown in Figure 4-4. Peak absorbance was observed to increase at the rate of carbamate formation at the reaction onset and decrease after a loading of 0.5 mol CO\(_2\) / mol amine. This decrease in peak absorbance was much more pronounced in Figure 4-2 and 4-4 for the piperidine / CO\(_2\) / H\(_2\)O system than that observed for the MEA or DEA / CO\(_2\) / H\(_2\)O systems discussed in the previous chapter (Section 3.2) and shown in Figure 3-1 and 3-2, and Figure 3-3 and 3-4 respectively. As mentioned in Section 3.2, this change in peak absorbance at high CO\(_2\) loadings was attributed to the sequential onset of a new reaction pathway such as the hydrolysis of the carbamate species to bicarbonate.
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Figure 4-4. Plot of the cumulative CO$_2$ absorption by piperidine (3 mol L$^{-1}$) against infrared peak absorbance for the bands assigned to the vibrational modes piperidine-1-carboxylate (1514, 1434, 1283 cm$^{-1}$), piperidine-H$^+$ (1477 cm$^{-1}$) and bicarbonate (1354 cm$^{-1}$).

The relationship between infrared peak absorbance and cumulative CO$_2$ absorption for the spectral peaks assigned to piperidine-1-carboxylate and piperidine-H$^+$ can be distinguished from that observed for the broad absorbance band that evolves in the 1400-1300 cm$^{-1}$ region (peak maxima at 1354 cm$^{-1}$). This band shows a corresponding increase in peak absorbance after a loading of 0.5 mol CO$_2$/mol amine, as shown in Figure 4-4. This band has been assigned to the $\nu_{\text{C-O}}$ of bicarbonate. The frequency of this band is in good agreement with literature values for aqueous bicarbonate (1360 cm$^{-1}$)$^{[115, 125]}$ as well as the spectral data collected for the MDEA and AMP / CO$_2$/ H$_2$O systems and shown in Figures 3-5 and 3-6 respectively (Section 3.2.1 and 3.3 respectively).

As mentioned in the preceding chapter there are two possible reaction pathways that can lead to the formation of bicarbonate in an amine / CO$_2$/ H$_2$O system, i.e. via the -

i. hydrolysis of the carbamate derivative (Section 4.3.5) or

ii. direct nucleophilic attack of OH$^-$ on dissolved CO$_2$ (base-catalysed) (Section 1.4.3).
The infrared spectral data collected for the piperidine / CO\textsubscript{2} / H\textsubscript{2}O system and presented in Figure 4-2 and 4-4 was illustrative of the first of these two pathways, with the simultaneous decline in absorbance of the \( \nu_{\text{asCOO}^-} \), \( \nu_{\text{sCOO}^-} \) and \( \nu_{\text{N-COO}^-} \) of piperidine-1-carboxylate and increase in bicarbonate absorbance.

Both the MEA and DEA / CO\textsubscript{2} / H\textsubscript{2}O systems discussed previously in Section 3.1 showed some evidence of bicarbonate formation, with a less intense broad peak evolving in the 1360-1350 cm\(^{-1}\) region at higher CO\textsubscript{2} loadings ( > 0.5 mol CO\textsubscript{2} / mol amine). However, MEA and DEA did not show to the same extent the simultaneous decline in carbamate absorbance and increase in bicarbonate absorbance as that observed for the piperidine / CO\textsubscript{2} / H\textsubscript{2}O system (c.f. Figure 3-2, 3-4 and 4-4 respectively). Based on the infrared spectral data collected for these amines, piperidine-1-carboxylate was much more susceptible to hydrolysis and the formation of bicarbonate at high CO\textsubscript{2} loadings compared with 2-hydroxyethylcarbamate and bis(hydroxyethyl)carbamate.

4.3.2 Effect of \( N\)-Methyl, Hydroxyl and Hydroxyalkyl Substituent’s

\( N\)-Methylpiperidine (1-MP), \( N\)-hydroxypiperidine (1-HP) and \( N\)-hydroxyethylpiperidine (1-PE) are cyclic tertiary amines and cannot react directly with CO\textsubscript{2} to form a carbamate. These amines form bicarbonate via the base-catalysed reaction pathway discussed in Section 1.4.3. For this reason their activity will not be compared to the set of secondary heterocyclic amines investigated here.

The infrared spectral data collected for these tertiary amines further demonstrate bicarbonate absorbance in an amine / CO\textsubscript{2} / H\textsubscript{2}O system. The results obtained for these amines also illustrate the effect different \( N\)-substituent’s can have on CO\textsubscript{2} absorption via the base-catalysis reaction pathway.

The sequential infrared spectral profile collected for a 1-PE / CO\textsubscript{2} / H\textsubscript{2}O system recorded in the 1750-950 cm\(^{-1}\) region is shown in Figure 4-5. The characteristic broad bicarbonate \( \nu_{\text{C-O}} \) absorbance band can be seen evolving in the 1400-1300 cm\(^{-1}\) region (peak maxima at 1354 cm\(^{-1}\)), similar to that observed for the MDEA / CO\textsubscript{2} / H\textsubscript{2}O system shown in Figure 3-5. This absorbance band was also accompanied by the smaller bicarbonate \( \nu_{\text{C-O}} \) band at 1300 cm\(^{-1}\). The same broad absorbance band was also observed in the infrared spectral data collected for the 1-MP / CO\textsubscript{2} / H\textsubscript{2}O system (peak maxima at 1360 cm\(^{-1}\)), for which the spectra is not shown.
Figure 4-5. Infrared spectral profile for 1-PE (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a loading of 0.27 mol CO\(_2\)/mol amine in the region of interest.

The 1-HP / CO\(_2\) / H\(_2\)O system was an exception. The infrared spectral profile obtained showed no spectral changes for the duration of the experiment, as shown in Figure 4-6. The tertiary amine 1-HP did not absorb CO\(_2\). It appears that the N-hydroxyl moiety in 1-HP inhibits a tertiary amine’s ability to act as a catalyst in the base-catalysed hydrolysis of CO\(_2\) to bicarbonate compared to the alkyl or hydroxyalkyl substituent in 1-PM and 1-PE respectively.
4.3.3 Effect of 2- Methyl and Hydroxyalkyl Substituent’s

2-Methylpiperidine (2-MP), 2-(hydroxymethyl)piperidine (2-PM) and 2-(2-hydroxyethyl)piperidine (2-PE) are the Cα-substituted analogues of piperidine (or ‘sterically-hindered amines’ in industry parlance). For this reason they were expected to form predominately bicarbonate on absorption of CO₂, similar to that of AMP (Cα-dimethyl substituted analogue of MEA).

The infrared spectral data collected for the 2-MP, 2-PM and 2-PE / CO₂ / H₂O systems differ significantly from that obtained for the piperidine / CO₂ / H₂O system. However, their spectra are similar to that of the 1-MP, 1-PE and AMP / CO₂/ H₂O systems. The infrared spectral profiles presented in Figures 4-7, 4-8 and 4-9 for 2-MP, 2-PM and 2-PE respectively, show the evolution of the characteristic broad bicarbonate absorbance band in the 1400-1300 cm⁻¹ region. This band is much more intense than that observed for the tertiary amine / CO₂ / H₂O systems.
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Figure 4-7. Infrared spectral profile for 2-MP (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.93 mol CO\(_2\)/mol amine in the region of interest.

Figure 4-8. Infrared spectral profile for 2-PM (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.85 mol CO\(_2\)/mol amine in the region of interest.
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![Infrared spectral profile for 2-PE (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.87 mol CO\(_2\)/mol amine in the region of interest.](image)

A noticeable difference between the infrared spectral data presented in Figures 4-7, 4-8 and 4-9 for the secondary C\(\alpha\)-substituted amine / CO\(_2\) / H\(_2\)O systems and that of the primary C\(\alpha\)-substituted amine (AMP) / CO\(_2\) / H\(_2\)O system shown in Figure 3-6 was the absence of the 1540 cm\(^{-1}\) absorbance band. This absorbance band was observed in the sequential infrared spectral data collected for the AMP / CO\(_2\) / H\(_2\)O system. The frequency of this band corresponds with the \(\nu_{\text{SCOO}}\) carbamate stretching frequency observed for the un-substituted MEA and DEA / CO\(_2\) / H\(_2\)O systems at 1567 cm\(^{-1}\) and 1533 cm\(^{-1}\) in Figures 3-1 and 3-3 respectively.

Another noticeable difference was the evolution of absorbance bands at 1420 cm\(^{-1}\) and 1279 cm\(^{-1}\) in Figures 4-7, 4-8 and 4-9. These bands were not observed for the AMP / CO\(_2\) / H\(_2\)O system (Figure 3-6). The 1420 cm\(^{-1}\) and 1279 cm\(^{-1}\) absorbance bands were seen to evolve at the reaction onset and cease to increase in intensity or decrease with respect to the 1420 cm\(^{-1}\) absorbance band after a loading of 0.4 mol CO\(_2\)/mol amine. With increasing CO\(_2\) absorption these two bands become superimposed by the broad bicarbonate peak. The frequency of these two bands correspond with the \(\nu_{\text{SCOO}}\) and \(\nu_{\text{NCOO}}\) carbamate stretching frequencies of the piperidine / CO\(_2\) / H\(_2\)O system at 1434 cm\(^{-1}\) and 1283 cm\(^{-1}\) respectively and shown on Figure 4-2.

Given the frequency of the absorbance bands at 1420 cm\(^{-1}\) and 1279 cm\(^{-1}\) in the 2-PM, 2-PM
and 2-PE / CO₂ / H₂O systems, and that at 1540 cm⁻¹ in the AMP / CO₂ / H₂O system, these bands were associated with a small degree of carbamate formation during the initial stages of CO₂ absorption. A closer look at the infrared spectral profiles of the un-substituted analogues piperidine and AMP respectively, further substantiated this.

A noticeable difference between the infrared spectral profile of the piperidine / CO₂ / H₂O system shown in Figure 4-2 and the MEA / CO₂ / H₂O system shown in Figure 3-1 was the difference in intensities of the bands assigned to the υₘCOO⁻ and υₛCOO⁻ of piperidine-1-carboxylate and 2-hydroxyethylcarbamate respectively. In the primary amine (MEA) system the υₘCOO⁻ of 2-hydroxyethylcarbamate was much more intense than υₛCOO⁻. It was also more intense than the υₘCOO⁻ of piperidine-1-carboxylate. In the secondary amine (piperidine) system the opposite was observed with the υₛCOO⁻ of piperidine-1-carboxylate being the more intense of the two absorbance bands and more intense than the υₘCOO⁻ of 2-hydroxyethylcarbamate (c.f. Figure 4-2 and 3-1). This trend was also reflected in the infrared spectral profile collected for the Cα-substituted analogues. The υₘCOO⁻ band was observable in the primary Cα-substituted amine AMP / CO₂ / H₂O system at 1540 cm⁻¹, however it was not observed in the secondary Cα-substituted amines 2-MP, 2-PM and 2-PE / CO₂ / H₂O systems. In contrast, the υₛCOO⁻ band was observable in the 2-MP, 2-PM and 2-PE / CO₂ / H₂O systems and not in the AMP / CO₂ / H₂O system.

### 4.3.3.1 Observation of the Carbamate Derivatives of Cα-Substituted Amines

As mentioned in Section 1.5.1, a common misconception for amines with one or more substituent’s at the α-carbon (e.g. AMP), or in this study 2-methyl, 2-hydroxymethyl and 2-hydroxyethyl substituted piperidine’s, is that they are sterically-hindered and unable to form a carbamate. Only recently has the direct observation of Cα-substituted carbamate anions been reported.⁴Jackson et al. [34] directly observed the carbamate derivatives of the Cα-substituted amines AMP and tris(hydroxymethyl)aminomethane (THAM) using negative-ion electrospray ionization mass spectrometry (ESI-MS). The carbamate derivatives were formed as a result of the reaction between sodium bicarbonate (NaHCO₃) and the Cα-substituted amines in aqueous solution. The results obtained provided evidence of the existence of Cα-substituted carbamate anions. However, it has still not been established whether they form directly via the reaction with CO₂ or bicarbonate during the absorption process.

In this study, in-situ ATR FT-IR spectroscopy has been used to observe the carbamate derivatives of 2-MP, 2-PM and 2-PE in real time as a result of the reaction with gaseous CO₂ at low partial pressures (13 %). Spectral data was collected during CO₂ absorption experiments
In the absence of water, bicarbonate formation via the CO$_2$ or carbamate hydrolysis pathway should be suppressed. To confirm the inhibition of bicarbonate formation spectral data was collected during the CO$_2$ irradiation of a tertiary amine (1-PE) / hexanol solution. The spectra presented in Figure 4-10 shows there to be no spectral changes in the 1750-950 cm$^{-1}$ region for the duration of the experiment (Run Time = 20 mins), as would be expected with a 1-PE / CO$_2$ / H$_2$O system and shown in Figure 4-5. The 1-PE / hexanol solution did not absorb any CO$_2$ due to the inhibition of bicarbonate formation.

![Figure 4-10](image-url)

**Figure 4-10.** Infrared spectral profile for a 1-PE / hexanol solution (3 mol L$^{-1}$) after exposure to CO$_2$ for 20 mins in the region of interest.

For comparison and to also establish the formation of carbamate species in a non-aqueous environment, spectral data was also collected for a piperidine / CO$_2$ / hexanol system and shown in Figure 4-11. The piperidine / hexanol solution absorbed CO$_2$ to an upper limit of 0.5 mol CO$_2$ / mol amine, as opposed to the upper limit of 0.76 mol CO$_2$ / mol amine obtained for the aqueous piperidine solution (Figure 4-2).
The spectra presented in Figure 4-11 shows the evolution of piperidine-1-carboxylate and piperidine-H⁺ absorbance bands including ν_{asCOO} at 1540 cm⁻¹, ν_{asCOO} at 1425 cm⁻¹, ν_{N-COO} at 1279 cm⁻¹ and ν_{C-N-C} at 1257 cm⁻¹; and one of the NH₂⁺ bending modes (scissoring) at 1643 cm⁻¹. The NH₂⁺ bending mode observed at 1643 cm⁻¹ in the piperidine / CO₂ / hexanol system was not observed in Figure 4-2 for the piperidine / CO₂ / H₂O system. This was due to the overlapping strong absorbance of water in this region of the aqueous amine system (Section 4.3.1.2). The NH₂⁺ wagging absorbance band observed at 1477 cm⁻¹ in the piperidine / CO₂ / H₂O system is not observable in the spectral data presented in Figure 4-11 for the piperidine / CO₂ / hexanol system. This was due to the overlapping strong absorbances of the original piperidine / hexanol solution in this region.

Also absent in the piperidine / CO₂ / hexanol system shown in Figure 4-11 was the broad absorbance band in the 1400-1300 cm⁻¹ region (peak maxima at 1354 cm⁻¹). This band was present in the piperidine / CO₂ / H₂O system shown in Figure 4-2 and was assigned to bicarbonate formation; however, Figure 4-11 does show a small peak growing at 1354 cm⁻¹. This small peak is similar to that observed at 1354 cm⁻¹ in the piperidine / CO₂ / H₂O system during the initial stages of CO₂ absorption. It was thought to arise from the ν_{N-COO}⁻ of
piperidine-1-carboxylate (Section 4.3.1.1). With increasing CO$_2$ absorption in the aqueous piperidine solution this peak was consumed by the evolution of the much broader bicarbonate absorbance band. The presence of this absorbance band in Figure 4-11 confirms its association with carbamate formation.

In the absence of water, 2-MP, 2-PM and 2-PE were found to absorb a small amount of CO$_2$, unlike the tertiary amine 1-PE. The infrared spectral profiles obtained for 2-MP, 2-PM and 2-PE showed the evolution of the same absorbance bands as observed for the piperidine / CO$_2$ / hexanol system. Although somewhat weaker the bands included the NH$_2^+$ bending mode of 2-MP-H$^+$, 2-PM-H$^+$ and 2-PE-H$^+$ at 1641-1638 cm$^{-1}$; and the 2-methylpiperidine-1-carboxylate, 2-(hydroxymethyl)piperidine-1-carboxylate and 2-(2-hydroxyethyl)piperidine-1-carboxylate $\nu_{\text{as COO}^-}$ at 1538-1536 cm$^{-1}$, $\nu_{\text{s COO}^-}$ at 1417-1416 cm$^{-1}$ and $\nu_{\text{N-COO}^-}$ at 1278-1276 cm$^{-1}$. Figures 4-12 and 4-13 show the sequential infrared spectra collected for a 2-PE and 2-MP / CO$_2$ / hexanol system respectively.

![Infrared spectral profile for a 2-PE / hexanol solution (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.30 mol CO$_2$ / mol amine in the region of interest.](image-url)
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As the intensity of these absorbance bands is weak, further confirmation of the existence of these anions was established by ESI-MS analysis and the method utilised by Jackson et al. in their detection of carbamate anions. Briefly, aqueous solutions of 2-MP, 2-PM and 2-PE (130-150 µg mL\(^{-1}\)) with NaHCO\(_3\) (50-70 µg mL\(^{-1}\)) (99.9 %, Sigma Aldrich) were analysed using a Waters Acquity HPLC-MS system. The carbamate derivatives of 2-MP (\(m/z = 141.9\)), 2-PM (\(m/z = 158.0\)), 2-PE (\(m/z = 172.0\)) were observed in the negative ion ESI-MS broad scan spectrum.

A peak corresponding to the loss of CO\(_2\) (\(m/z = 44\)) was also evident in the multiple collision-induced dissociation (CID) spectrum of the 2-MP-carbamate parent ion (2-methylpiperidine-1-carboxylate) as shown in Figure 4-14. However in the case of the 2-PM and 2-PE carbamate parent ions (2-(hydroxymethyl)piperidine-1-carboxylate and 2-(2-hydroxyethyl)piperidine-1-carboxylate respectively), a mass loss of 46 was evident in their CID spectrum. Figure 4-15 presents the CID spectrum obtained for 2-(2-hydroxyethyl)piperidine-1-carboxylate. A mass loss of 46 was also observed by Jackson et al. in the CID spectrum they obtained for the carbamate derivative of DEA. The carbamate derivatives of 2-PM and 2-PE, as well as DEA, both have exchangeable hydrogen’s on the hydroxyl group of the alkyl side chain.
that is within close proximity of the carboxylate moiety, similar to that of the anions of α-
hydroxy carboxylic acids. These anions are known to dissociate by eliminating a mass of 46,
which corresponds to the loss of formic acid.\cite{138}

The infrared spectral and ESI-MS data presented in this section confirms our observation of
carbamate hydrolysis in the amine / CO\textsubscript{2} / H\textsubscript{2}O systems.

Figure 4-14. Negative-ion low energy CID spectrum of 2-methylpiperidine-1-carboxylate (m/z =
141.9).\cite{137}
4.3.4 Effect of 3- and 4- Methyl, Hydroxyl and Hydroxyalkyl Substituent’s

The infrared spectral data obtained for the 3- and 4- methylpiperidine (3-MP and 4-MP), 3- and 4- hydroxy piperidine (3-HP and 4-HP), 3- and 4- (hydroxymethyl)piperidine (3-PM and 4-PM) and 4-(2-hydroxyethyl)piperidine (4-PE) / CO\textsubscript{2} / H\textsubscript{2}O systems illustrate a high degree of similarity with that of the piperidine / CO\textsubscript{2} / H\textsubscript{2}O system. This is in terms of both their infrared spectral profile and the relationship between peak absorbance and cumulative CO\textsubscript{2} absorption for the peaks assigned to carbamate, protonated amine and bicarbonate.

Table 4-1 provides a brief summary of the frequencies assigned to the protonated amine and carbamate \(\nu_{\text{amCOO}}, \nu_{\text{COO}},\) and \(\nu_{\text{NCOO}}\) stretching frequencies. For comparison the vibrational frequencies of piperidine-1-carboxylate and piperidine-H\textsuperscript{+} have also been included. From Table 4-1 it can be seen that there is excellent correlation with difference in frequencies not exceeding 7 cm\(^{-1}\). There are a few differences in the infrared spectral data collected, particularly with regards to bicarbonate formation and carbamate hydrolysis in the 3-HP and 4-HP / CO\textsubscript{2} / H\textsubscript{2}O systems. These are discussed below.
Table 4-1. Comparison of the frequencies assigned to $\nu_{\text{asCOO}^-}$, $\nu_{\text{sCOO}^-}$, $\nu_{\text{N-COO}^-}$ and $\text{NH}_2^+$ for piperidine and the 3- and 4- methyl, hydroxyl and hydroxyalkyl substituted piperidines.

<table>
<thead>
<tr>
<th>Amine / CO$_2$ / H$_2$O System</th>
<th>Infrared Vibrational Modes and Frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu_{\text{asCOO}^-}$</td>
</tr>
<tr>
<td>piperidine</td>
<td>1514</td>
</tr>
<tr>
<td>3-MP</td>
<td>1519</td>
</tr>
<tr>
<td>4-MP</td>
<td>1519</td>
</tr>
<tr>
<td>3-HP</td>
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<tr>
<td>4-PM</td>
<td>1516</td>
</tr>
<tr>
<td>4-PE</td>
<td>1520</td>
</tr>
</tbody>
</table>

4.3.4.1 3- and 4- methylpiperidine

For the 3-MP and 4-MP / CO$_2$ / H$_2$O systems, Figures 4-16 and 4-17 respectively presents:

a) The infrared spectral profile as CO$_2$ is absorbed into solution, and 

b) A plot of cumulative CO$_2$ absorption against the intensity of infrared peak absorbance for the spectral peaks assigned to carbamate, protonated amine and bicarbonate.

The spectral data presented in Figures 4-16a and 4-17a both show a single broad peak emerging in the 1300-1250 cm$^{-1}$ region (peak maxima at 1276 cm$^{-1}$ and 1272-1261 cm$^{-1}$ respectively). This differed from the piperidine / CO$_2$ / H$_2$O system in Figure 4-2, which showed two peaks in this region including $\nu_{\text{N-COO}^-}$ at 1283 cm$^{-1}$ and $\nu_{\text{C-N-C}}$ at 1261 cm$^{-1}$. 

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Figure 4-16. **a)** Infrared spectral profile for 3-MP (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.75 mol CO\(_2\) / mol amine in the region of interest; and **b)** Plot of cumulative CO\(_2\) absorption against infrared peak absorbance for the bands assigned to 3-methylpiperidine-1-carboxylate (1519, 1429, 1276 cm\(^{-1}\)), 3-MP-H\(^+\) (1474 cm\(^{-1}\)) and bicarbonate (1354 cm\(^{-1}\)).
Figure 4-17.  a) Infrared spectral profile for 4-MP (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.76 mol CO$_2$ / mol amine in the region of interest; and b) Plot of cumulative CO$_2$ absorption against infrared peak absorbance for the bands assigned to 4-methylpiperidine-1-carboxylate (1519, 1429, 1272 cm$^{-1}$), 4-MP-H$^+$ (1477 cm$^{-1}$) and bicarbonate (1358 cm$^{-1}$).
In the 3-MP and 4-MP / CO\(_2\) / H\(_2\)O systems a peak can also be seen evolving at 1313 cm\(^{-1}\). This peak was not evident in the piperidine / CO\(_2\) / H\(_2\)O system. This was attributed to the strong absorbance of the original aqueous piperidine solution in this region. This band has been assigned to the \(\nu_{C,N-C}\) of 3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate.

The B3LYP calculations placed the \(\nu_{N-COO^-}\) of 3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate as a single intense band in the 1285-1271 cm\(^{-1}\) region. These values were calculated to be 1286-1284 cm\(^{-1}\) using the MP2 approach. Absorbance due to the \(\nu_{C,N-C}\) of 3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate were also placed in the same region with less intense absorbances at 1289 cm\(^{-1}\) and 1290 cm\(^{-1}\) respectively. These values were calculated to be 1255 cm\(^{-1}\) and 1298 cm\(^{-1}\); and 1254 cm\(^{-1}\) respectively using the MP2 approach.

The superimposition of \(\nu_{C,N-C}\) (minor) and \(\nu_{N-COO^-}\) (major) absorbance would contribute to the broad character of the single peak observed in the 1300-1250 cm\(^{-1}\) region of the 3-MP and 4-MP / CO\(_2\) / H\(_2\)O systems. For ease this band has been simply assigned \(\nu_{N-COO^-}\) in Table 4-1, given that this vibrational mode is the largest contributor of the two N-C stretching vibrations. The \(\nu_{C,N-C}\) and \(\nu_{N-COO^-}\) of piperidine-1-carboxylate were better resolved in this region.

The \(\nu_{C,N-C}\) of 3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate were also predicted to give rise to a smaller absorbance band at around 1313 cm\(^{-1}\) and 1321 cm\(^{-1}\) respectively. These values were calculated to be 1303 cm\(^{-1}\) and 1309 cm\(^{-1}\) respectively using the MP2 approach. These values agree well with the observed band at 1313 cm\(^{-1}\) in the 3-MP and 4-MP / CO\(_2\) / H\(_2\)O systems. The nearby strong absorbance of the original aqueous 4-MP solution contributes to the increased intensity of this band in Figure 4-17a, compared to that observed for 3-MP in Figure 4-16a.

The small \(\nu_{N-COO^-}\) absorbance band in the 1360-1350 cm\(^{-1}\) region can be seen in Figures 16a and 17a. Similar to that of the piperidine / CO\(_2\) / H\(_2\)O system this band becomes consumed by the broad bicarbonate absorbance band with increasing CO\(_2\) absorption. B3LYP calculations placed this band at 1338 cm\(^{-1}\) and 1339 cm\(^{-1}\) for 3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate respectively. These values were calculated to be 1346 cm\(^{-1}\) and 1355 cm\(^{-1}\) respectively using the MP2 approach.

Table 4-2 provides a summary of the calculated frequency values for the carbamate \(\nu_{N-COO^-}\) and \(\nu_{C,N-C}\) stretching frequencies. The results highlight the coincidence of these two absorbances in the 1300–1250 cm\(^{-1}\) region. Of the two vibrational modes \(\nu_{N-COO^-}\) absorbance is the most
significant, with $\nu_{C-N-C}$ being much weaker.

Table 4-2. B3LYP and MP2 calculated frequencies for the carbamate $\nu_{N-COO}$ and $\nu_{C-N-C}$ absorbance bands.

<table>
<thead>
<tr>
<th>Carbamate</th>
<th>B3LYP</th>
<th>MP2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\nu_{N-COO}$ (cm$^{-1}$)</td>
<td>$\nu_{C-N-C}$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>Piperidine-1-carboxylate</td>
<td>1289</td>
<td>1289</td>
</tr>
<tr>
<td></td>
<td>1337</td>
<td>1313</td>
</tr>
<tr>
<td>3-methylpiperidine-1-carboxylate</td>
<td>1280</td>
<td>1271</td>
</tr>
<tr>
<td></td>
<td>1287</td>
<td>1289</td>
</tr>
<tr>
<td></td>
<td>1338</td>
<td>1313</td>
</tr>
<tr>
<td>4-methylpiperidine-1-carboxylate</td>
<td>1271</td>
<td>1290</td>
</tr>
<tr>
<td></td>
<td>1339</td>
<td>1321</td>
</tr>
<tr>
<td>3-hydroxypiperidine-1-carboxylate</td>
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<td>1258</td>
</tr>
<tr>
<td></td>
<td>1351</td>
<td>1284</td>
</tr>
<tr>
<td>4-hydroxypiperidine-1-carboxylate</td>
<td>1287</td>
<td>1289</td>
</tr>
<tr>
<td></td>
<td>1333</td>
<td>1310</td>
</tr>
<tr>
<td>3-(hydroxymethyl)piperidine-1-carboxylate</td>
<td>1289</td>
<td>1271</td>
</tr>
<tr>
<td></td>
<td>1353</td>
<td>1289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1308</td>
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<tr>
<td>4-(hydroxymethyl)piperidine-1-carboxylate</td>
<td>1270</td>
<td>1289</td>
</tr>
<tr>
<td></td>
<td>1291</td>
<td>1298</td>
</tr>
<tr>
<td></td>
<td>1339</td>
<td>1321</td>
</tr>
<tr>
<td>4-(2-hydroxyethyl)piperidine-1-carboxylate</td>
<td>1280</td>
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</tr>
<tr>
<td></td>
<td>1309</td>
<td>1291</td>
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<td></td>
<td>1336</td>
<td>1309</td>
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</tbody>
</table>

Both the sequential infrared spectral data and the peak absorbance versus cumulative CO$_2$ absorption curve, presented in Figures 4-16 and 4-17, clearly illustrate the hydrolysis of the 3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate to bicarbonate at high CO$_2$ loadings (> 0.5 mol CO$_2$ / mol amine).
4.3.4.2 3- and 4- hydroxyalkylpiperidine

For 3-PM, 4-PM and 4-PE / CO\textsubscript{2} / H\textsubscript{2}O systems, Figures 4-18, 4-19 and 4-20 respectively, presents:

a) The infrared spectral profile as CO\textsubscript{2} is absorbed into solution, and

b) A plot of cumulative CO\textsubscript{2} absorption against the intensity of infrared peak absorbance for the spectral peaks assigned to carbamate, protonated amine and bicarbonate.

Both the 3-PM and 4-PE / CO\textsubscript{2} / H\textsubscript{2}O systems show the evolution of a single broad $\nu_{N-COO^-}$ absorbance band in the 1300-1250 cm\textsuperscript{-1} region (peak maxima at 1276 cm\textsuperscript{-1} and 1281 cm\textsuperscript{-1} respectively), along with a smaller $\nu_{C-N-C}$ peak at 1300 cm\textsuperscript{-1} and 1315 cm\textsuperscript{-1} respectively. This could be distinguished from the 4-PM / CO\textsubscript{2} / H\textsubscript{2}O system which shows the evolution of multiple peaks in this region (1274 cm\textsuperscript{-1} and 1296 cm\textsuperscript{-1}), arising from both $\nu_{N-COO^-}$ and $\nu_{C-N-C}$ vibrations. The superimposition of absorbance from the two different N-C stretching modes, $\nu_{N-COO^-}$ (major) and $\nu_{C-N-C}$ (minor), contributes to the broad character of the bands in this region.

The increased intensity of the $\nu_{C-N-C}$ absorbance band evolving at 1317 cm\textsuperscript{-1} in the spectral data collected for 4-PM, compared to that of 3-PM and 4-PE, was attributed to the strong absorbance of the original aqueous 4-PM solution in this region. The small 1360-1350 cm\textsuperscript{-1} $\nu_{N-COO^-}$ absorbance band was evident in the infrared spectral data collected for 3-PM and 4-PM. With increasing CO\textsubscript{2} absorption this band was consumed by the broad bicarbonate absorbance band.

The calculated $\nu_{N-COO^-}$ and $\nu_{C-N-C}$ frequencies presented in Table 4-2 were in good agreement with experimental values obtained for 3-(hydroxymethyl)piperidine-1-carboxylate, 4-(hydroxymethyl)piperidine-1-carboxylate and 4-(2-hydroxyethyl)piperidine-1-carboxylate.

Both the sequential infrared spectral data and peak absorbance versus cumulative CO\textsubscript{2} absorption curve presented in Figures 4-18, 4-19 and 4-20 clearly illustrate the hydrolysis of the 3-(hydroxymethyl)piperidine-1-carboxylate, 4-(hydroxymethyl)piperidine-1-carboxylate and 4-(2-hydroxyethyl)piperidine-1-carboxylate to bicarbonate at high CO\textsubscript{2} loadings (≥ 0.5 mol CO\textsubscript{2} / mol amine) respectively.
4. Heterocyclic Amines I: Functionalised Piperidines

**Figure 4-18.** a) Infrared spectral profile for 3-PM (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.74 mol CO$_2$ / mol amine in the region of interest; and b) Plot of cumulative CO$_2$ absorption and infrared peak absorbance for the bands assigned to 3-(hydroxymethyl)piperidine-1-carboxylate (1516, 1430, 1276 cm$^{-1}$), 3-PM-H$^+$ (1477 cm$^{-1}$) and bicarbonate (1354 cm$^{-1}$).
Figure 4-19.  

a) Infrared spectral profile for 4-PM (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.74 mol CO$_2$/mol amine in the region of interest; and b) Plot of cumulative CO$_2$ absorption against infrared peak absorbance for the bands assigned to 4-(hydroxymethyl)piperidine-1-carboxylate (1516, 1434, 1274 cm$^{-1}$), 4-PM-H$^+$ (1477 cm$^{-1}$) and bicarbonate (1356 cm$^{-1}$).
4. Heterocyclic Amines I: Functionalised Piperidines

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**Figure 4-20.**

a) Infrared spectral profile for 4-(2-hydroxyethyl)piperidine (4-PE) (3 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.74 mol CO$_2$ / mol amine in the region of interest; and b) Plot of cumulative CO$_2$ absorption against infrared peak absorbance for the bands assigned to 4-(2-hydroxyethyl)piperidine-1-carboxylate (1520, 1432, 1281 cm$^{-1}$), 4-PE-H$^+$ (1477 cm$^{-1}$) and bicarbonate (1356 cm$^{-1}$).
4.3.4.3 3- and 4- hydroxypiperidine

For 3-HP and 4-HP / CO\textsubscript{2} / H\textsubscript{2}O systems, Figures 4-21 and 4-22 respectively presents:

a) The infrared spectral profile as CO\textsubscript{2} is absorbed into solution, and

b) A plot of cumulative CO\textsubscript{2} absorption against the intensity of infrared peak absorbance for the spectral peaks assigned to carbamate, protonated amine and bicarbonate.

The 3-HP / CO\textsubscript{2} / H\textsubscript{2}O system shows a single broad $\nu_{N\text{-}COO^-}$ absorbance band in the 1300-1250 cm\textsuperscript{-1} region (peak maxima at 1278 cm\textsuperscript{-1}), along with the smaller $\nu_{C\text{-}N\text{-}C}$ absorbance band at 1313 cm\textsuperscript{-1}. This could be distinguished from the 4-HP / CO\textsubscript{2} / H\textsubscript{2}O system which showed two sharp absorbance bands at 1276 cm\textsuperscript{-1} ($\nu_{N\text{-}COO^-}$) and 1250 cm\textsuperscript{-1} ($\nu_{C\text{-}N\text{-}C}$) in this region, similar to that of the piperidine / CO\textsubscript{2} / H\textsubscript{2}O system shown on Figure 4-2. The smaller $\nu_{C\text{-}N\text{-}C}$ absorbance band above 1300 cm\textsuperscript{-1} was not as evident in the 4-HP / CO\textsubscript{2} / H\textsubscript{2}O system. This was attributed to the nearby strong absorbance of the original aqueous 4-HP solution, as well as the broad $\nu_{N\text{-}COO^-}$ peak at 1276 cm\textsuperscript{-1}. The small $\nu_{N\text{-}COO^-}$ absorbance band in the 1360-1350 cm\textsuperscript{-1} region was evident in both the 3-HP and 4-HP / CO\textsubscript{2} / H\textsubscript{2}O systems.

The calculated $\nu_{N\text{-}COO^-}$ and $\nu_{C\text{-}N\text{-}C}$ frequencies presented in Table 4-2 were in good agreement with experimental values obtained for 3-hydroxypiperidine-1-carboxylate and 4-hydroxypiperidine-1-carboxylate.

Based on the infrared spectral data presented in Figures 4-21 and 4-22, 3-hydroxypiperidine-1-carboxylate and 4-hydroxypiperidine-1-carboxylate were less susceptible to hydrolysis than piperidine-1-carboxylate and the other 3- and 4- substituted carbamate derivatives.

Hydrolysis of 3-hydroxypiperidine-1-carboxylate and 4-hydroxypiperidine-1-carboxylate at high CO\textsubscript{2} loadings (> 0.5 mol CO\textsubscript{2} / mol amine) was evident in the infrared spectral data presented in 4-21a and 4-22a respectively. However, the bicarbonate absorbance band in the 1400-1300 cm\textsuperscript{-1} region was not as prominent as that seen to evolve within the piperidine, 3MP, 4MP, 3PM, 4PM and 4PE / CO\textsubscript{2} / H\textsubscript{2}O systems shown in Figures 4-2 and 4-16 to 4-20 respectively. The strong absorbance of the original aqueous 4-HP solution in this region contributed to the intensity and odd shape of the absorbance band seen to evolve.
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Figure 4-21.  

**a)** Infrared spectral profile for 3-HP (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.61 mol CO\(_2\)/mol amine in the region of interest; and **b)** Plot of cumulative CO\(_2\) absorption against infrared peak absorbance for the bands assigned to 3-hydroxypiperidine-1-carboxylate (1521, 1429, 1278 cm\(^{-1}\)), 3-HP-H\(^+\) (1477 cm\(^{-1}\)) and bicarbonate (1354 cm\(^{-1}\)).
4. Heterocyclic Amines I: Functionalised Piperidines

Figure 4-22. a) Infrared spectral profile for 4-HP (3 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.61 mol CO\(_2\)/mol amine in the region of interest; and b) Plot of cumulative CO\(_2\) absorption against infrared peak absorbance for the bands assigned to 4-hydroxypiperidine-1-carboxylate (1521, 1432, 1276 cm\(^{-1}\)), 4-HP-H\(^+\) (1478 cm\(^{-1}\)) and bicarbonate (1354 cm\(^{-1}\)).
The peak absorbance versus cumulative CO$_2$ absorption curve presented in Figures 4-21b and 4-22b also, does not show to the same extent the simultaneous decline in carbamate absorbance and increase in bicarbonate absorbance as that observed for piperidine and the other 3- and 4- substituted piperidines. Further evidence with regards to the carbamate derivatives of 3-HP and 4-HP being less susceptible to hydrolysis is discussed below in terms of their absorption capacity (Section 4.4).

4.3.5 Carbamate Hydrolysis

From the infrared spectral data presented in this and the preceding chapter, we have been able to observe the hydrolysis of secondary amine carbamate derivatives at high CO$_2$ loadings (> 0.5 mol CO$_2$ / mol amine) during the CO$_2$ absorption process. In this section the mechanism by which these carbamate species are hydrolysed will be discussed. It is important when considering the hydrolysis of the carbamate species (R'R"NCOO') formed as result of the reaction between CO$_2$ and primary or secondary amines, is that these species are differentiated from the ester type carbamates of general formula R'R"NCOOR, which hydrolyse to generate an alcohol and carbamic acid (R'R"NCOOH).

The hydrolysis of primary carbamate esters (R' or R" = H) (1) proceeds via an elimination pathway with an isocyanate intermediate (2), which reacts further with H$_2$O or OH$^-$ to afford the carbamic acid (3), as shown in Scheme 4-1. Secondary carbamates (4) proceed via a base catalysed mechanism involving the direct nucleophilic attack of OH on the carbonyl carbon and the formation of a tetrahedral intermediate (5). The intermediate breaks down into the alcohol and carbamic acid (3), as shown in Scheme 4-2. For both primary and secondary carbamate esters the alkoxide (OR) is the leaving group. The carbamate species analysed in this study (R'R"NCOO') cannot hydrolyse via ether of these mechanisms.

The direct nucleophilic attack of OH on secondary (R' or R" = H) and tertiary amides of general formula R'R"NOR (6) follows a course analogous to that of secondary carbamate esters. With the exception that N'R'R" (amide anion), rather than OR (alkoxide), is the leaving group. The reaction mechanism is shown in Scheme 4-3. The addition of the OH ion to an amide occurs with relative ease to produce a monoanion tetrahedral intermediate (7). However, the thermodynamically preferred route for the breakdown of the intermediate is the loss of the hydroxide to regenerate the amide (6) rather than expulsion of the N'R'R" group. For this reason, the base-catalysed hydrolysis of secondary amides in aqueous solution is not a very efficient process, with the expulsion of water being competitive with expulsion of the leaving group.
Scheme 4-1. Hydrolysis of primary esterified carbamates (1), via an elimination pathway to produce an isocyanate intermediate (2) and the corresponding alcohol. The intermediate reacts further with H₂O or `OH to afford the carbamic acid (3).

Scheme 4-2. Hydrolysis of secondary esterified carbamates (4) via the direct nucleophilic attack of OH⁻ on the carbonyl carbon to form a monoanion tetrahedral intermediate (5). From which cleavage of the `OR group generates the corresponding alcohol and carbamic acid (3).
Scheme 4-3. Hydrolysis of tertiary amides (6) via the direct nucleophilic attack of \( \text{OH} \) on the carbonyl carbon to form a monoanion tetrahedral intermediate (7). In the presence of an excess of strong base (\( \text{OH} \)) a dianion tetrahedral intermediate (8) can form. From which cleavage of the \( \text{-NR}^\prime\text{R}'' \) group occurs to generate the corresponding carboxylate anion (9) and amine (10).

However, in the case of tertiary amides the presence of an excess of strong base (\( \text{OH} \)) can remove the hydroxylic proton of the monoamine intermediate (7) to generate a dianion tetrahedral intermediate (8) (Scheme 4-3). From this intermediate cleavage of the \( \text{-NR}^\prime\text{R}'' \) group can occur with ease to generate the corresponding carboxylate anion (9) and amine (10).

It has not been established whether the expelled amide anion does exist as a discrete entity or whether on expulsion from the tetrahedral intermediate it is simultaneously protonated by the aqueous solvent. In an aqueous environment the participation of water molecules have been shown to play a key role in the base-catalysed hydrolysis pathway. The direct reaction of amide with a water molecule (neutral hydrolysis) has also been found to play a role, however the preferred mechanism is the direct nucleophilic attack by \( \text{OH} \).

In summary, the mechanistic pathways by which amides and esterfied carbamates are hydrolysed are well characterised and have been extensively studied experimentally and theoretically.

The secondary amine carbamate derivatives (11) investigated in this study, e.g. piperidine-1-
carboxylate, have been shown to hydrolyse in an aqueous environment (pH 8-10) to generate the corresponding amine (10) and bicarbonate. The hydrolytic breakdown of these species involves hydrolysis of essentially an N, N-disubstituted amide bond. The proposed reaction mechanism is provided in Scheme 4-4. Analogous to the hydrolysis of tertiary amides, the reaction may proceed via the direct nucleophilic attack of \( \text{OH}^- \) on the highly electrophilic carbonyl carbon of the carbamate species to form a dianion tetrahedral intermediate (12). The intermediate decomposes to bicarbonate and the corresponding amine (10). Given the presence of a negatively charged oxygen atom in the carbamate species itself, addition of the hydroxide ion would lead directly to the dianion intermediate without the need of excess base to remove the hydroxylic proton, such as that required for tertiary amides (Scheme 4-3).

Scheme 4-4. Hydrolysis of secondary carbamates (11), such as piperidine-1-carboxylate, in an aqueous environment (pH 8-10) via the direct nucleophilic attack of \( \text{OH}^- \) on the carbonyl carbon of the carbamate species to form a dianion tetrahedral intermediate (12), which could decompose to bicarbonate and the corresponding amine (10).

The infrared spectral data presented in this and the preceding chapter shows secondary amine carbamate derivatives, e.g. piperidine-1-carboxylate and bis(hydroxyethyl)carbamate, to be
more susceptible to hydrolysis than primary amine carbamate derivatives, e.g. 2-hydroxyethylcarbamate. This was consistent with the base-catalysed hydrolysis of tertiary and secondary amides. Tertiary amides preferentially hydrolyse compared to secondary amides. The tetrahedral intermediates of primary and secondary amides tended to regenerate reactants\textsuperscript{[144, 145, 151, 152]} This has been attributed to the amine leaving ability from the tetrahedral intermediate, with $R_2NH > RNH_2 > NH_3$.\textsuperscript{[152]}

In this study the presence of a hydroxyl group 2-3 carbon atoms removed from the amino nitrogen, such as that in 3- and 4-hydroxypiperidine-1-carboxylate and bis(hydroxyethyl)carbamate, was also shown to reduce the susceptibility of the carbamate species to hydrolysis (Section 4.3.4.3 and 3.2.2 respectively).

### 4.4 CO\textsubscript{2} Absorption Capacity and Initial Absorption Rate

To quantify the effect molecular structure has on CO\textsubscript{2} / amine reactivity the CO\textsubscript{2} absorption capacity ($C_A$) and initial absorption rate ($K_G$) were determined for each amine.

The CO\textsubscript{2} absorption capacity was measured simultaneously with the infrared spectral data during a typical absorption / FT-IR experiment (Section 2.1). The WWC technique described in Section 2.2.2 was used to analyse the initial absorption rate of CO\textsubscript{2} into 1 mol L\textsuperscript{-1} aqueous amine solutions. The change in concentration from 3 mol L\textsuperscript{-1} to 1 mol L\textsuperscript{-1} between the two different experimental techniques arose from the large volume of solution (1L) required for a WWC experiment and consequently the availability of the amines. A typical CO\textsubscript{2} absorption / FT-IR experiment required a solution volume of only 30 mL, allowing for a higher concentration to be tested.

The measured $C_A$ and $K_G$ values are presented in Table 4-3. For comparison of reactivity, the $C_A$ and $K_G$ values obtained for conventional amine-based absorbents MEA, DEA and AMP (dimethyl substituted MEA) have been included in Table 4-3. Table 4-3 also provides the selected atomic properties including, electrostatic potential (ESP) partial charge on the amino nitrogen and the exposed area on the nitrogen for optimised geometries of the heterocyclic amines. The trend in results at the two levels of theory was found to be in good agreement of one another. For computational details see Section 4.2.
Table 4-3. Measured absorption capacity ($C_A$) at 40 °C and 3 mol L$^{-1}$ amine concentrations; and mass transfer coefficient ($K_G$) at 40 °C, zero loading and 1 mol L$^{-1}$ amine concentrations, for aqueous solutions of the heterocyclic monoamines. For comparison the reactivity of conventional absorbents MEA, DEA and AMP have been included. Also provided are the atomic properties including ESP charge on the nitrogen and the exposed area on the nitrogen atom for all optimised amine structures.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A$ (mol CO$_2$/mol amine)</th>
<th>$K_G$ (mol/s cm$^2$ Pa) ($\times 10^{-6}$)</th>
<th>ESP Charge on Nitrogen</th>
<th>Exposed Area on Nitrogen (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B3LYP</td>
<td>MP2</td>
</tr>
<tr>
<td>piperidine</td>
<td>0.76</td>
<td>3.85</td>
<td>-0.643</td>
<td>-0.671</td>
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<td><strong>Tertiary Amines</strong></td>
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<td>N'-methylpiperidine (1-MP)</td>
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<td><strong>Conventional Absorbents</strong></td>
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<td>monoethanolamine (MEA)</td>
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</tr>
<tr>
<td>diethanolamine (DEA)</td>
<td>0.60</td>
<td>0.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>0.84</td>
<td>0.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Nm= Not measured
The $C_A$ and $K_G$ results presented in Table 4-3 highlight the significant increase in reactivity of heterocyclic amines compared to conventional acyclic amines MEA and DEA. Table 4-3 shows the current industry standard amine, MEA to have a $C_A$ value of 0.56 mol CO$_2$ / mol amine and a $K_G$ value of 1.48 mol / s cm$^2$ Pa ($x10^{10}$). DEA exhibited a slightly higher $C_A$ value of 0.60 mol CO$_2$ / mol amine and lower $K_G$ value of 0.61 mol / s cm$^2$ Pa ($x10^{10}$). Heterocyclic amine $C_A$ values ranged from 0.61 (3-HP) to 0.93 (2-MP) mol CO$_2$ / mol amine and $K_G$ values from 1.86 (4-PM) to 3.85 (piperidine) mol / s cm$^2$ Pa ($x10^{10}$). Particularly noteworthy was the increase in initial absorption rates of the $C_\alpha$-substituted cyclic amines 2-MP, 2-PM and 2-PE (2.38, 1.11 and 1.23 mol / s cm$^2$ Pa ($x10^{10}$) respectively) compared to that of the $C_\alpha$-substituted acyclic amine AMP (0.61 mol / s cm$^2$ Pa (x10$^{10}$)), given the similarity in structure (sterically-hindered). The $K_G$ values obtained for 2-MP, 2-PM and 2-PE are even comparable / improved compared to that of MEA.

The heterocyclic monoamines exhibit a significant increase in the exposed area of the amino nitrogen compared to that of conventional secondary amine DEA (3.53 Å$^2$ (B3LYP) and 3.47 Å$^2$ (MP2)), with the exception of 2-PE (2.99 Å$^2$ (B3LYP)). Å$^2$ values ranged from 4.66 (piperidine) and 4.68 (4-PM) to 3.88 (2-PM) (B3LYP) for the heterocyclic amines. This could account for the higher initial absorption rates obtained for these amines, with an increase in exposure of the electron density of the reactive site increasing the amine’s nucleophilicity, especially when considering the increased reactivity of the $C_\alpha$-substituted heterocyclic amines.

Based on the infrared spectral data and MS / MS data presented in Section 4.3.3.1, it has been established that these amines (‘sterically-hindered’) form a carbamate derivative during the initial stages of CO$_2$ absorption.

Table 4-3 shows piperidine and the 3- and 4- alkyl and hydroxyalkyl substituted piperidines to exhibit similar $C_A$ values of 0.76 (piperidine), 0.75 (3-MP), 0.76 (4-MP), 0.74 (3MP), 0.74 (4-PM) and 0.74 (4-PE) mol CO$_2$ / mol amine. This is consistent with the interpretation of the infrared spectral data presented Section 4.3. These amines react with CO$_2$ to form a relatively stable carbamate derivative, which at higher CO$_2$ loadings ($> 0.5$ mol CO$_2$ / mol amine) begins to hydrolyse forming bicarbonate. The hydrolysis of the carbamate species permits the CO$_2$ loading of these amines to well exceed 0.5 mol CO$_2$ / mol amine, despite the consumption of two molecules of amine per molecule of CO$_2$ in the carbamate reaction pathway. The infrared spectral data and $C_A$ values obtained for DEA (Figure 3-3) and MEA (Figure 3-1) are also consistent with a small degree of carbamate hydrolysis, however to a much lesser extent than that observed for piperidine and the 3- and 4- alkyl and hydroxyalkyl substituted piperidines. This is reflected in the lower $C_A$ values obtained for both MEA and DEA of 0.56 and 0.60 mol
Methyl substitution in 3-MP and 4-MP had a relatively small effect on the ESP charge on the amino nitrogen or on the exposed area of the reactive site. This is reflected in the $K_G$ values obtained for these amines of 3.73 and 3.75 mol / s cm$^2$ Pa ($x10^{-10}$) respectively, which are almost identical to that of piperidine (3.85 mol / s cm$^2$ Pa ($x10^{10}$)). A similar trend in predicted electronic properties was observed for the 3- and 4- hydroxylalkyl substituted amines 3-PM, 4-PM and 4-PE. Hydroxylalkyl substitution in these amines had a relatively small effect on the ESP charge on the amino nitrogen or on the exposed area of the reactive site. However, on absorption of CO$_2$ the formation of the carbamate derivatives of the 3 and 4 –hydroxylalkyl substituted piperidines was found to be kinetically less favourable than the carbamate derivatives of 3- and 4- methyl substituted piperidines. 3-PM and 4-PM exhibited lower $K_G$ values of 2.32 and 1.86 mol / s cm$^2$ Pa ($x10^{-10}$) respectively. Across the subset of functionalised piperidines, both the MP2 and B3LYP calculated trends in the ESP charge on the amino nitrogen and the exposed area on the nitrogen atom are in good agreement of one and other.

Hydroxyl substitution in 3-HP and 4-HP lead to both reduced $C_A$ values (0.61 and 0.64 mol CO$_2$ / mol amine respectively) and $K_G$ values (2.24 and 2.28 mol / s cm$^2$ Pa ($x10^{10}$) respectively) compared to piperidine, as well as its methyl substituted analogues. The lower $C_A$ values obtained for these amines is consistent with the interpretation of the infrared spectral data, that their carbamate derivatives are less susceptible to hydrolysis at higher CO$_2$ loadings compared to the carbamate derivatives of piperidine and its methyl and hydroxyalkyl substituted analogues. These amines still however exhibited higher initial absorption rates than MEA and DEA (1.48 and 0.61 mol / s cm$^2$ Pa ($x10^{10}$) respectively), but with similar $C_A$ values. Both 3-HP and 4-HP share a structural similarity with MEA and DEA that being a hydroxyl group 2-3 carbon atoms removed from the amino nitrogen. The presence of the hydroxyl moiety in 3-HP and 4-HP was found to have little effect on the ESP charge on the amino nitrogen ($N = -0.640$ and -0.651 respectively) relative to piperidine ($N = -0.643$) (B3LYP). The hydroxyl group in 3-HP was however found to reduce the exposed area of the nitrogen atom to 3.96 Å$^2$ compared to 4.66 Å$^2$ in piperidine. It should also be noted that presence of an oxygen atom directly bonded to the nitrogen atom in the tertiary amine N-hydroxypiperidine completely hindered CO$_2$ absorption via the base-catalysis mechanism, as opposed to the methyl or hydroxyethyl substitution. Table 4-3 shows 1-MP and 1-PE to have $C_A$ values of 0.31 and 0.27 respectively; and $K_G$ values of 0.50 and 0.34 respectively. 1-HP did not react with CO$_2$. 

The electrostatic potential maps shown in Figure 4-23, were generated by overlaying the electrostatic potential onto the electron density, for the B3LYP optimised geometries of the
heterocyclic monoamines. Analysis of these maps revealed the electron distribution in 3-HP and 4-HP to be much more delocalised than that of piperidine and the 3- and 4- methyl substituted piperidines. A similar effect was also observed for 3-PM, 4-PM and 4-PE. This was reflected in the lower $K_G$ values also obtained for these amines. These amines have a hydroxyl group 3-4 carbon atoms removed from the amino nitrogen.

![Electrostatic potential map for optimised geometries (B3LYP / 6-31+G**) of](image)

Figure 4-23. Electrostatic potential map for optimised geometries (B3LYP / 6-31+G**) of a) piperidine; b) 3-HP; c) 4-HP; d) 3-MP; e) 3-PM and f) 4-PM. The maximum absolute value of the negative potential (red / yellow region) at the amino nitrogen is -182 kJ mol$^{-1}$, -107 kJ mol$^{-1}$, -161 kJ mol$^{-1}$, -181 kJ mol$^{-1}$, -169 kJ mol$^{-1}$ and -168 kJ mol$^{-1}$ respectively. The blue region represents a positive potential.
The residual electronic delocalisation between the lone pair of electrons on the amino nitrogen and those on the hydroxyl oxygen atom (crossing the CH₂ groups) decreased the availability of the nitrogen lone pair in the nucleophilic attack on CO₂ and hence the amines reactivity in terms of initial absorption rates.¹⁵³ The increased susceptibility of the 3-PM, 4-PM and 4-PE carbamate derivatives to hydrolysis at higher CO₂ loadings accounts for the higher $C_A$ values obtained for these amines compared to 3-HP and 4-HP.

The heterocyclic tertiary amines investigated further exemplify the effect of this electronic delocalisation on CO₂ / amine reactivity in the base-catalysed reaction pathway. Table 4-3 shows the hydroxyethyl substitution in 1-PE to reduce the $K_G$ value (0.34 mol/s cm² Pa ($x10^{-10}$)) compared to the methyl substitution in 1-MP (0.50 mol/s cm² Pa ($x10^{-10}$)). Electronic delocalisation and steric effects (hydroxyethyl group is bulky compared to a methyl group) reduces the accessibility of the lone pair of electrons on the amino nitrogen in 1-PE and hence their efficacy as a proton acceptor site and the amines role in facilitating the hydrolysis of CO₂.¹⁵³ When the highly electronegative oxygen atom is directly bonded to the amino nitrogen, the amine’s reactivity is completely inhibited, as observed for 1-HP.

For 2- methyl and hydroxyalkyl substituted piperidines, the tendency to favour bicarbonate formation, as indicated by the infrared spectral data, was reflected in the higher $C_A$ and lower $K_G$ values obtained for these amines relative to piperidine (0.76 mol CO₂/mol amine and 3.85 mol/s cm² Pa ($x10^{-10}$) respectively). Table 4-3 shows 2-MP, 2-PM and 2-PE to have $C_A$ values of 0.93, 0.85 and 0.87 mol CO₂/mol amine respectively and $K_G$ values of 2.38, 1.11 and 1.23 mol/s cm² Pa ($x10^{-10}$) respectively. The role of these substituent’s in significantly altering the reactivity of the amino nitrogen towards CO₂ and destabilising the carbamate derivative seems to manifest itself through both electronic effects and by reducing the exposed area of the nitrogen atom.

The methyl substitution in 2-MP significantly increased the negative ESP charge on the amino nitrogen (N = -0.836) compared to piperidine (N = -0.643) and the 3- and 4- substituted piperidine derivatives (N = -0.640 (3-HP) to N = -0.741 (3-MP)) (B3LYP). This electronic influence on the reactive site was found to be far less pronounced in 2-PM (N = -0.723) and 2-PE (N = -0.729) (B3LYP). The electrostatic potential map generated for 2-MP and 2-PE showed delocalisation of the electron distribution compared to that of 2-MP, which showed an increase in electron density at the amino nitrogen (Figure 4-24). However, the hydroxyl alkyl side chain in 2-PM and 2-PE was found to significantly reduce the exposed area on the nitrogen atom ($Å^2 = 3.88$ and 2.99 respectively) compared to piperidine ($Å^2 = 4.66$), the methyl side chain in 2-MP
(Å² = 4.59) and the hydroxyalkyl side chain in 3-PM (Å² = 4.67), 4-PM (Å² = 4.68) and 4-PE (Å² = 4.69) (B3LYP).

![Electrostatic potential map for optimised geometries (B3LYP / 6-31+G**) of a) 2-MP and b) 2-PM. The maximum absolute value of the negative potential (red / yellow region) at the amino nitrogen is -190 kJ mol⁻¹, -115 kJ mol⁻¹ respectively. Blue region represents a positive potential.](image)

In terms of $C_A$ and $K_G$ values 2-MP stands out from the rest of the amines. Whilst the amine has been identified in this study as forming predominantly bicarbonate on absorption of CO₂, it showed a significant improvement in the $K_G$ value compared to 2-PM and 2-PE. Although the 2-methyl substituent was found to have the largest electronic influence on the amino nitrogen, in terms of ESP charge, it exerted the smallest effect in terms of reducing the exposed area on the nitrogen atom. A plausible explanation for the increased $K_G$ value may be that the increased exposure of the nitrogen lone pair of electrons in 2-MP, compared to 2-PM and 2-PE, facilitates the initial uptake of CO₂ to form an unstable carbamate derivative. The electronic effect exerted by the neighbouring methyl group, combined with a small steric effect, facilitates the destabilisation of the carbamate derivative, which is then readily hydrolysed to bicarbonate. In contrast, both the 2-hydroxyalkyl substituent’s in 2-PM and 2-PE were found to have the smallest effect on the electronic environment of the amino nitrogen, in terms of ESP charge, but substantially reduced the exposed area on the nitrogen atom. These amines were also found to have a more delocalised electron distribution. Table 4-3 shows 2-PM and 2-PE to have the smallest $K_G$ values.
4.5 Effect of Substituent’s on Carbamate Structure

To investigate the effect alkyl, hydroxyl and hydroxyalkyl substituent’s had on carbamate structure the N-COO⁻ carbamate bond and the resonance structure of the carboxylate moiety were analysed. For computational details see Section 4.2.

For the lowest energy conformer of each carbamate derivative, Table 4-4 shows the calculated N-COO⁻ (\(r_{N-C}\)) bond length (Å), \(r_{C1-O1} / r_{C1-O2}\) (Å) (see Figure 4-25) and ESP partial negative charge on both oxygen atoms as a measure of charge delocalisation. The trend in results obtained at the two levels of theory was found to be in good agreement.

![Diagram](image)

Figure 4-25. Structural reference for Table 4-4, with regards to \(r_{N-C}, r_{C-O1} / r_{C-O2}\), \(R_1, R_2\) and \(R_3\) are the positioning of the alkyl, hydroxy and hydroxyalkyl substituents in the different functionalised piperdines i.e. \(R_1\) refers to the position of the 2 -methyl and -hydroxyalkyl substituents in 2-MP, 2-PE and 2-PM; \(R_2\) refers to the 3 -methyl, -hydroxy and -hydroxyalkyl substituents in 3-MP, 3-HP, 3-MP and 3-PE; \(R_3\) refers to the 4 -methyl, -hydroxy and -hydroxyalkyl substituents in 4-MP, 4-HP, 4-MP and 4-PE.
Table 4-4. The calculated N-COO\(^-\)(r\(_{\text{nc}}\)) bond length (Å), r\(_{\text{C-O1}}\)/r\(_{\text{C-O2}}\)(Å) and ESP partial charge on both oxygen atoms for optimised geometries of the carbamate derivatives of the subset of functionalised piperidines analysed.

<table>
<thead>
<tr>
<th>Carbamate Derivative</th>
<th>r(_{\text{nc}})(Å)</th>
<th>r(<em>{\text{C-O1}})/r(</em>{\text{C-O2}})(Å)</th>
<th>ESP Charge on O(_1)/O(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP</td>
<td>MP2</td>
<td>B3LYP</td>
</tr>
<tr>
<td>Piperidine-1-carboxylate</td>
<td>1.469</td>
<td>1.475</td>
<td>1.258 / 1.258</td>
</tr>
<tr>
<td>2-methylpiperidine-1-carboxylate</td>
<td>1.464</td>
<td>1.469</td>
<td>1.259 / 1.260</td>
</tr>
<tr>
<td>3-methylpiperidine-1-carboxylate</td>
<td>1.469</td>
<td>1.475</td>
<td>1.258 / 1.258</td>
</tr>
<tr>
<td>4-methylpiperidine-1-carboxylate</td>
<td>1.469</td>
<td>1.475</td>
<td>1.258 / 1.258</td>
</tr>
<tr>
<td>3-hydroxypiperidine-1-carboxylate</td>
<td>1.459(^a, c)</td>
<td>1.460(^b, c)</td>
<td>1.250 / 1.274(^a, c)</td>
</tr>
<tr>
<td></td>
<td>1.482(^b)</td>
<td>1.486(^b)</td>
<td>1.255 / 1.255(^b)</td>
</tr>
<tr>
<td>4-hydroxypiperidine-1-carboxylate</td>
<td>1.470</td>
<td>1.476</td>
<td>1.257 / 1.258</td>
</tr>
<tr>
<td>2-(hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.450(^a, c)</td>
<td>1.455(^b)</td>
<td>1.251 / 1.275(^a, c)</td>
</tr>
<tr>
<td></td>
<td>1.459(^a, d)</td>
<td>1.457(^a, d)</td>
<td>1.252 / 1.272(^b)</td>
</tr>
<tr>
<td>3-(hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.449(^b, c)</td>
<td>1.450(^b, c)</td>
<td>1.252 / 1.275(^a, c)</td>
</tr>
<tr>
<td></td>
<td>1.469(^b)</td>
<td>1.477(^b)</td>
<td>1.257 / 1.258(^b)</td>
</tr>
<tr>
<td>4-(hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.471</td>
<td>1.475</td>
<td>1.257 / 1.257</td>
</tr>
<tr>
<td>2-(2-hydroxyethyl)piperidine-1-carboxylate</td>
<td>1.444(^a, c)</td>
<td>1.445(^a, c)</td>
<td>1.253 / 1.275(^a, c)</td>
</tr>
<tr>
<td></td>
<td>1.458(^b)</td>
<td>1.473(^b)</td>
<td>1.259 / 1.262(^b)</td>
</tr>
<tr>
<td>4-(2-hydroxyethyl)piperidine-1-carboxylate</td>
<td>1.471</td>
<td>1.477</td>
<td>1.257 / 1.257</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Conformer exhibits hydrogen bonding between the hydroxyl proton of the hydroxy or hydroxalkyl side chain and the carboxylate moiety; \(^{[b]}\) Conformer with no hydrogen bonding present; \(^{[c]}\) Calculated to be the lowest energy conformer of a and b; \(^{[d]}\) Out of the subset of low energy conformers analysed all exhibited hydrogen bonding.
Table 4-4 shows the lowest energy conformers for the carbamate derivatives of 3-HP (3-hydroxypiperidine-1-carboxylate), 2-PM (2-(hydroxymethyl)piperidine-1-carboxylate), 3-PM (3-(hydroxymethyl)piperidine-1-carboxylate) and 2-PE (2-(2-hydroxyethyl)piperidine-1-carboxylate) all exhibited intramolecular hydrogen bonding between the hydroxyl proton of the hydroxyl or hydroxyalkyl side chain and the carboxylate moiety. For 3-hydroxypiperidine-1-carboxylate and 3-(hydroxymethyl)piperidine-1-carboxylate conformers the presence of intramolecular hydrogen bonding is shown to affect both the N-COO bond length and resonance structure of the carboxylate moiety, when compared to conformers with no hydrogen bonding present, as shown in Table 4-4.

It should be noted that the calculated conformers are gas phase conformers and may not be dominant in the solution phase and that solvation effects will also influence the stability of the carbamate derivative, along with electronic / steric effects and intramolecular hydrogen bonding.

The data presented in Table 4-4 shows the carbamate N-COO bond to be single bond in character. Standard single r\textsubscript{N-C} in piperidine is 1.466 Å (B3LYP) and 1.464 Å (MP2) However, the carbamate derivatives of the 2-methyl and hydroxyalkyl substituted 2-MP (2-methylpiperidine-1-carboxylate) (r\textsubscript{N-C} = 1.464 Å), 2-PM (2-(hydroxymethyl)piperidine-1-carboxylate) (r\textsubscript{N-C} = 1.450 Å) and 2-PE (2-(2-hydroxyethyl)piperidine-1-carboxylate) (r\textsubscript{N-C} = 1.444 Å) respectively, were found to have a shorter N-C bond length compared to the carbamate derivatives of piperidine (piperidine-1-carboxylate) (r\textsubscript{N-C} = 1.469 Å), 3 and 4 -MP (3-methylpiperidine-1-carboxylate and 4-methylpiperidine-1-carboxylate) (r\textsubscript{N-C} = 1.469 Å), 3 and 4 –PM (3-(hydroxymethyl)piperidine-1-carboxylate and 4-(hydroxymethyl)piperidine-1-carboxylate) (r\textsubscript{N-C} = 1.469 and 1.471 Å), and 4- PE (4-(2-hydroxyethyl)piperidine-1-carboxylate) (r\textsubscript{N-C} = 1.471 Å) (B3LYP).

The negative charge on the resonance structure of the carboxylate moiety in piperidine-1-carboxylate (O1 = -0.748; O2 = -0.748), 3-methylpiperidine-1-carboxylate (O1 = -0.767; O2 = -0.764), 4-methylpiperidine-1-carboxylate (O1 = -0.760; O2 = -0.760), 3-hydroxy piperidine-1-carboxylate (conformer with no hydrogen bonding) (O1 = -0.738; O2 = -0.730), 4-hydroxy piperidine-1-carboxylate (O1 = -0.751; O2 = -0.750), 3-(hydroxymethyl)piperidine-1-carboxylate (conformer with no hydrogen bonding) (O1 = -0.726; O2 = -0.715), 4-(hydroxymethyl)piperidine-1-carboxylate (O1 = -0.750; O2 = -0.741), and 4-(2-hydroxyethyl)piperidine-1-carboxylate (O1 = -0.759; O2 = -0.750) (B3LYP) are shown to be centred equally on the two oxygen atoms. The calculated ESP charge on both oxygen atoms are equivalent, along with both C-O bond lengths. Bond lengths ranged from r\textsubscript{C-O} = 1.255 Å (3-
hydroxypiperidine-1-carboxylate) to 1.258 Å (piperidine) and $r_{C-O2} = 1.255$ Å (3-hydroxypiperidine-1-carboxylate) to 1.258 Å (piperidine) (B3LYP).

In contrast, the electron distribution in the carboxylate moiety of 2-(hydroxymethyl)piperidine-1-carboxylate ($O1 = -0.716; O2 = -0.763$) and 2-(2-hydroxyethyl)piperidine-1-carboxylate ($O1 = -0.713; O2 = -0.778$) (B3LYP) are less delocalised across the two oxygen atoms. One oxygen atom increases in negative charge while the other decreases. The C-O bond length incorporating the more negatively charged oxygen atom also increases in double bond character while the C-O bond length incorporating the less negatively charge oxygen atom becomes more single bond in character. For 2-(hydroxymethyl)piperidine-1-carboxylate $r_{C-O1} = 1.251; r_{C-O2} = 1.275$ and 2-(2-hydroxyethyl)piperidine-1-carboxylate $r_{C-O1} = 1.253; r_{C-O2} = 1.275$. This effect was much less pronounced in 2-methylpiperidine-1-carboxylate with $O1 = -0.753; O2 = -0.765$ and $r_{C-O1} = 1.259; r_{C-O2} = 1.260$ (B3LYP).

In light of the infrared spectral data, the increased $C_A$ values and lower $K_G$ values obtained for 2-MP, 2-PM and 2-PE, a shorter N-COO$^-$ bond length and significant shift in electron distribution of the carboxylate moiety seems to reduce the stability of the carbamate derivative and thus its resilience to hydrolysis.
5  Heterocyclic Amines II: Diamines

5.1  Introduction

In the previous chapter the structure-activity relationship study of a series of heterocyclic monoamines was reported. The amines investigated included piperidine, as well as commercially available methyl, hydroxyl and hydroxyalkyl substituted analogues. This chapter will outline a structure-activity relationship study on a series of heterocyclic diamines.

The diamines investigated include piperazine, methyl piperazines and novel hexahydropyrimidine, methyl hexahydropyrimidines and hexahydropyridazine. Figure 5-1 provides the names and chemical structures of the heterocyclic diamines analysed. The hexahydropyrimidine and hexahydropyridazine compounds were not commercially available and were therefore synthesised as described in Section 6.

All the analogues evaluated retain piperazine’s two ring nitrogens varying in their relative positions and ring substituents. This approach allowed for rapid determination of the effect of the position of the nitrogen atoms within the six member ring and the CO₂ / amine reactivity. It also provided for a series of potential novel CO₂ capture absorbents that possessed enhanced CO₂ capture characteristics, but with improved aqueous solubility.

The second amine moiety present in these amines offers the potential for enhanced CO₂ absorption characteristics either in the form of a second reactive site for carbamate formation or proton acceptance or in modifying / enhancing the reactivity of the first amine site.
Piperazine and Methyl Substituted Derivatives (Commercially available)

- Piperazine (PZ)
- 2,6-dimethylpiperazine (2,6-DMPZ)
- 2,5-dimethylpiperazine (2,5-DMPZ)

Hexahydropyrimidine and Methyl Substituted Derivatives (Synthesised)

- Hexahydropyrimidine (HHPY)
- 2-methylhexahydropyrimidine (MHHPY)
- 2,2-dimethylhexahydropyrimidine (DMHHPY)

Hexahydropyridazine (Synthesised)

Hexahydropyridazine (HHPZ)

Figure 5-1 Chemical structures of the heterocyclic diamines examined for CO₂ absorption properties.
The effect of structure on CO$_2$ / amine reactivity has been investigated as follows:

i. The infrared active reaction products including, carbamate versus bicarbonate formation with cumulative CO$_2$ absorption.

ii. CO$_2$ absorption capacity. This parameter was measured simultaneously with the infrared spectral data, as described in Section 2.1.

iii. Initial rate of CO$_2$ absorption. This parameter was measured using thermal gravimetric analysis (TGA) technique described in Section 2.2.3.

iv. Correlation between the atomic properties of the amine and carbamate derivative with the infrared spectral data, CO$_2$ absorption capacity and initial absorption rate. The computational approach used to calculate atomic properties is described in Section 4.2.

In the previous chapter a 3 mol L$^{-1}$ amine concentration was used in the CO$_2$ absorption / in-situ FT-IR experiments. A 1.5 mol L$^{-1}$ amine concentration was used for the diamines in this chapter. The lower concentration was used based on the solubility constraints of PZ and its carbamate derivative, as well as the availability of the synthesised amines investigated. PZ, as the base molecule against which the remaining diamines were compared has an aqueous solubility of 1.7 mol L$^{-1}$ (146 g L$^{-1}$) at 20°C$^{[154]}$ The piperazine carbamate has a solubility of 1.3 mol L$^{-1}$ (170 g L$^{-1}$) before precipitation.$^{[70]}

### 5.2 Infrared Spectral Data

In the preceding chapter the carbamate derivatives of heterocyclic monoamines were identified as giving rise to several strong absorbance bands in the 1600-1260 cm$^{-1}$ region including the asymmetric ($\nu_{as\text{COO}^-}$, 1600-1500 cm$^{-1}$) and symmetric ($\nu_{s\text{COO}^-}$, 1450-1350 cm$^{-1}$) vibrations of the carboxylate moiety; and the N-C stretching vibrations ($\nu_{N\text{-COO}^-}$ and $\nu_{C\text{-N-C}}$, 1315-1260 cm$^{-1}$) of the carbamate species. The protonated amine generated on absorption of CO$_2$ gave rise to an absorbance band in the 1478-1474 cm$^{-1}$ region due to the NH$_2^+$ bending mode (wagging).

The carbamate derivative of the acyclic secondary amine DEA (Section 3.1.2) was also found to give rise to similar absorbance bands in 1600-1260 cm$^{-1}$ with $\nu_{as\text{COO}^-}$ at 1533 cm$^{-1}$, $\nu_{s\text{COO}^-}$ at 1414 cm$^{-1}$, $\nu_{N\text{-COO}^-}$ and $\nu_{C\text{-N-C}}$ at 1302-1261 cm$^{-1}$ and NH$_2^+$ at 1481 cm$^{-1}$.
For the first time, hydrolysis of the amine carbamate species to bicarbonate was also observed with increasing CO₂ absorption.

Bicarbonate was identified as giving rise to a broad absorbance band in the 1360-1350 cm⁻¹ region (υsC-O) in an amine / CO₂ / H₂O system. Assignment was based on the spectral data acquired for a MDEA / CO₂ / H₂O system (Section 3.2.1) and an AMP / CO₂ / H₂O system (Section 3.3.1). As mentioned previously, tertiary amines cannot react directly with CO₂ to form a carbamate species rather they act as a catalyst in the direct nucleophilic attack of -OH on dissolved CO₂. It is also known that absorption by aqueous AMP (α-dimethyl substituted MEA) leads to the formation of mostly bicarbonate with no significant carbamate formation.

The ability of Cα-substituted heterocyclic amines 2-MP, 2-PM and 2-PE to form a carbamate on reaction with gaseous CO₂ in a non-aqueous environment was also established. Infrared spectral data was collected during CO₂ absorption experiments with amine / hexanol solutions. The spectral profiles obtained for the 2-MP, 2-PM and 2-PE / CO₂ / hexanol systems showed the evolution of weak carbamate absorbance bands including υasCOO⁻ at 1538-1536 cm⁻¹, υsCOO⁻ at 1417-1416 cm⁻¹ and υN-COO⁻ at 1278-1276 cm⁻¹; and the NH₂⁺ bending mode (scissoring) of protonated 2-MP, 2-PM and 2-PE at 1641-1638 cm⁻¹. Further confirmation of the existence of these anions was also established by ESI-MS analysis of aqueous solutions of 2-MP, 2-PM and 2-PE reacted with NaHCO₃. The carbamate derivatives of 2-MP (m/z = 141.9), 2-PM (m/z = 158.0) and 2-PE (m/z = 172.0) were observed in the negative ion ESI-MS broad scan spectrum (Section 4.3.3.1).

The infrared spectral data collected for the heterocyclic diamines PZ, 2,6-DMPZ, 2,5-DMPZ, HHPY, MHHPY, DMHHPY and HHPZ investigated in this chapter have been interpreted according to the above carbamate and bicarbonate peak assignments.

### 5.2.1 Piperazine

The sequential infrared spectra collected for a PZ / CO₂ / H₂O system recorded in the 1750-950 cm⁻¹ region is shown in Figure 5-2.
Five major FT-IR peaks were seen to evolve with CO₂ absorption and hence were related to the vibrational modes of the potential ionic reaction products including:

i. Piperazine-1-carboxylate and 1-piperazinium-4-carboxylate (PZ-carbamate and \(^{13}\)H-PZ-carbamate respectively);

ii. Protonated PZ (PZ-H⁺);

iii. Piperazine-1,4-dicarboxylate (PZ-dicarbamate); and

iv. Bicarbonate.

PZ is a secondary diamine and therefore capable of reacting with CO₂ in aqueous solution to form three possible carbamate species: the amine carbamate, a protonated amine carbamate and a dicarbamate. Of these forms the protonated amine carbamate (1-piperazinium-4-carboxylate) was expected to be the main reaction product.\(^{[58, 61]}\) One amine moiety acts as the binding site for CO₂ and the second as proton acceptor. PZ has also been reported to form the dicarbamate species. This species has been detected by \(^{1}\)H and \(^{13}\)C NMR at CO₂ loadings between 0.2-0.8.

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Figure 5-2 Infrared spectral profile for PZ (1.5 mol L\(^{-1}\)) from no CO₂ loading to a maximum loading of 0.92 mol CO₂ / mol amine in the region of interest.
mol CO$_2$ / mol amine.$^{[58, 61]}$ Assignment of the spectral peaks that evolved is detailed below.

### 5.2.1.1 Vibrational Modes of the PZ-carbamate Species

The infrared spectrum presented in Figure 5-2 for the PZ / CO$_2$ / H$_2$O system closely resembled that previously reported for the monoamine analogue piperidine / CO$_2$ / H$_2$O system (Figure 4-2), differing only in slight shifts in key infrared stretching frequencies.

Of the five main peaks observed, three have been assigned to the vibrational modes of 1-piperazinium-4-carboxylate, and piperazine-1, 4-dicarboxylate, as shown in Figure 5-2:

i. **1276-1294 cm$^{-1}$** - $\nu_{N-COO}^-$

ii. **1432 cm$^{-1}$** - $\nu_{sCOO}^-$, shifts to 1423 cm$^{-1}$ with cumulative CO$_2$ absorption

iii. **1524 cm$^{-1}$** - $\nu_{asCOO}^-$, shifts to 1546 cm$^{-1}$ with cumulative CO$_2$ absorption

At low levels of CO$_2$ absorbed the PZ / CO$_2$ / H$_2$O system exhibits the $\nu_{asCOO}^-$ (1524 cm$^{-1}$), $\nu_{sCOO}^-$ (1432 cm$^{-1}$) and $\nu_{N-COO}^-$ (1276 cm$^{-1}$) of 1-piperazinium-4-carboxylate. With increasing CO$_2$ absorption levels, these peaks shift in frequency to 1546 cm$^{-1}$, 1423 cm$^{-1}$ and 1289 cm$^{-1}$ respectively. The 1276 cm$^{-1}$ peak was accompanied by a smaller peak which emerged at 1294 cm$^{-1}$, that also shifts to 1289 cm$^{-1}$ with increasing CO$_2$ absorption. The shift in frequency and intensity of the peaks in the 1294-1276 cm$^{-1}$region with increasing CO$_2$ absorption was attributed to the formation of the piperazine-1, 4-dicarboxylate species. Further details relating to these assignments are provided below.

For the spectral peaks assigned to $\nu_{asCOO}^-$, $\nu_{sCOO}^-$ and PZ-H$^+$ a near linear relationship was found to exist between cumulative CO$_2$ absorption and infrared peak absorbance, as shown in Figure 5-3. Increased peak absorbance was concomitant with the rate of carbamate formation at the reaction onset, plateauing as a maximum CO$_2$ loading of 0.92 mol CO$_2$ / mol amine was approached. The near linear relationship could be distinguished from that observed for the $\nu_{N-COO}^-$ absorbances at 1276 cm$^{-1}$ and 1294 cm$^{-1}$. From the data presented in Figure 5-2 and 5-3 the primary $\nu_{N-COO}^-$ absorbance emerges at 1276 cm$^{-1}$ and is the dominant peak. This peak increased with initial CO$_2$ absorption up to a loading of about 0.4-0.5 mol CO$_2$ / mol amine, at which point it ceased to increase in intensity and a corresponding sharp increase in intensity of the absorbance band at 1294 cm$^{-1}$ was observed, along with a frequency shift to 1289 cm$^{-1}$.
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Figure 5-3  Plot of cumulative CO$_2$ absorption by PZ (1.5 mol L$^{-1}$) and infrared peak absorbance for the bands assigned to the vibrational modes of the carbamate species (1546, 1425, 1289, 1276 cm$^{-1}$), PZ-H$^+$ (1470 cm$^{-1}$) and bicarbonate (1358 cm$^{-1}$).

The observed frequency shift and emergence of the intense 1289 cm$^{-1}$ peak has been attributed to the formation of piperazine-1,4-dicarboxylate. The infrared absorbance of the PZ / CO$_2$ / H$_2$O system in this region (1294 - 1276 cm$^{-1}$) differed from the previously investigated, with all other heterocyclic amine systems thus far reported (Section 4.2), and the remaining heterocyclic diamines analysed in this chapter, displaying a single $\nu_{\text{N-COO}^-}$ absorbance band in the 1283-1272 cm$^{-1}$ region.

The infrared stretching frequencies of 1-piperazinium-4-carboxylate, piperazine-1-carboxylate and piperazine-1, 4-dicarboxylate have not been previously reported. It was for this reason gas phase frequency and intensity calculations were used to facilitate the assignment of key vibrational modes, in particular $\nu_{\text{N-COO}^-}$. For computational details see Section 4.2.

For 1-piperazinium-4-carboxylate the B3LYP calculations placed the $\nu_{\text{N-COO}^-}$ stretch as a single intense band at 1282 cm$^{-1}$, similar in shape, but not as broad as that which initially emerged at 1276 cm$^{-1}$ in Figure 5-2. The MP2 calculations positioned this band at 1284 cm$^{-1}$.

For piperazine-1,4-dicarboxylate the B3LYP calculations predicted two $\nu_{\text{N-COO}^-}$ absorbances at 1297-1266 cm$^{-1}$ and 1348-1345 cm$^{-1}$. The MP2 calculations positioned these bands at 1302-
1274 cm\(^{-1}\) and 1364-1355 cm\(^{-1}\). The calculated values corresponded well with the experimentally observed peaks at 1266 cm\(^{-1}\), 1276 cm\(^{-1}\) and 1294 cm\(^{-1}\) in Figure 5-2. The 1276 cm\(^{-1}\) and 1294 cm\(^{-1}\) absorbance bands shift to 1289 cm\(^{-1}\) with increasing CO\(_2\) absorption.

For both 1-piperazinium-4-carboxylate and piperazine-1,4-dicarboxylate the B3LYP calculations also placed a weak \(\nu_{C,N-C}\) absorbance in the 1297-1266 cm\(^{-1}\) region, at 1293 cm\(^{-1}\) and 1267 cm\(^{-1}\). The MP2 calculations placed these bands at 1293 cm\(^{-1}\) and 1295 cm\(^{-1}\). The B3LYP and MP2 calculations confirm our peak assignments for the PZ carbamate absorption species above.

For 1-piperazinium-4-carboxylate the B3LYP calculations also placed a weak \(\nu_{C,N-C}\) absorbance band at 1315 cm\(^{-1}\). The MP2 calculations placed this band at 1341 cm\(^{-1}\). These values agreed well with the small peak observed to evolve at 1334 cm\(^{-1}\) in Figure 5-2.

The evolution of a weak broad absorbance band in the 1300-1400 cm\(^{-1}\) region of the PZ / CO\(_2\) / H\(_2\)O system was assigned to the \(\nu_{C,O}\) of bicarbonate. This absorbance band was far less prominent than that observed for the piperidine / CO\(_2\) / H\(_2\)O system shown in Figure 4-2. Peak absorbance in the PZ / CO\(_2\) / H\(_2\)O system (Figure 5-3) also did not follow the same trend as that observed for the corresponding piperidine system (Figure 4-4). Figures 5-2 and 5-3 do not show the depletion of the \(\nu_{\text{asCOO}}\), \(\nu_{\text{sCOO}}\) and \(\nu_{\text{NCOO}}\) carbamate absorbances and concomitant increase in bicarbonate absorbance with increasing CO\(_2\) loading. The trend in carbamate and bicarbonate peak absorbance observed for the piperidine / CO\(_2\) / H\(_2\)O system has been attributed to the hydrolysis of piperidine-1-carboxylate, which strongly suggested, and was consistent with the infrared spectral data presented in Figure 5-2 and 5-3, that the PZ system forms a hydrolysis resistant carbamate.

### 5.2.1.2 Vibrational Modes of PZ-H\(^+\) and 1-piperazinium-4-carboxylate

The absorbance band that appears at 1470 cm\(^{-1}\) in Figure 5-2 has been assigned to the NH\(_2\)^+ bending mode of PZ-H\(^+\) and 1-piperazinium-4-carboxylate. This absorbance resides at a slightly lower frequency than that of piperidine-H\(^+\) (1477 cm\(^{-1}\)). Further confirmation of this assignment is provided in Figure 5-4, which shows a small band to appear at 1466 cm\(^{-1}\) on protonation of the original aqueous PZ solution after acidification with hydrochloric acid. The B3LYP calculations placed the NH\(_2\)^+ bending mode of PZ-H\(^+\) and 1-piperazinium-4-carboxylate as a small absorbance band in the 1425-1407 cm\(^{-1}\) region. These values were calculated to be 1457-1417 cm\(^{-1}\) using the MP2 approach. The calculated values correspond well with the experimentally observed peak at 1470 cm\(^{-1}\) in Figure 5-2 and 1466 cm\(^{-1}\) in Figure 5-4.
5.2.2 2,6- and 2,5- Dimethyl Substituted Piperazine Derivatives

The effect of alkyl group substituent on the PZ $\text{CO}_2$ absorption characteristics was examined with 2,6-dimethylpiperazine (2,6-DMPZ) and 2,5-dimethylpiperazine (2,5-DMPZ).

Both 2,6-DMPZ and 2,5-DMPZ are dimethyl substituted analogues of PZ, differing only in the position of the methyl substituent’s on the PZ ring. In 2,6-DMPZ one amino group has two $\alpha$-methyl moieties, with a methyl substituent on both adjacent carbon atoms, while the second amino group was not substituted. In 2,5-DMPZ both amino groups have one $\alpha$-methyl moiety as shown in Figure 5-1. The infrared spectral data collected for the 2,6-DMPZ and 2,5-DMPZ / $\text{CO}_2$ / H$_2$O systems are presented in Figure 5-5 and 5-6 respectively.
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Figure 5-5  

a) Infrared spectral profile for 2,6-DMPZ (1.5 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.86 mol CO$_2$/mol amine in the region of interest; and b) Plot of cumulative CO$_2$ absorption against infrared peak absorbance for the bands assigned to the vibrational modes of the carbamate species (1550, 1425, 1289 cm$^{-1}$), 2,6-DMPZ-H$^+$ (1464 cm$^{-1}$) and bicarbonate (1354 cm$^{-1}$).
The infrared spectral data presented in Figure 5-5a and b for the 2,6-DMPZ / CO$_2$ / H$_2$O system illustrates a high degree of similarity with that of the PZ / CO$_2$ / H$_2$O system (Figure 5-2 and 5-3) in terms of signal positioning and the relationship between peak absorbance and cumulative CO$_2$ absorption. While the $\nu_{\text{asCOO}^-}$ and $\nu_{\text{sCOO}^-}$ absorbance bands were less intense and only a single $\nu_{\text{N-COO}^-}$ absorbance band emerges in the 1289-1276 cm$^{-1}$ region, all major absorbances of the 2,6-DMPZ system were within 6 cm$^{-1}$ of the PZ system: $\nu_{\text{asCOO}^-}$ at 1526 cm$^{-1}$, $\nu_{\text{COO}^-}$ at 1425 cm$^{-1}$ and $\nu_{\text{N-COO}^-}$ at 1279 cm$^{-1}$ of the 2,6-DMPZ carbamate species (2,6-dimethylpiperazinium-4-carboxylate); the NH$_2^+$ bending of 2,6-DMPZ-H$^+$ and 2,6-dimethylpiperazinium-4-carboxylate at 1464 cm$^{-1}$; and bicarbonate absorbance at 1400-1300 cm$^{-1}$ (peak maxima at 1354 cm$^{-1}$). The $\nu_{\text{asCOO}^-}$ and $\nu_{\text{N-COO}^-}$ absorbances shift to 1550 cm$^{-1}$ and 1289 cm$^{-1}$ respectively, with increasing absorbed CO$_2$. The lack of a second $\nu_{\text{N-COO}^-}$ absorbance was reflected in the relationship between peak absorbance and cumulative CO$_2$ absorption shown in Figure 5-5.

For 2,6-dimethylpiperazinium-4-carboxylate the B3LYP calculations placed $\nu_{\text{N-COO}^-}$ as a single intense band at 1284 cm$^{-1}$ accompanied by a weak $\nu_{\text{C-N-C}}$ absorbance at 1261 cm$^{-1}$ and the NH$_2^+$ bending mode (wag) in the 1427-1417 cm$^{-1}$ region. The MP2 calculations positioned these
bands at 1284 cm\(^{-1}\), 1281 cm\(^{-1}\) and 1456-1441 cm\(^{-1}\) respectively. The calculated values corresponded well with the experimentally observed peaks at 1289-1279 cm\(^{-1}\) and 1464 cm\(^{-1}\) in Figure 5-5.

The B3LYP calculations also placed \(\nu_{C-N-C}\) absorbance as a small peak at 1325-1319 cm\(^{-1}\). The MP2 calculations positioned this band at 1348-1335 cm\(^{-1}\). These values corresponded well with the small peak observed to evolve at 1340 cm\(^{-1}\) in Figure 5-5 at low levels of CO\(_2\) absorbed (< 0.4 mol CO\(_2\)/mol amine). This peak was also observed in the infrared spectra collected for the PZ / CO\(_2\) / H\(_2\)O system at 1334 cm\(^{-1}\) (Figure 5-2). However in the 2,6-DMPZ / CO\(_2\) / H\(_2\)O spectra it was consumed by the broad bicarbonate absorbance emerging in this region.

Due to steric congestion arising from the 2\(\alpha\)-CH\(_3\) moieties in 2,6-DMPZ, the initial CO\(_2\) absorption most likely occurred at the less hindered and more nucleophilic amine moiety resulting in carbamate formation. The reduced nucleophilicity of the \(\alpha\)-dimethylamine moiety reduced 2,6-DMPZ’s reactivity towards CO\(_2\) and hindered dicarbamate formation, correlating with the observation of a single \(\nu_{N-COO^-}\) peak in the infrared spectral data shown in Figure 5-5. The reduced prevalence for dicarbamate formation results in increased hydrolysis and bicarbonate formation, as evidenced by the rapid growth of the \(\nu_{C-O}\) band at 1354 cm\(^{-1}\) in Figure 5-5b, compared to that of the PZ system (c.f. Figure 5-3). The \(\alpha\)-dimethylamine moiety acts catalytically, in a manner analogous to that reported for sterically-hindered amines, accelerating the formation of bicarbonate.

The subtle structural variations between 2,6-DMPZ and 2,5-DMPZ resulted in a significant change in the infrared spectral profile obtained. For the 2,5-DMPZ / CO\(_2\) / H\(_2\)O system the most dominant feature was bicarbonate as evidenced by the broad intense \(\nu_{C-O}\) peak in the 1400-1300 cm\(^{-1}\) region (peak maxima at 1356 cm\(^{-1}\)) of Figure 5-6. There was little evidence to support the formation of a stable carbamate.

In Chapter 4 we have provided unequivocal evidence that \(\alpha\)-substituted amines do form a carbamate derivative, one that is inherently susceptible to hydrolysis in an aqueous environment. Close examination of the infrared spectral profile presented in Figure 5-6 for 2,5-DMPZ shows the evolution of weak carbamate (2,5-dimethylpiperazinium-4-carboxylate) absorbance bands including \(\nu_{asCOO^-}\) at 1524 cm\(^{-1}\), \(\nu_{sCOO^-}\) at 1421 cm\(^{-1}\) and \(\nu_{N-COO^-}\) at 1278 cm\(^{-1}\) during the initial stages of CO\(_2\) absorption. The 1421 cm\(^{-1}\) and 1278 cm\(^{-1}\) bands become superimposed by the bicarbonate peak with increasing CO\(_2\) absorption. The frequency of the observed 2,5-dimethylpiperazinium-4-carboxylate peaks corresponded with those assigned to the \(\nu_{asCOO^-}\), \(\nu_{sCOO^-}\) and \(\nu_{N-COO^-}\) of 2,6-dimethylpiperazinium-4-carboxylate at 1526 cm\(^{-1}\), 1425
cm\(^{-1}\) and 1279 cm\(^{-1}\) respectively in Figure 5-5a.

### 5.2.3 Hexahydropyrimidine

The infrared spectral data collected for the HHPY / CO\(_2\) / H\(_2\)O system recorded in the 1750-950 cm\(^{-1}\) region is shown in Figure 5-7. Figure 5-7a exhibits some similarity with that of the PZ / CO\(_2\) / H\(_2\)O system (Figure 5-2) in terms of signal positioning but with weaker signal evident, in particular \(\nu_\text{asCOO}^-\) and \(\nu_\text{sCOO}^-\). The weaker signals in part were due to a reduced concentration of HHPY present in solution then initially thought. This could arise from the presence of residual water remaining in the final product of the in-house synthesised HHPY. However, examination of the final product by \(^1\)H NMR revealed no peak due to the presence of water. For synthesis details see Section 6.3.1.

The formation of a more hydrolytically labile carbamate derivative will also result in weaker \(\nu_\text{asCOO}^-\) and \(\nu_\text{sCOO}^-\) absorbances. This is evidenced by comparing the \(\nu_\text{asCOO}^-\) and \(\nu_\text{sCOO}^-\) absorbances in the spectral data collected for the piperidine (3 mol L\(^{-1}\)) / CO\(_2\) / H\(_2\)O system in Figure 4-2 to that of the PZ (1.5 mol L\(^{-1}\)) / CO\(_2\) / H\(_2\)O system in Figure 5-2. Despite the higher amine concentration of the piperidine / CO\(_2\) / H\(_2\)O system, the carbamate \(\nu_\text{asCOO}^-\) and \(\nu_\text{sCOO}^-\) absorbances were weaker than that observed for the PZ / CO\(_2\) / H\(_2\)O system. In Section 4.3.1.3 piperidine was shown to form a more hydrolytically labile carbamate derivative.

Notwithstanding the weaker signal, the HHPY / CO\(_2\) / H\(_2\)O system in Figure 5-7a showed the evolution of carbamate (protonated tetrahydropyrimidine-1(2H)-carboxylate) \(\nu_\text{asCOO}^-\) at 1570-1520 cm\(^{-1}\), \(\nu_\text{sCOO}^-\) at 1427 cm\(^{-1}\) and \(\nu_\text{N-COO}^-\) at 1293 cm\(^{-1}\) as a single strong absorbance band; the NH\(^+\) bending mode of HHPY-H\(^+\) and protonated tetrahydropyrimidine-1(2H)-carboxylate at 1479 cm\(^{-1}\); and \(\nu_\text{C-O}\) of bicarbonate at 1354 cm\(^{-1}\).

The bicarbonate absorbance band in Figure 5-7a was more prominent than that observed for the PZ / CO\(_2\) / H\(_2\)O system in Figure 5-2. This indicated that HHPY formed a more hydrolytically labile carbamate derivative. Further evidence of this was provided in Figure 5-7b, which shows the depletion in carbamate \(\nu_\text{sCOO}^-\) and concomitant increase in bicarbonate \(\nu_\text{C-O}\), with increasing CO\(_2\) absorbed. This trend was not observed for \(\nu_\text{asCOO}^-\) due to the weak signal and undefined shape of the peak in this region.
Figure 5-7  Infrared spectral profile for HHPY (1.5 mol L$^{-1}$) from no CO$_2$ loading to a maximum loading of 0.85 mol CO$_2$/mol amine in the region of interest; and b) Plot of cumulative CO$_2$ absorption against infrared peak absorbance for the bands assigned to the vibrational modes of the carbamate species (1570, 1427, 1294 cm$^{-1}$), HHPY-H$^+$ (1479 cm$^{-1}$) and bicarbonate (1354 cm$^{-1}$).
The B3LYP calculations placed the $\nu_{N-COO^-}$ of protonated tetrahydropyrimidine-1(2H)-carboxylate as a single intense band in at $1308 \text{ cm}^{-1}$, accompanied by a weaker $\nu_{C,N-C}$ absorbance at $1281 \text{ cm}^{-1}$. These values were calculated to be $1263 \text{ cm}^{-1}$ and $1306 \text{ cm}^{-1}$ using the MP2 approach. The calculated values correspond well with the experimentally observed broad peak at $1293 \text{ cm}^{-1}$ in Figure 5-7a.

Figure 5-7a shows a small peak to appear at $1391 \text{ cm}^{-1}$ with increasing carbamate formation. The B3LYP calculations revealed protonated tetrahydropyrimidine-1(2H)-carboxylate to have a small absorbance in the 1384-1367 cm$^{-1}$ region arising from the combination of the NH$_2^+$ wag and N-C stretching vibrations ($\nu_{N-COO^-}$ and $\nu_{C,N-C}$), in addition to the NH$_2^+$ bending mode at 1446-1425 cm$^{-1}$. The MP2 calculations positioned these absorbances at 1393-1386 cm$^{-1}$ and 1465-1452 cm$^{-1}$. These values correspond well with the experimentally observed peaks at 1391 cm$^{-1}$ and 1479 cm$^{-1}$ in Figure 5-7a. On close examination of the 2,6-DMPZ infrared spectral data in Figure 5-5, a similar absorbance can also be observed at 1391 cm$^{-1}$, though somewhat obscured by the dominate absorbance of the original aqueous 2,6-DMPZ solution in this region.

### 5.2.4 2-Methylhexahydropyrimidine

2-Methylhexahydropyrimidine (MHHPY) is the $\alpha$-methyl substituted analogue of HHPY, with the CH$_3$ moiety located on the carbon atom adjoining the two amino groups.

The sequential infrared spectra collected for the MHHPY / CO$_2$ / H$_2$O system recorded in the 1750-950 cm$^{-1}$ region is shown in Figure 5-8. Figure 5-8 shows the spectral profile to be dominated by the broad bicarbonate absorbance band in the 1400-1300 cm$^{-1}$ region, which was characteristic of C$\alpha$-substituted amines. Given the intensity of the bicarbonate band, MHHPY was readily hydrolysed under the study conditions with bicarbonate formation dominating on absorption of CO$_2$. 
The weak broad absorbance bands emerging in the 1570-1530 cm$^{-1}$ and 1500-1480 cm$^{-1}$ region in Figure 5-8 were thought to be due to a small amount of MHHPY-carbamate formation. The frequency of the 1570-1530 cm$^{-1}$ peak corresponded with that assigned to the $\nu_{\text{asCOO}^-}$ of protonated tetrahydropyrimidine-1(2$H$)-carboxylate in the 1570-1520 cm$^{-1}$ region of the un-substituted analogue HHPY / CO$_2$ / H$_2$O system (Figure 5-7). For the observed 1500-1480 cm$^{-1}$ peak the B3LYP calculations placed absorbance in this region due to the combination of a NH$_2^+$ wag and CH$_3$ twist for both $^1$H-MHHPY-carbamate at 1493-1477 cm$^{-1}$ and MHHPY-H$^+$ at 1495-1482 cm$^{-1}$. The MP2 calculations positioned this absorbance at 1490 cm$^{-1}$ and 1486-1475 cm$^{-1}$ respectively. This absorbance resides at a slightly higher frequency than that observed for the NH$_2^+$ wag at 1479 cm$^{-1}$ in the HHPY system (Figure 5-7).

On closer examination of the spectra presented in Figure 5-8 for the MHHPY / CO$_2$ / H$_2$O system absorbance in the 1295-1290 cm$^{-1}$ region can be observed as a shoulder peak to the dominant broad bicarbonate peak. The frequency of this peak corresponded well with the $\nu_{\text{NCOO}^-}$ absorbance at 1294 cm$^{-1}$ in the HPPY / CO$_2$ / H$_2$O system.
5.2.5 Hexahydropyridazine

The heterocyclic diamine HHPZ was found to absorb no CO$_2$ during a typical CO$_2$ absorption / FT-IR experiment. For this reason the infrared spectral data collected will not be discussed.

HHPZ is a hydrazine derivative that is reported to have a pKa value of 7.9\textsuperscript{[155]} which is much lower than that of PZ (9.73)\textsuperscript{[156]} HHPY (9.75)\textsuperscript{[157]} or 2,5-DMPZ (9.66)\textsuperscript{[158]} The low basicity of HHPZ compared to the other diamines (pKa values > 9.5) would be expected to significantly reduce the amines reactivity towards CO$_2$.

5.2.6 Blended Amine Systems

5.2.6.1 2,2-Dimethylhexahydropyrimidine

2,2-Dimethylhexahydropyrimidine (DMHHPY) is the dimethyl substituted analogue of MHHPY, as well as HHPY. Given the structural similarity between DMHHPY and MHHPY, DMHHPY was anticipated to form predominately bicarbonate on absorption of CO$_2$.

The sequential infrared spectra collected for the DMHHPY / CO$_2$ / H$_2$O system recorded in the 1750-950 cm$^{-1}$ region is shown in Figure 5-9a. This spectral profile was significantly different to that obtained for the MHHPY / CO$_2$ / H$_2$O system in Figure 5-8, as well as that of the HHPY and PZ / CO$_2$ / H$_2$O systems in Figure 5-7 and 5-2 respectively. Here the DMHHPY was acting more in keeping with a blended amine absorbent system.

The starting material used in the synthesis of DMHHPY was 1,3-diaminopropane (DAP) (Section 6.3.3), the diamine analogue of the aliphatic primary amine MEA. Examination of the in-house synthesized DMHHPY by $^1$H NMR and infrared spectroscopy revealed the presence of unreacted DAP which had unavoidably carried forward to the final product. Hence the contamination of the DMHHPY with DAP explains the observed blended system-like infrared profile presented in Figure 5-9.
Figure 5-9  

**a)** Infrared spectral profile for DMHHPY (1.5 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 1.10 mol CO\(_2\)/mol amine in the region of interest; and **b)** plot of cumulative CO\(_2\) absorption against infrared peak absorbance for the bands assigned to the vibrational modes of the DAP-carbamate species (1565, 1440, 1328 cm\(^{-1}\)), DAP-H\(^+\) (1492 cm\(^{-1}\)) and bicarbonate (1360 cm\(^{-1}\)).
The DMMHPY infrared spectrum identified the NH bending mode of DAP at 1602 cm\(^{-1}\) (Section 6.3.3), confirmed by analysis of the infrared spectrum of pure DAP (\(\nu(N-H)\) 1602 cm\(^{-1}\)). The DNHHPY blended absorbent system, therefore consisted of an \(\alpha\)-dimethyl substituted heterocyclic secondary diamine and an aliphatic primary diamine. Based on the percent concentrations determined by \(^1\)H NMR the concentration of DAP (approximately 37\%, 1.91 g) and DMHHPY (63 \%, 3.24 g) in the DMHHPY / CO\(_2\) / H\(_2\)O system was 0.85 and 0.96 mol L\(^{-1}\) respectively, with a total concentration of 1.81 mol L\(^{-1}\). While the DAP and DMHHPY concentrations were approaching equimolar, the DMHHPY / CO\(_2\) / H\(_2\)O system formed predominately the corresponding DAP-carbamate on CO\(_2\) absorption.

To allow potential deconvolution of the DAP and DMHHPY signals in the DMHHPY / CO\(_2\) / H\(_2\)O infrared spectral profile, data was collected separately during a typical CO\(_2\) absorption experiment with an aqueous solution of DAP (0.6 mol L\(^{-1}\)). The sequential infrared spectra collected for the DAP / CO\(_2\) / H\(_2\)O system recorded in the 1750-950 cm\(^{-1}\) region is shown in Figure 5-10. From Figure 5-10 it was apparent that the DMHHPY / CO\(_2\) / H\(_2\)O system (Figure 5-9a) is dominated by the reactivity of DAP (c.f. Figure 5-9 and 5-10). Both systems show the evolution of DAP-carbamate absorbance bands including \(\nu_{\text{asCOO}^-}\) at 1565 cm\(^{-1}\) and 1568 cm\(^{-1}\) respectively, \(\nu_{\text{sCOO}^-}\) at 1440 cm\(^{-1}\) and 1330 cm\(^{-1}\) respectively; and the NH\(_3^+\) bending mode of protonated DAP at 1492 cm\(^{-1}\). For the blended DMHHPY / CO\(_2\) / H\(_2\)O system, weaker absorbance bands were also observed to be emerging at 1385 cm\(^{-1}\) and 1370-1350 cm\(^{-1}\), at CO\(_2\) loadings of > 1.0 mol CO\(_2\) / mol amine (Figure 5-9b). These new peaks are consistent with carbamate hydrolysis and bicarbonate formation. Carbamate hydrolysis was not observed for the pure DAP / CO\(_2\) / H\(_2\)O system.

In the DMHHPY / CO\(_2\) / H\(_2\)O system (Figure 5-9) the DAP-carbamate absorbance bands dominate the infrared spectra. However, in the DAP / CO\(_2\) / H\(_2\)O systems the carbamate absorbances were considerably weaker. Initially the effect of this was thought to be that the DAP concentration in the DMHHPY / H\(_2\)O /CO\(_2\) system appears to be significantly higher than the 0.85 mol L\(^{-1}\) determined by \(^1\)H NMR. However, a similar difference in intensity between the carbamate absorbance bands of a blended AMP (2.4 mol L\(^{-1}\)) / PZ (0.6 mol L\(^{-1}\)) system versus an unblended PZ (0.6 mol L\(^{-1}\)) system was also observed. Carbamate absorbance in the unblended PZ system was found to be considerably weaker than that observed for the AMP / PZ blended system, despite equivalent PZ concentrations (0.6 mol L\(^{-1}\)). The blended AMP / PZ / CO\(_2\) / H\(_2\)O system is discussed further in Section 5.1.5.2.
Figure 5-10  Infrared spectral profile for DAP (0.6 mol L\textsuperscript{-1}) from no CO\textsubscript{2} loading to a maximum loading of 0.95 mol CO\textsubscript{2} / mol amine in the region of interest.

5.2.6.2  AMP / PZ Blended Amine System

An AMP / PZ blended amine system was investigated for comparative purposes. Blend formulation was 2.4 mol L\textsuperscript{-1} AMP and 0.6 mol L\textsuperscript{-1} PZ. The AMP / PZ blend consists of an amine that forms predominately bicarbonate on absorption of CO\textsubscript{2} (AMP, major constituent) and an amine that forms a hydrolytically stable carbamate (PZ, minor constituent), similar to that of the blended DMHHPY system.

The sequential infrared spectra collected for the AMP / PZ / CO\textsubscript{2} / H\textsubscript{2}O system recorded in the 1750-950 cm\textsuperscript{-1} region is shown in Figure 5-11. Figure 5-11 shows a similar trend in infrared absorbance as that observed for the DMHHPY / CO\textsubscript{2} / H\textsubscript{2}O system in Figure 5-9a. The PZ-carbamate absorbance bands dominate the infrared spectral profile, despite PZ being the minor constituent of the amine blend. Figures 5-11a and b shows the evolution of 1-piperazinium-4-carboxylate $\nu_{\text{asCOO}^-}$ at 1533 cm\textsuperscript{-1}, $\nu_{\text{sCOO}^-}$ at 1421 cm\textsuperscript{-1}, $\nu_{\text{N-COO}^-}$ at 1276 cm\textsuperscript{-1} and NH\textsubscript{2}\textsuperscript{+} bending mode at 1471 cm\textsuperscript{-1}. The $\nu_{\text{N-COO}^-}$ band at 1276 cm\textsuperscript{-1} shifted to 1263 cm\textsuperscript{-1} with increasing CO\textsubscript{2} absorption. Bicarbonate absorbance can be seen to evolve in the 1400-1300 cm\textsuperscript{-1} region after a CO\textsubscript{2} loading of about 0.5 mol CO\textsubscript{2} / mol amine (Figure 11b).
Figure 5-11  a) Infrared spectral profile for an AMP / PZ blend (2.4 mol L$^{-1}$ / 0.6 mol L$^{-1}$ respectively) from no CO$_2$ loading to a maximum loading of 1.00 mol CO$_2$ / mol amine in the region of interest; and b) Plot of the cumulative CO$_2$ absorption and infrared peak absorbance for the bands assigned to the vibrational modes of the PZ-carbamate species (1533, 1421, 1263 cm$^{-1}$), PZ-H$^+$ (1471 cm$^{-1}$) and bicarbonate (1358 cm$^{-1}$).
Infrared spectral data was also collected for an equivalent unblended PZ (0.6 mol L\(^{-1}\)) / CO\(_2\) / H\(_2\)O system for comparison. Figure 5-12 shows the sequential infrared spectra recorded in the 1750-950 cm\(^{-1}\) region. Carbamate absorbance in this unblended system is considerably weaker than that observed for the blended system, despite equivalent PZ concentrations. For the infrared spectral profile of an equivalent unblended AMP (3 mol L\(^{-1}\)) / CO\(_2\) / H\(_2\)O system see Figure 3-6 in Section 3.3.1.

![Figure 5-12](image-url)

**Figure 5-12** Infrared spectral profile for unblended PZ (0.6 mol L\(^{-1}\)) from no CO\(_2\) loading to a maximum loading of 0.92 mol CO\(_2\) / mol amine in the region of interest.

The bicarbonate absorbance band is more prominent in the infrared spectra of the AMP / PZ / CO\(_2\) / H\(_2\)O system, compared to that of the DMHHPY / CO\(_2\) / H\(_2\)O system. This was most likely due to the difference in amine concentrations, with the AMP component of the AMP / PZ blend having a concentration of 2.4 mol L\(^{-1}\) and the DMHHPY component of the DMHHPY / DAP blend having a concentration close to 1 mol L\(^{-1}\). The extent of bicarbonate signal reduction due to change in concentrations was further evident in the infrared spectral profile obtained for the 2,5-DMPZ and MHHPY (1.5 mol L\(^{-1}\)) / CO\(_2\) / H\(_2\)O systems (Figure 5-6 and 5-8 respectively) compared to that obtained for the AMP (3 mol L\(^{-1}\)) system (Figure 3-6).
5.2.6.1 AMP / Piperidine Blended Amine System

Piperidine is the monoamine analogue of PZ. In this work it has been shown to possess an enhanced CO$_2$ absorption capacity and initial absorption rate (Table 4-3). It has also been shown to form a more hydrolytically labile carbamate derivative at higher CO$_2$ loadings (> 0.5 mol CO$_2$/mol amine) (Figures 4-2 and 4-4) compared to the PZ and DAP carbamate species (c.f. Figures 5-2 and 5-10). It was for this reason that an AMP / piperidine blended system was investigated. Blend formulation was 2.4 mol L$^{-1}$ AMP and 0.6 mol L$^{-1}$ piperidine.

The sequential infrared spectra collected for the AMP / piperidine / CO$_2$/H$_2$O system recorded in the 1750-950 cm$^{-1}$ region is shown in Figure 5-13. The spectral profile presented in Figure 5-13 is significantly different to that of the AMP / PZ and DMHHPY blended systems shown in Figure 5-11 and 5-9 respectively. Figure 5-13 shows the bicarbonate absorbance band to dominate the infrared spectral profile. Carbamate formation is evident in the initial stages of CO$_2$ absorption. The $\nu_{\text{asCOO}^-}$, $\nu_{\text{sCOO}^-}$ and $\nu_{\text{N-COO}^-}$ of piperidine-1-carboxylate; and NH$_2^+$ bending mode of piperidine$^+\cdot$H can be seen to evolve at 1518 cm$^{-1}$, 1436 cm$^{-1}$, 1283 cm$^{-1}$ and 1471 cm$^{-1}$ respectively.

Figure 13b shows carbamate formation to be prominent up to a CO$_2$ absorption level of 0.3–0.4 mol CO$_2$/mol amine. With increasing CO$_2$ absorption bicarbonate formation rapidly increases and becomes the prominent absorbance. This trend in infrared peak absorbance and the weaker carbamate signal in Figure 5-13 were consistent with the lability of piperidine-1-carboxylate and the conclusion that PZ forms a hydrolysis resistant carbamate species. Further delineation of the role PZ, compared to piperidine, has on altering the CO$_2$ absorption characteristics of AMP in a blended system is discussed below in Section 5.5 in terms of CO$_2$ absorption rates.
Figure 5-13  

a) Infrared spectral profile for an AMP / piperidine blend (2.4 mol L\(^{-1}\) / 0.6 mol L\(^{-1}\) respectively) from no CO\(_2\) loading to a maximum loading of 0.90 mol CO\(_2\) / mol amine in the region of interest; and b) Plot of cumulative CO\(_2\) absorption and infrared peak absorbance for the bands assigned to the vibrational modes of piperidine-1-carboxylate (1518, 1436, 1283 cm\(^{-1}\)), piperidine-H\(^+\) (1477 cm\(^{-1}\)) bicarbonate (1354 cm\(^{-1}\)).
5.3 Absorption Capacity and Absorption Rate

To quantify the effect molecular structure has on CO₂ / amine reactivity the CO₂ absorption capacity (Cₐ) and initial absorption rate (Rᵢₐ) were determined for each amine.

The CO₂ absorption capacity was measured simultaneously with the infrared spectral data during a typical absorption / FT-IR experiment (Section 2.1). The TGA method described in Section 2.2.3 was used to analyse initial CO₂ absorption rates. The TGA method was used here as opposed to the WWC technique described in Section 2.2.2 as it requires only milligrams of amine. This allowed testing of those amines more difficult to obtain or synthesised in small quantities. The WWC technique was the method of choice for analysing initial CO₂ absorption rates. However it required 1L solution volumes and a much larger quantity of amine, up to 86-114 g amine per run. The results obtained by the TGA method are satisfactory for comparing the reactivity of a specific group of amines, as is the case in this instance.

The measured Cₐ and Rᵢₐ values are presented in Table 5-1. For comparison, the reactivity of conventional absorbents MEA, DEA and AMP have been included.

Table 5-1 shows the current industry standard amine, MEA to have a Cₐ value of 0.56 mol CO₂ / mol amine and an Rᵢₐ value of 0.027 mol CO₂ / mol amine min⁻¹. From the data amassed for PZ, 2,6-DMPZ, HHPY, and DMHHPY in Table 5-1, superior Cₐ and Rᵢₐ values are observed for all these diamines relative to MEA. Superior Cₐ values were also observed for 2,5-DMPZ and MHHPY, but with lower Rᵢₐ values. HHPZ did not react with CO₂, and DMHHPY is blended with DAP. Diamine Cₐ values ranged from 0.85 (HHPY) to 0.92 (PZ) mol CO₂ / mol amine and Rᵢₐ values from 0.018 (2,5-DMPZ) to 0.045 (PZ) mol CO₂ / mol amine min⁻¹.

In absolute terms PZ was the standout pure diamine with the highest Cₐ and Rᵢₐ values. However it is important to recognise that Cₐ and Rᵢₐ are not the sole factors to be considered in determining the most efficient absorbent system. Aqueous solubility and carbamate lability also play an important role.
Table 5-1  Measured absorption capacity ($C_A$), at 40 °C with an amine concentration of 1.5 mol L$^{-1}$ and initial absorption rate ($R_{IA}$) at 40 °C and amine concentration of 1.5 mol L$^{-1}$, for aqueous solutions of PZ, 2,6-DMPZ, 2,5-DMPZ and synthesized amines HHPY, MHHPY, DMHHY and HHPZ. For comparison, the reactivity of conventional absorbents, such as MEA, DEA and AMP (1.5 - 3 mol L$^{-1}$), have been included.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A$ (mol CO$_2$/mol amine)</th>
<th>$R_{IA}$ (mol CO$_2$/mol amine, min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piperazine (PZ)</td>
<td>0.92</td>
<td>0.045</td>
</tr>
<tr>
<td>2,6-dimethylpiperazine (2,6-DMPZ)</td>
<td>0.86[a]</td>
<td>0.025[b]</td>
</tr>
<tr>
<td>2,5-dimethylpiperazine (2,5-DMPZ)</td>
<td>0.88</td>
<td>0.018[c]</td>
</tr>
<tr>
<td>Hexahydropyrimidine (HHPY)</td>
<td>0.85</td>
<td>0.032</td>
</tr>
<tr>
<td>2-methylhexahydropyrimidine (MHHPY)</td>
<td>0.86</td>
<td>0.018</td>
</tr>
<tr>
<td>2,2-dimethylhexahydropyrimidine (DMHHPY)</td>
<td>1.10</td>
<td>0.032</td>
</tr>
<tr>
<td>Hexahydropyridazine (HHPZ)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Conventional Amines**

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A$ (mol CO$_2$/mol amine)</th>
<th>$R_{IA}$ (mol CO$_2$/mol amine, min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>0.56[d]</td>
<td>0.027[e]</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>0.60[d]</td>
<td>0.015[e]</td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>0.84[d]</td>
<td>0.006[e]</td>
</tr>
</tbody>
</table>

[a] A precipitate formed during CO$_2$ absorption / FT-IR run; [b] A precipitate formed during the CO$_2$ and N$_2$ run of the TGA experiment; [c] A precipitate formed during the CO$_2$ run only of the TGA experiment. This would be mainly due to the evaporation of water; [d] 3 mol L$^{-1}$; [e] 1.5 mol L$^{-1}$.

The low aqueous solubility of PZ limits its use as a sole CO$_2$ capture absorbent, rather, it is commonly used in catalytic quantities as an absorption accelerator in sterically-hindered or tertiary amine / CO$_2$ / H$_2$O systems. HHPY displays higher water solubility than PZ. This was determined based on observation when preparing 1.5 mol L$^{-1}$ amine solutions. HHPY was readily soluble at this concentration as opposed to PZ that required heating and stirring for dissolution. Table 5-1 also shows HHPY to have high $C_A$ and $R_{IA}$ values. The infrared spectral data collected for the HHPY / CO$_2$ / H$_2$O systems and presented in Figure 5-7 displayed clear evidence of the formation of a hydrolysis susceptible carbamate.
The dimethyl substituted analogues of PZ, 2,6-DMPZ and 2,5-DMPZ, exhibited significantly lower $R_{IA}$ values (0.025 and 0.018 mol CO$_2$/mol amine min$^{-1}$ respectively) than that of PZ. As these analogues differ only in the number of methyl substituents and the positioning of these methyl groups, this data suggests that the introduction of methyl moieties has an adverse effect on the initial rate of CO$_2$ absorption. 2,6-DMPZ placed both methyl groups $\alpha$ to a single NH, while 2,5-DMPZ placed one methyl group $\alpha$ to each NH. The measured $R_{IA}$ values indicate that the addition of $\alpha$-methyl groups is cumulative with the $R_{IA}$ dropping from 0.045 (PZ) to 0.025 (2,6-DMPZ) to 0.018 (2,5-DMPZ) mol CO$_2$/mol amine min$^{-1}$ with each $\alpha$-methyl addition. Concurrent with the reduction in $R_{IA}$ is an increased prevalence towards bicarbonate formation with 2,5-DMPZ favouring bicarbonate production (Figure 5-6).

2,5-DMPZ’s propensity for bicarbonate formation was similar to that observed with MHHPY, as shown in Figures 5-6 and 5-8 respectively. This was reflected in the almost identical $C_A$ and $R_{IA}$ values obtained for these amines and given in Table 5-1. Despite forming predominately bicarbonate, Table 5-1 shows the initial absorption rate obtained for both MHHPY and 2,5-DMPZ (0.018 mol CO$_2$/mol amine, min$^{-1}$) to be much higher than that obtained for AMP (0.006 mol CO$_2$/mol amine, min$^{-1}$) and comparable to that of MEA and DEA (0.027 and 0.015 mol CO$_2$/mol amine, min$^{-1}$).

2,6-DMPZ’s reactivity towards CO$_2$ was found to be similar to that of MEA, with the exception of a higher $C_A$ value. Figure 5-5 shows 2,6-DMPZ to form predominantly carbamate on absorption CO$_2$, similar to that of HHPY. The propensity for carbamate hydrolysis and subsequent bicarbonate formation is also similar to that observed with HHPY (c.f. Figure 5-4 and 5-7). This is reflected in the almost identical $C_A$ values obtained for these amines. However, Table 5-1 shows 2,6-DMPZ to have a much lower $R_{IA}$ value.

Of the diamines examined DMHHPY exhibited the highest $C_A$ value (1.10 mol CO$_2$/mol amine) and an $R_{IA}$ value (0.032 mol CO$_2$/mol amine, min$^{-1}$) higher than MHHPY (0.015 mol CO$_2$/mol amine, min$^{-1}$) and equal to that of HHPY (0.032 mol CO$_2$/mol amine, min$^{-1}$). This was an artefact of the blending with DAP. The primary amine constituent (DAP) contributed significantly towards the observed CO$_2$ absorption capacity, particularly so given that it is a diamine, which allowed for a 1:1 stoichiometric reaction with CO$_2$. A $C_A$ of 0.95 mol CO$_2$/mol amine was obtained for an unblended aqueous solution of DAP (0.6 mol L$^{-1}$). In the blended DMHHPY / DAP system the bicarbonate forming DMHHPY constituent further promoted CO$_2$ absorption, resulting in a $C_A$ value greater than 0.95 mol CO$_2$/mol amine (Table 5-1). DAP’s un-substituted primary amine groups contributed towards DMHHPY’s increased initial reaction rate, when compared to its less substituted analogue MHHPY.
Overall the results presented in Table 5-1 highlighted the increased reactivity of heterocyclic diamines, with the exception of HHPZ, compared to the equivalent conventional amines MEA, DEA and AMP.

### 5.4 Effect of Molecular Structure on Carbamate Stability

To investigate the effect PZ structural modifications had on carbamate stability the N-COO\(^{-}\) carbamate bond and resonance structure of the carboxylate moiety were analysed. For computational details see Section 4.2.

Geometry optimisations were initially performed on PZ, 2,6-DMPZ, 2,5-DMPZ, HHPY, MHHPY, DMHHPY and HHPZ. Table 5-2 details selected atomic properties including electrostatic potential (ESP) partial charge on the amino nitrogen and the exposed area on the nitrogen atom for these diamines. The trend in results obtained at the two levels of theory was found to be in good agreement of one another.

**Table 5-2** Atomic properties, including ESP charge on nitrogen and the exposed area on the nitrogen atom (Å\(^2\)) for optimised forms of the structurally variant diamines analysed.

<table>
<thead>
<tr>
<th>Amine</th>
<th>ESP Charge on Nitrogen</th>
<th>Exposed Area on Nitrogen (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP</td>
<td>MP2</td>
</tr>
<tr>
<td>PZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.584</td>
<td>-0.584</td>
</tr>
<tr>
<td>N2</td>
<td>-0.584</td>
<td>-0.584</td>
</tr>
<tr>
<td>2,6-DMPZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.718</td>
<td>-0.752</td>
</tr>
<tr>
<td>N2</td>
<td>-0.752</td>
<td>-0.778</td>
</tr>
<tr>
<td>2,5-DMPZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.746</td>
<td>-0.746</td>
</tr>
<tr>
<td>N2</td>
<td>-0.746</td>
<td>-0.785</td>
</tr>
<tr>
<td>HHPY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.874</td>
<td>-0.874</td>
</tr>
<tr>
<td>N2</td>
<td>-0.874</td>
<td>-0.907</td>
</tr>
<tr>
<td>MHHPY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.851</td>
<td>-0.728</td>
</tr>
<tr>
<td>N2</td>
<td>-0.728</td>
<td>-0.759</td>
</tr>
<tr>
<td>DMHHPY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.959</td>
<td>-0.957</td>
</tr>
<tr>
<td>N2</td>
<td>-0.957</td>
<td>-0.982</td>
</tr>
<tr>
<td>HHPZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-0.525</td>
<td>-0.386</td>
</tr>
<tr>
<td>N2</td>
<td>-0.525</td>
<td>-0.386</td>
</tr>
</tbody>
</table>
As anticipated, Table 5-2 shows methyl substitution to significantly increase the partial negative charges on the amino nitrogens of 2,6-DMPZ (N1 = -0.718; N2 = -0.752), 2,5-DMPZ (N1 = N2 = -0.746), MHHPY (N1 = -0.851; N2 = -0.728) and DMHHPY (N1 = -0.959; N2 = -0.957) relative to PZ (N1 = N2 = -0.584). Table 5-2 also shows a reduced exposed area on the amino nitrogen of 2,6-DMPZ (N1 = 4.21 Å²; N2 = 4.70 Å²), 2,5-DMPZ (N1 = N2 = 4.45 Å²), MHHPY (N1 = 4.77 Å²; N2 = 4.57 Å²) and DMHHPY (N1 = 4.50 Å²; N2 = 4.51 Å²) relative to PZ (N1 = N2 = 4.71 Å²) (B3LYP). HHPZ was found to exhibit a significant decrease in the partial negative charges on the amino nitrogens (N1 = -0.525; N2 = -0.386), which was reflected its lower basicity (pKa = 7.9). These changes in electronic effects both impact on the resonance structure of the carboxylate moiety and hence overall stability of the carbamate derivative.

As mentioned previously, diamines can react with CO₂ in an aqueous environment to form three possible forms of carbamate species: amine-carbamate (HNR₁R₂NCOO₂⁻), protonated amin-carbamate (H₂NHR₁R₂NCOO⁻) and dicarbamate (OOCNR₁R₂NCOO₂⁻). Protonated amine-carbamate is expected to be the main reaction product. Geometry optimisations were next performed for the protonated amine-carbamate and amine-carbamate species. Table 5-3 provides the calculated N-COO⁻ (r_{N,C}) bond length (Å), r_{C1,O1} / r_{C1,O2} (Å) (see Figure 5-14) and ESP partial charge on both oxygen atoms for the lowest energy conformer of each protonated amine-carbamate and amine-carbamate derivative.

Figure 5-14  Chemical structures associated with Table 5-3, with regards to r_{N,C}, r_{C1,O1} / r_{C1,O2} for a) 2,6-DMPZ (1. R₂=R₃=CH₃, R₁=R₄=H and 2. R₁=R₄=CH₃, R₂=R₃=H) and 2,5-DMPZ (R₂=R₃=CH₃, R₁=R₄=H); b) HHPY (R₂=R₃=H), MHHPY (R₁= CH₃, R₂=H) and DMHHPY (R₁=R₄=CH₃); and c) HHPZ.
The calculated N-COO⁻ \( (r_{NC}) \) bond length (Å), \( r_{C1-O1} / r_{C1-O2} \) (Å) and ESP partial charge on both oxygen atoms for optimised geometries of the H⁺-HNR,R₂N-COO⁻ and HNR,R₂NCOO⁻ derivatives of the subset of diamines analysed.

<table>
<thead>
<tr>
<th>Carbamate Derivative</th>
<th>( r_{NC} ) [Å]</th>
<th>( r_{C-O1} / r_{C-O2} ) [Å]</th>
<th>ESP Charge on O1 / O2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP</td>
<td>MP2</td>
<td>B3LYP</td>
</tr>
<tr>
<td>H⁺-PZ-carbamate</td>
<td>1.513</td>
<td>1.507</td>
<td>1.247 / 1.247</td>
</tr>
<tr>
<td>PZ-carbamate</td>
<td>1.471</td>
<td>1.477</td>
<td>1.257 / 1.257</td>
</tr>
<tr>
<td>H⁺-2,6-DMPZ-carbamate</td>
<td>1.508</td>
<td>1.505</td>
<td>1.248 / 1.249</td>
</tr>
<tr>
<td>2,6-DMPZ-carbamate</td>
<td>1.469</td>
<td>1.477</td>
<td>1.258 / 1.258</td>
</tr>
<tr>
<td>H⁺-2,6-DMPZ-carbamate</td>
<td>1.523</td>
<td>1.527</td>
<td>1.247 / 1.247</td>
</tr>
<tr>
<td>2,6-DMPZ-carbamate</td>
<td>1.461</td>
<td>1.463</td>
<td>1.260 / 1.260</td>
</tr>
<tr>
<td>H⁺-2,5-DMPZ-carbamate</td>
<td>1.505</td>
<td>1.503</td>
<td>1.249 / 1.247</td>
</tr>
<tr>
<td>2,5-DMPZ-carbamate</td>
<td>1.465</td>
<td>1.470</td>
<td>1.259 / 1.258</td>
</tr>
<tr>
<td>H⁺-HHHPY-carbamate</td>
<td>1.507</td>
<td>1.503</td>
<td>1.227 / 1.277[d]</td>
</tr>
<tr>
<td>HHPY-carbamate</td>
<td>1.475</td>
<td>1.478</td>
<td>1.257 / 1.259</td>
</tr>
<tr>
<td>H⁺- MHHPY-carbamate</td>
<td>1.417</td>
<td>1.417</td>
<td>1.211 / 1.354[d]</td>
</tr>
<tr>
<td>MHHPY-carbamate</td>
<td>1.463</td>
<td>1.469</td>
<td>1.258 / 1.260</td>
</tr>
<tr>
<td>H⁺- DMHHPY-carbamate</td>
<td>1.555</td>
<td>1.550</td>
<td>1.235 / 1.244</td>
</tr>
<tr>
<td>DMHHPY-carbamate</td>
<td>1.501</td>
<td>1.500</td>
<td>1.252 / 1.261</td>
</tr>
<tr>
<td>H⁺- HHPZ-carbamate</td>
<td>1.390</td>
<td>1.396</td>
<td>1.215 / 1.350[d]</td>
</tr>
<tr>
<td>HHPZ-carbamate</td>
<td>1.460</td>
<td>1.470</td>
<td>1.254 / 1.263</td>
</tr>
</tbody>
</table>

[a] Isomer 1: \( R_2 = R_3 = \text{CH}_3 \) and \( R_1 = R_4 = \text{H} \) (Figure 5-14); [b] Isomer 2: \( R_1 = R_3 = \text{CH}_3 \) and \( R_2 = R_4 = \text{H} \) (Figure 5-14); [c] \( R_2 = R_4 = \text{CH}_3 \) and \( R_1 = R_3 = \text{H} \) (Figure 5-14); [d] Hydrogen bonding between ‘O2’ of the carbamate moiety and a proton of the NH₂⁺ group (Figure 5-14).
In this chapter PZ has been shown to form a hydrolysis resistant carbamate, as per Figure 5-2 and 5-3. It was for this reason that the optimised geometries of H\textsuperscript+-PZ-carbamate and PZ-carbamate were used as the baseline against which the remaining amine carbamate derivatives were compared.

For both H\textsuperscript+-PZ-carbamate and PZ-carbamate resonance stabilisation of the carboxylate moiety was evident. Table 5-3 shows identical charges on O1 and O2 and identical r\textsubscript{C-O} bond lengths. The r\textsubscript{C-O} bond lengths display partial double bond character at 1.247 Å and 1.257 Å for the H\textsuperscript+-PZ-carbamate and PZ-carbamate respectively (B3LYP). The N-COO\textsuperscript{-} bond length of both PZ carbamate species is of single bond character at 1.513 Å (H\textsuperscript+-PZ-carbamate) and 1.471 Å (PZ-carbamate) (B3LYP). Standard single r\textsubscript{N-C} in PZ is 1.466 Å (B3LYP) and 1.465 Å (MP2). H\textsuperscript+-2,6-DMPZ-carbamate and 2,6-DMPZ-carbamate also exhibit this stable resonance structure, albeit with slightly shorter N-COO\textsuperscript{-} bond lengths. These findings were in keeping with our infrared studies with PZ and 2,6-DMPZ and presented in Figure 5-2 and 5-5 respectively. Both amines gave very similar outcomes with the exception of the emergence of a small bicarbonate \(\nu\textsubscript{C-O}\textsuperscript{-}\) absorbance band in Figure 5-5 for 2,6-DMPZ. The protonated and unprotonated 2,6-DMPZ-carbamate forms of isomer 2 (Figure 5-14), the minor reaction component, contribute to bicarbonate formation.

H\textsuperscript+-HHPY-carbamate displayed a lower level of charge delocalisation to the two oxygen atoms, relative to H\textsuperscript+-PZ-carbamate. Changes in charge distribution and bond length were noted with a r\textsubscript{C-O1} of 1.227 Å and r\textsubscript{C-O2} of 1.277 Å, which was mirrored in the change in electron density at O1 (-0.641) and O2 (-0.735) (B3LYP). The shift in electron distribution was much less pronounced in the HHPY-carbamate species with a r\textsubscript{C-O1} of 1.257 Å and a r\textsubscript{C-O2} of 1.259 Å which was mirrored in the change in electron density at O1 (-0.762) and O2 (-0.767) (B3LYP). Table 5-3 shows the N-COO\textsuperscript{-} bond length of H\textsuperscript+-HHPY-carbamate and HHPY-carbamate to be similar to that of the PZ carbamate species. These findings were in keeping with our infrared studies (Figure 5-7) in which HHPY was identified as forming a more labile carbamate derivative that is more susceptible to hydrolysis than that of PZ.

The lowest energy conformer obtained for H\textsuperscript+-HHPY-carbamate, as opposed to HHPY-carbamate species, exhibited intramolecular hydrogen bonding between the COO\textsuperscript{-} functionality of the carboxylate group and the NH\textsubscript{2}\textsuperscript{+} moiety. The low energy conformers of H\textsuperscript+-MHHPY-carbamate and H\textsuperscript+-HHPZ-carbamate were also found to exhibit the same intramolecular hydrogen bonding. The resonance structure of the H\textsuperscript+-MHHPY-carbamate was even less delocalised with a r\textsubscript{C-O1} of 1.211 Å and a r\textsubscript{C-O2} of 1.354 Å which was mirrored in the change in electron density at O1 (-0.650) and O2 (-0.772) (B3LYP). The N-COO\textsuperscript{-} bond length of H\textsuperscript+-
MHHPY-carbamate was also found to be much shorter at 1.417 Å. The shift in electron distribution of the carboxylate resonance structure was again much less pronounced in the MHHPY-carbamate species compared to the H⁺-MHHPY-carbamate species. However, MHHPY-carbamate displayed a shorter N-COO⁻ bond length than PZ-carbamate and HHPY-carbamate. MHHPY was found to form predominantly bicarbonate on absorption of CO₂ (Figure 5-8) as does 2,5-DMPZ (Figure 5-6). Both species display shorter N-COO⁻ bond lengths and lower levels of resonance stabilisation.

In our infrared studies DMHHPY was found to be representative of a blended amine system. Nonetheless, optimised geometries of the H⁺-DMHHPY-carbamate and DMHHPY-carbamate were still analysed. Both species exhibited reduced resonance in the carboxylate moiety with a \( r_{C-O1} \) of 1.235 Å and a \( r_{C-O2} \) of 1.244 Å which was mirrored in the change in electron density at O1 (-0.653) and O2 (-0.699) and with a \( r_{C-O1} \) of 1.252 Å and a \( r_{C-O2} \) of 1.261 Å which was mirrored in the change in electron density at O1 (-0.758) and O2 (-0.819) (B3LYP) respectively. DMHHPY was expected to form predominantly bicarbonate on absorption of CO₂, given the structural similarity of DMHHPY with MHHPY.

HHPZ was found to be un-reactive towards CO₂, with no measurable CO₂ absorption. Table 5-3 shows H⁺-HHPZ-carbamate to have a significantly shorter N-COO⁻ bond length of 1.390 Å, which was more double bond in character. H⁺-HHPZ-carbamate was also shown to have the largest displacement in electron distribution of the carboxylate resonance structure with a \( r_{C-O1} \) of 1.215 Å and a \( r_{C-O2} \) of 1.350 Å which was mirrored in the change in electron density at O1 (-0.575) and O2 (-0.660) (B3LYP). This was much less pronounced in the HHPZ-carbamate species, nonetheless in a diamine system it is typical for one amine functionality to act as the binding site for CO₂ while the other amine group becomes protonated. These data support our experimental observations.

### 5.5 Heterocyclic Diamines as Promoters in Blended Amine Systems

The advantage of blended amine systems was first realised in this study on the FT-IR analysis of the DMHHPY / CO₂ / H₂O system. The in house synthesised DMHHPY was blended with primary diamine DAP and found to exhibit significantly enhanced \( C_A \) and \( R_{IA} \) values compared to its single methyl substituted analogue MHHPY (Table 5-1). An AMP / PZ blended system was also investigated to aid in the interpretation of the infrared spectral profile obtained for the DMHHPY / CO₂ / H₂O system (Figure 5-9). Similar CO₂ absorption characteristics were observed for both blended systems (c.f. Figure 5-9 and 5-11).
As mentioned previously, PZ is commonly used as an additive in tertiary and Cα-substituted amine absorbent systems.\cite{66, 68, 72, 76-78, 98, 99, 159} Furthermore, it has been reported that the presence of the tertiary and Cα-substituted amine at significantly higher concentrations than PZ (4 mol L$^{-1}$/0.4 mol L$^{-1}$ respectively) appears to catalyse the carbamate forming reaction between CO$_2$ and PZ.\cite{68, 99} This suggested that some sort of amine-amine interaction contributed to the enhanced CO$_2$ absorption of the blended systems, rather than the two amines simply acting as separate entities in solution and the enhancement being an additive effect.

In this study further interest was shown in the CO$_2$ absorption characteristics of blended amine systems and in the effect other heterocyclic amines, such as piperidine, may have if added in catalytic quantities to a Cα-substituted amine such as AMP. Both piperidine and PZ are cyclic amines, with PZ being the diamine analogue of piperidine, and they both react rapidly with CO$_2$ to form a carbamate species. Despite the subtle change in structure the piperidine carbamate species has been identified in this study as being more hydrolytically labile than the PZ carbamate species. This effect has a considerable impact on CO$_2$ absorption, particularly at high CO$_2$ loadings (>0.5 mol CO$_2$/mol amine).

Having observed \textit{in-situ} the different CO$_2$ absorption characteristics of piperidine and PZ as sole CO$_2$ capture absorbents, we went onto investigate \textit{in-situ} the CO$_2$ absorption characteristics of an AMP / piperidine blended amine system. The infrared spectral profile obtained and presented in Figure 5-13 was found to be significantly different from that of the AMP / PZ and DMHHPY system.

To further investigate the advantages of amine blends, as well as the effect PZ versus piperidine has on the CO$_2$ absorption characteristics of AMP, absorption capacity (C$_A$) and rate data (K$_G$) was collected for both the AMP / PZ and AMP / piperidine blended systems. For comparison data was also collected for the equivalent unblended systems.

C$_A$ was measured simultaneously with the infrared spectral data during a typical CO$_2$ absorption / FT-IR experiment, as per Section 2.1. The AMP / PZ and AMP / piperidine formulation was 2.4 mol L$^{-1}$/0.6 mol L$^{-1}$, respectively.

The wetted-wall column (WWC) technique described in Section 2.2.2 was used to analyse K$_G$ over a range of CO$_2$ loadings (0-0.6 mol CO$_2$/mol amine). A total amine concentration of 1 mol L$^{-1}$ was analysed. The AMP / PZ and AMP / piperidine formulation was 0.75 mol L$^{-1}$/0.25 mol L$^{-1}$ respectively. For the unblended PZ and piperidine systems a concentration of 0.25 mol L$^{-1}$ was used and 1 mol L$^{-1}$ for the unblended AMP system. The blended and unblended amines were preloaded to the desired CO$_2$ loading by bubbling a pure CO$_2$ gas stream through the solution and gravimetrically measuring the amount of CO$_2$ absorbed. Following the procedure
outlined in Section 2.2.2.3 absorption flux experiments were then conducted for each amine or amine blend at liquid CO\textsubscript{2} loadings of 0, 0.2, 0.35-0.4 and 0.5-0.6 mol CO\textsubscript{2} / mol amine. A gas flow rate of 3 L min\textsuperscript{-1} and liquid flow rate of 133 ml L\textsuperscript{-1} was used for all experiments.

Table 5-4 provides the C\textsubscript{A} and K\textsubscript{G} values obtained for the blended and unblended systems. Figure 5-15 plots K\textsubscript{G} as a function of CO\textsubscript{2} loading. As anticipated, K\textsubscript{G} decreased with increasing CO\textsubscript{2} loading, as a result of the subsequent decrease in the amount of free amine available to react with CO\textsubscript{2}.

Table 5-4  The overall mass transfer coefficient (K\textsubscript{G}), at 40°C, and liquid CO\textsubscript{2} loading for aqueous solutions of AMP (1 mol L\textsuperscript{-1}), PZ (0.25 mol L\textsuperscript{-1}), piperidine (0.25 mol L\textsuperscript{-1}), AMP / PZ (0.75 / 0.25 mol L\textsuperscript{-1}) and AMP / Piperidine (0.75 / 0.25 mol L\textsuperscript{-1}). The exact CO\textsubscript{2} loading of the test solutions is provided in parenthesis. The CO\textsubscript{2} absorption capacity (C\textsubscript{A}) for each amine systems has also been provided.

<table>
<thead>
<tr>
<th>Amine System</th>
<th>C\textsubscript{A} (mol CO\textsubscript{2} / mol amine)</th>
<th>K\textsubscript{G} ([d]) (mol / s cm\textsuperscript{2} Pa) (x10\textsuperscript{-10})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>AMP</td>
<td>0.84\textsuperscript{[a]}</td>
<td>0.61</td>
</tr>
<tr>
<td>PZ</td>
<td>0.92\textsuperscript{[b]}</td>
<td>1.30</td>
</tr>
<tr>
<td>Piperidine</td>
<td>0.76\textsuperscript{[c]}</td>
<td>1.26</td>
</tr>
<tr>
<td>AMP / PZ</td>
<td>1.0\textsuperscript{[c]}</td>
<td>1.63</td>
</tr>
<tr>
<td>AMP / Piperidine</td>
<td>0.90\textsuperscript{[c]}</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Concentrations: \(\textsuperscript{[a]}3\) mol L\textsuperscript{-1}; \(\textsuperscript{[b]}1.5\) mol L\textsuperscript{-1}; \(\textsuperscript{[c]}3\) mol L\textsuperscript{-1} (AMP= 2.4 mol L\textsuperscript{-1} / PZ or Piperidine= 0.6 mol L\textsuperscript{-1}); \(\textsuperscript{[d]}\) For rate study unblended AMP= 1 mol L\textsuperscript{-1}, unblended PZ and Piperidine= 0.25 mol L\textsuperscript{-1}, AMP / PZ and AMP / Piperidine Blends= 1 mol L\textsuperscript{-1} (AMP= 0.75 mol L\textsuperscript{-1} / PZ and piperidine= 0.25 mol L\textsuperscript{-1}).
Figure 5-15  The overall mass transfer coefficient \( (K_G) \), at 40°C, as a function of CO\(_2\) loading for aqueous solutions of AMP (1 mol L\(^{-1}\)), PZ (0.25 mol L\(^{-1}\)), piperidine (0.25 mol L\(^{-1}\)), AMP / PZ (0.75 / 0.25 mol L\(^{-1}\)) and AMP / Piperidine (0.75 / 0.25 mol L\(^{-1}\)).

Table 5-4 shows unblended PZ and piperidine to exhibit similar initial rates of CO\(_2\) absorption returning almost identical \( K_G \) values at zero loading of 1.30 and 1.26 mol / s.cm\(^2\).Pa \((x10^{-10})\) respectively. This was mirrored in the initial \( K_G \) values obtained for the equivalent AMP / PZ and AMP / piperidine blended systems of 1.66 and 1.54 mol / s.cm\(^2\).Pa \((x10^{-10})\) respectively.

The blended AMP / PZ and AMP / piperidine systems exhibited enhanced CO\(_2\) absorption characteristics compared to the corresponding unblended counterparts, returning higher \( C_A \) and initial \( K_G \) values. This is consistent with the results obtained for DMHHHPY and given in Table 5-1.

The enhancement in initial \( K_G \) values of the blended systems was equivalent to the combined \( K_G \) values of the corresponding unblended systems. For instance AMP returned an initial \( K_G \) value of 0.61, PZ 1.30 and piperidine 1.26 mol / s.cm\(^2\).Pa \((x10^{-10})\). If the \( K_G \) values were additive in a blended system, theoretically an AMP / PZ and AMP / piperidine blend should return an initial \( K_G \) value close to 1.91 and 1.86 mol / s.cm\(^2\).Pa \((x10^{-10})\) respectively, or between these values and that of the unblended equivalents. The AMP / PZ and AMP / piperidine
blended system returned an initial $K_G$ value of 1.66 and 1.54 mol / s.cm$^2$.Pa ($x10^{-10}$) respectively, confirming that $K_G$ was additive in the blended systems. PZ or piperidine reacted preferentially and rapidly with CO$_2$, with the slower reacting AMP also contributing but to a much lesser extent. This resulted in a higher CO$_2$ absorption rate compared to the corresponding unblended system but nothing beyond an additive effect.

Figure 5-14 shows piperidine $K_G$ values to decline rapidly with increasing CO$_2$ loading. By 0.5 mol CO$_2$ / mol amine $K_G$ becomes equivalent to that of AMP and bicarbonate formation. This can be attributed to the piperidine molecule containing only one NH group. This imparted a 2:1 stoichiometry on the reaction with CO$_2$, whereby a second amine molecule is required to act as proton acceptor in the carbamate reaction pathway. By a loading of 0.5 mol CO$_2$ / mol amine all free amine had been consumed, either in the form of piperidine-1-carboxylate or piperidine-H$^+$, and the rate of CO$_2$ absorption then becomes dependent on carbamate hydrolysis and the subsequent catalytic formation of bicarbonate.

The trend in $K_G$ values obtained for the AMP / piperidine blend traced that of piperidine after a CO$_2$ loading of 0.2 mol CO$_2$ / mol amine. An enhancement in the CO$_2$ absorption rate is observed in the initial stages of the reaction but declines rapidly up to a loading of 0.2 mol CO$_2$ / mol amine. By a loading of 0.5 mol CO$_2$ / mol amine the rate of CO$_2$ absorption falls to that of AMP and becomes dependent on carbamate hydrolysis and subsequent bicarbonate formation. These results are in keeping with the infrared spectral data presented in Figure 4-2 and 5-13 for the piperidine and AMP / piperidine / CO$_2$ / H$_2$O systems respectively. Figure 4-2 shows the hydrolysis of piperidine-1-carboxylate at CO$_2$ loadings above 0.5 mol CO$_2$ / mol amine and Figure 5-13 shows bicarbonate formation to dominate at CO$_2$ loadings above 0.3-0.4 mol CO$_2$ / mol amine.

The $K_G$ value obtained for PZ was almost identical to that of piperidine at zero loading. However, Figure 5-15 shows $K_G$ to decline at a much slower rate with increasing CO$_2$ loading. This was attributed to the PZ molecule containing two NH groups. There is a greater amount of free amine available to react with CO$_2$, when compared to piperidine at equivalent CO$_2$ loadings.

The $K_G$ values obtained for the AMP / PZ system traces that of PZ. Figure 5-15 shows an enhancement in $K_G$ up to a loading of 0.4 mol CO$_2$ / mol amine, after which it falls to that of PZ. This enhancement is greater than that observed for the AMP / piperidine blend and again can be attributed to the diamine nature of PZ. These results are consistent with the infrared spectral data given in Figure 5-2 and 5-11 for the PZ and AMP / PZ / CO$_2$ / H$_2$O systems respectively. Figure 5-2 and 5-11 show carbamate formation to dominate up to CO$_2$ loadings of
0.92-1.0 mol CO\textsubscript{2} / mol amine. For the AMP / PZ / CO\textsubscript{2} / H\textsubscript{2}O system bicarbonate absorbance can be seen evolving in the background with a rapid increase in formation occurring at CO\textsubscript{2} loadings > 0.5 mol CO\textsubscript{2} / mol amine, but to a much lesser extent then that observed for the corresponding AMP / piperidine system (c.f. Figure 5-11 and 5-13). The observed increase in bicarbonate was concomitant with the decrease in free PZ.

The data presented in Table 5-4 and Figure 5-14 highlighted the advantages of using a diamine, such as PZ or even DAP, as an absorption accelerator in Ca-substituted amine systems when compared to a monoamine such as piperidine.

The success and widespread application of PZ as an absorption accelerator in blended amine systems, as opposed to a sole CO\textsubscript{2} capture absorbent, was attributed to two main factors:

i. PZ forms a hydrolysis resistant carbamate derivative in the reaction with CO\textsubscript{2}, as evidenced in the infrared spectral data presented in Figure 5-2, and

ii. The diamine nature of PZ, as evidenced by the CO\textsubscript{2} absorption rate data presented in Figure 5-15.

Both of the above factors contributed to an increased enhancement in CO\textsubscript{2} absorption by the blended AMP / PZ system over a wider range of CO\textsubscript{2} loadings when compared to the AMP / piperidine system and unblended piperidine and PZ systems, whilst maintaining prominent bicarbonate formation.

Capture absorbents that form more bicarbonate are economically desirable from the viewpoint that it is more cost-effective to re-release the CO\textsubscript{2} in the stripping stage of the PCC process. On the other hand amines that exhibit enhanced CO\textsubscript{2} absorption rates are economically desirable from the viewpoint that a smaller absorption column is required to capture CO\textsubscript{2}. Blended amine systems, such as AMP / PZ or DMHHPY / DAP offer a compromise between the two. However, it has also been demonstrated in this chapter and the previous chapter that the same compromise can be reached using sole CO\textsubscript{2} capture absorbents, such as piperidine or HHPY. These amines react rapidly with CO\textsubscript{2} to form labile carbamate species that is readily hydrolysed to bicarbonate at high CO\textsubscript{2} loadings (> 0.5 mol CO\textsubscript{2} / mol amine).
6 Synthesis of Hexahydropyrimidine, Methylhexahydropyrimidines and Hexahydropyridazine

6.1 Introduction

Hexahydropyrimidine (HHPY), 2-methylhexahydropyrimidine (MHHPY), 2,2-dimethylhexahydropyrimidine (DMHHPY) and hexahydropyridazine (HHPZ) have been synthesised for characterisation of their reaction with CO$_2$ and subsequent testing as novel CO$_2$ capture absorbents.

6.1.1 Hexahydropyrimidines

Hexahydropyrimidine and its methyl substituted analogues can be obtained by the condensation of 1, 3-diaminopropane (DAP) (1) with carbonyl compounds (2) such as formaldehyde, acetaldehyde and acetone (Scheme 6-1).\textsuperscript{[157, 160-162]} The reaction proceeded first via the formation of a monoimine (3). The free amino group of the monoimine attacked the imine carbon in a 6-endo-trig ring closure to yield the hexahydropyrimidine (4).\textsuperscript{[163, 164]} Generally imine formation required an acid catalyst to expel water or the reaction is very slow. However under acidic conditions a tautomeric mixture of (3) and (4) is often obtained.\textsuperscript{[157, 160, 162]} On prolonged contact with acid the open chained form (3) is readily hydrolysed to DAP and the carbonyl compound.\textsuperscript{[157, 162]}
6. Synthesis of Hexahydropyrimidine, Methyl Hexahydropyrimdines and Hexahydropyridazine

Scheme 6-1. Condensation of 1,3-diaminopropane (1) with a carbonyl compound (2) (where \( R' = R'' = H \) or \( R' = H, R'' = CH_3 \) or \( R' R'' = CH_3 \)), via the direct nucleophilic attack of the \( 1^\circ \) amine group on the carbonyl carbon to form a monomine (3), which undergoes a 6-endotrig ring closure to yield the corresponding hexahydropyrimidine (4).

The earliest reports found on the preparation of HHPY utilised the reaction between the monoprotonated form of DAP (1,3-diaminopropane monohydrochloride) and formaldehyde (37 wt % solution).\(^{157, 161, 162}\) In this work HHPY was prepared as described by Evans.\(^{157}\) One equivalent of DAP was first titrated with concentrated hydrochloric acid to a methyl orange endpoint, followed by the addition of a second equivalent of DAP and then the gradual addition of formaldehyde. This method was found to afford a low conversion of DAP to HHPY. Examination of the \(^1\)H-NMR spectra revealed an almost 1:1 mixture of DAP (47 %, ) and HHPY.
6. Synthesis of Hexahydropyrimidine, Methyl Hexahydropyrimdines and Hexahydropyridazine

(53 %). This method is described in more detail in Section 6.3.1.1.

Alternatively the reaction between free DAP and the carbonyl compounds was also explored and found to afford solely the hexahydropyrimidine, with the exception of acetone.\cite{157, 160, 165} A tautomeric mixture of the monoamine (3) and hexahydropyrimidine (4) has been observed for the reaction between free DAP and acetone.\cite{160} Subsequently, HHPY was prepared as described by Locke.\cite{165} This method involved the reaction between formaldehyde (37 wt % solution) and DAP, but with a much longer reaction time of 24 hrs as opposed to 3 hrs.\cite{162} Examination of the $^1$H-NMR spectra of the final product contained no signals from unreacted DAP. In contrast, the method reported by Locke\cite{165} was found to give a product contaminated with unreacted DAP (10 %). Removal of water from the reaction product was achieved by azeotropic distillation with cyclohexane. However water and cyclohexane also formed an azeotrope with HHPY resulting in the loss of product during the dehydration procedure and consequently a low yield of anhydrous HHPY (20 %). The method is described in more detail in Section 6.3.1.2.

MHHPY and DMHHPY were also prepared utilising the reaction between the free amine and carbonyl compound (acetaldehyde and acetone respectively) in a non-aqueous environment. For DMHHPY examination of the $^1$H-NMR spectra revealed the presence of DAP (37 %). The methods are further described in Sections 6.3.2 and 6.3.3 respectively.

6.1.2 Hexahydropyridazine

Hexahydropyridazine was obtained by the base-catalysed hydrolysis of a dicarboalkoxyhexahydropyridazine (5), such as dicarbethoxyhexahydropyridazine (Scheme 6-2).\cite{166-168} The reaction proceeds via the same general mechanism as that described for secondary carbamate esters in Section 4.2.5 but stepwise, with one carboalkoxy group being hydrolysed to a considerable extent before the second carboalkoxy group is attacked.\cite{166} The reaction involves the direct nucleophilic attack of $\text{OH}$ on one of the carbonyl carbons of (5) to form a monoanion tetrahedral intermediate (6). Cleavage of the alkoxide group (OR) occurs to generate the corresponding alcohol and carboxylate (7). The carboxylate rapidly decomposes to $\text{CO}_2$ and the monocarboalkoxyhexahydropyridazine (8). The monocarboxyhexahydropyridazine was then hydrolysed accordingly to generate hexahydropyridazine (9).
6. Synthesis of Hexahydropyrimidine, Methyl Hexahydropyrimdines and Hexahydropyridazine

Dicarboalkoxyhexahydropyridazines (5), such as dicarbethoxyhexahydropyridazine, can be obtained by the alkylation and subsequent cyclization of a hydrazine dicarboxylate (10) with a dihalogenobutane (11), such as diethylhydrazine dicarboxylate and dibromobutane (X = Br) respectively.\textsuperscript{167, 168} The reaction proceeds via a S\textsubscript{N}2 pathway. Stepwise, one amino group is alkylated followed by the second amino group resulting in cyclization (Scheme 6-3). The N-alkylation involves the nucleophilic attack of a 2° amino group in (10) on an electrophilic
6. Synthesis of Hexahydropyrimidine, Methyl Hexahydropyrimidines and Hexahydropyridazine

carbon of (11), displacing the halide (X) and forming an ammonium cation intermediate (12). The intermediate is deprotonated by base ‘B’, e.g. ‘OH. The subsequent N-alklyation of the second amino group in (10) gives the dicarboalkoxyhexahydropyridazine (5).

Scheme 6-3. Alkylation, and subsequent cyclization, of a hydrazine dicarboxylate (10) (where R=alkyl group such as CH₃, CH₂CH₃) with a dihalogenobutane (11) (where X= halide such as Cl, Br, I) to obtain the corresponding dicarboalkoxyhexahydropyridazine (5).
Hexahydropyridazine has been synthesised in a two-step procedure. Firstly, dicarbethoxyhexahydropyridazine was prepared by reacting diethylhydrazine dicarboxylate and dibromobutane. The prepared and isolated dicarbethoxyhexahydropyridazine was then hydrolysed and decarboxylated to obtain hexahydropyridazine. The method is described in more detail in Section 6.4.

### 6.2 General Experimental

All starting materials are provided in Table 6-1 and were used without further purification. Solvents were bulk and distilled prior to use. \(^1\)H and \(^13\)C NMR spectra were recorded on a Bruker Avance™ AMX 300 MHz spectrometer at 300.1315 and 75.4762 MHz respectively. Chemical shifts (\(\delta\)) are reported in parts per million (ppm) measured relative to the internal standards, and coupling constants (\(J\)) are expressed in Hertz (Hz). Mass spectra were recorded on a Shimadzu LCMS-2010 EV spectrometer and obtained via the ESI method. Infrared spectra were recorded by ATR FT-IR on a Mettler-Toledo ic10 FT-IR spectrometer. Where applicable, product ratios in the final reaction products were determined from integration of the \(^1\)H NMR spectra.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>(\geq 99.5%)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Acetone</td>
<td>(\geq 99.9%)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Anhydrous potassium Carbonate (K(_2)CO(_3))</td>
<td>(\geq 99.0%)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Anhydrous 1,3-dimainopropane (DAP)</td>
<td>(\geq 99.0%)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Dibromobutane</td>
<td>99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Diethylhydrazine dicarboxylate</td>
<td>97.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Formaldehyde Solution</td>
<td>37 wt %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Hydrochloric Acid (HCl)</td>
<td>37 wt %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Anhydrous Sodium Hydroxide pellets (NaOH)</td>
<td>(\geq 98.0%)</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
6.3 Synthesis of Hexahydropyrimidine and Methylhexahydropyrimidines

6.3.1 Preparation of Hexahydropyrimidine (HHPY)

6.3.1.1 Method 1

Firstly HHPY was prepared as described by Evans. An ice-cooled stirred aliquot of DAP (0.2 mol, 17.0 mL, 15.10 g) in water (50 mL) was titrated with concentrated HCl (37 wt % solution, 0.4 mol, 35 mL) to a methyl orange end-point. 1,3-Diaminopropane (0.2 mol, 17.0 mL, 15.10 g) was added and the solution cooled and maintained at 20-25°C using an ice-bath. Formaldehyde (37 wt % solution, 0.4 mol, 30 mL, 32.70 g) was added drop wise to the ice-cooled stirred solution over 30 mins. The reaction mixture was then stirred for 3 hours at room temperature, cooled in an ice-bath and NaOH added (2 mol, 80.00 g). The organic layer was transferred to a Dean-Stark apparatus and azeotropically distilled with cyclohexane (100 mL). The cyclohexane was removed in vacuo and the residue fractionally distilled to afford a clear oil (14.37 g, 42%) (b.p. 57-60°C / 27 mbar, lit. [157, 165] b.p. 55-60°C / 27 mbar).

Examination of the $^1$H-NMR spectra revealed a mixture of DAP (47%, 6.75 g) and HHPY (53%, 7.62 g). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.00 (2H, m), 2.47 (4H, t, $J$ = 5.5 Hz), 3.27 (2H, s), with DAP signals at $\delta$ 0.84 (4H, s), 1.07 (2H, m), 2.24 (4H, t, $J$ = 6.9 Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 28.1, 45.0, 62.2, with DAP signals at $\delta$ 36.6, 39.1.

6.3.1.2 Method 2

HHPY was prepared as described by Locke. Formaldehyde (37 wt % solution, 1.5 mol, 126.00 g) was added drop wise to an ice-cooled, stirred aliquot of anhydrous DAP (1 mol, 74.10 g) over 30 mins. The reaction mixture was then stirred for 24 hours at room temperature, cooled in an ice-bath and NaOH added (1 mol, 40.00 g). The organic layer was transferred to a Dean-Stark apparatus and azeotropically distilled with cyclohexane (100 mL). The cyclohexane was removed in vacuo and the residue fractionally distilled to afford anhydrous HHPY (17.00 g, 20%) as a clear oil (b.p. 57-60°C / 27 mbar, lit. [157, 165] b.p. 58-60°C / 27 mbar).

The $^1$H-NMR spectra of the reaction product contained no signals from unreacted DAP. $^1$H and $^{13}$C NMR data were consistent with the literature values. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$
1.36 (2H, m), 1.96 (2H, bs), 2.82 (4H, t, \( J = 5.5 \text{ Hz} \)), 3.63 (2H, s); \(^{13}\text{C NMR (75 MHz, CDCl}\text{)} \delta 28.6, 45.7, 62.8; \text{MS (ESI\( ^{+} \)) m/z }87 \text{ (M+1); FT-IR } \nu(\text{N-H}) \text{ 3267 cm}^{-1}.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 & + & \text{H}_2\text{O} \\
\text{r.t, 24h} & & & \\
\text{H}_2\text{N} & \quad \text{NH} & & \\
\text{Scheme 6-4. Synthesis of hexahydropyrimidine (HHPY).}
\end{align*}
\]

### 6.3.2 Preparation of 2-Methylhexahydropyrimidine (MHHPY)

MHHPY was prepared as described by Zelenin.\(^{[160]}\) Acetaldehyde (0.215 mol, 9.50 g) in diethyl ether (100 mL) was added drop wise to an ice-cooled, stirred aliquot of anhydrous DAP (0.2 mol, 14.80 g). The reaction mixture was then stirred over K\(_2\text{CO}_3\) (0.4 mol, 55.40 g) for 24 hours at room temperature. The solvent was removed \textit{in vacuo} and the residue fractionally distilled to afford MHHPY (17.50 g, 87\%) as a clear oil (b.p. 56-59°C / 30 mbar, lit.\(^{[160]}\) b.p. 60°C / 30 mbar).

\(^1\text{H} \text{and } ^{13}\text{C NMR data were consistent with the literature values.}^{[160,169]} \(^1\text{H NMR (300 MHz, CDCl}_3)) \delta 0.80 (3\text{H, d, } J = 6.0 \text{ Hz}), 1.09 (2\text{H, m}), 2.48 (2\text{H, m}), 2.76 (4\text{H, m}), 3.25 (1\text{H, q, } J = 6.0 \text{ Hz}); ^{13}\text{C NMR (75 MHz, CDCl}_3)) \delta 22.8, 26.8, 45.4, 67.1; \text{MS (ESI\( ^{+} \)) m/z 101 (M+1); FT-IR } \nu(\text{N-H}) \text{ 3266 cm}^{-1}.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 & + & \text{(C}_2\text{H}_3)_2\text{O, K}_2\text{CO}_3 \\
\text{r.t, 24h} & & & \\
\text{H}_2\text{N} & \quad \text{NH} & & \\
\text{Scheme 6-5. Synthesis of 2-methylhexahydropyrimidine (MHHPY).}
\end{align*}
\]

### 6.3.3 Preparation of 2,2-Dimethylhexahydropyrimidine (DMHHPY)

DMHHPY was prepared as described by Zelenin.\(^{[160]}\) A solution of acetone (0.215 mol, 12.50 g) in diethyl ether (100 mL) was added drop wise to an ice-cooled, stirred aliquot of anhydrous DAP (0.2 mol, 14.83 g). The reaction mixture was then stirred over K\(_2\text{CO}_3\) (0.4 mol,
55.40 g) for 24 hours at room temperature. The solvent was removed \textit{in vacuo} and the residue fractionally distilled to afford DMHHPY (16.17 g, 71\%) as a clear oil (b.p. 50-54°C / 25 mbar, lit.\cite{160} b.p. 65°C / 33 mbar).

\(^1\)H NMR and \(^{13}\)C NMR data was consistent with the literature values.\cite{160} \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.90 (6H, s), 1.05 (2H, m), 1.45 (2H, s), 2.60 (4H, t, \(J = 5.7\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 27.6, 36.9, 40.0, 64.3; MS (ESI\(^+\)) \(m/\ell\) 115 (M+1); FT-IR \(\nu(\text{N-H})\) 3271 cm\(^{-1}\), \(\nu(\text{NH}_2)\) 1602 cm\(^{-1}\). Examination of the \(^1\)H-NMR spectra also revealed the presence of DAP (37 \%, 5.98 g), with signals at \(\delta\) 0.98 (4H, s), 1.20 (2H, m), 2.37 (4H, t, \(J = 6.9\) Hz).

![Scheme 6-6. Synthesis of 2,2-dimethylhexahydropyrimidine (DMHHPY).](image)

### 6.4 Synthesis of Hexahydropyridazine

#### 6.4.1 Step 1: Preparation of Dicarbethoxyhexahydropyridazine

Dicarbethoxyhexahydropyridazine was prepared as described by Nakayama.\cite{167} Dibromobutane (0.1 mol, 21.6g) was added drop wise to a stirred solution of diethylhydrazine dicarboxylate (0.1 mol, 17.6 g), K\(_2\)CO\(_3\) (0.2 mol, 27.7g) and acetonitrile (100ml) at room temperature. The reaction mixture was then refluxed for 24 hours, cooled and filtered. The solvent was removed \textit{in vacuo} and the residue fractionally distilled to afford dicarbethoxyhexahydropyridazine (18.5g, 80\%) as a clear oil (b.p. 110-114°C / 2-3 mbar, lit.\cite{167} 106-114°C / 3 mbar).

\(^1\)H NMR data was consistent with the literature values.\cite{170} \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.07 (6H, m), 1.49 (4H, s), 2.74 (4H, bs), 3.97 (4H, m); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 14.4, 23.2, 44.8, 61.9, 155.2; MS (ESI\(^+\)) \(m/\ell\) 231 (M+1); FT-IR \(\nu(\text{C=O})\) 1706cm\(^{-1}\).
6. Synthesis of Hexahydropyrimidine, Methyl Hexahydropyrimdines and Hexahydropyridazine

Scheme 6-7. Synthesis of dicarboxhexahydropyridazine.

6.4.2 Step 2: Preparation of Hexahydropyridazine (HHPZ)

HHPZ was prepared as described by Sugiyama.\textsuperscript{[168]} dicarboxhexahydropyridazine (0.13 mol, 30.10 g) was added to a solution of NaOH (0.72 mol, 20.80 g), water (20 mL) and methanol (150 mL). The reaction mixture was then refluxed for 20 hours, cooled and the precipitated inorganic salt removed by filtration. The filtrate was refluxed for a further 20 hours, cooled, filtered and the solvent removed \textit{in vacuo}. The residue was extracted well with dichloromethane (40 mL x 3), concentrated \textit{in vacuo} and fractionally distilled to afford HHPZ (6.75 g, 60%) as a yellow oil (b.p. 38-40°C / 11 mbar, lit.\textsuperscript{[168]} b.p. 38°C / 11mbar).

\textsuperscript{1}H NMR (300 MHz, MeOD) $\delta$ 2.39 (4H, m), 3.73 (4H, m), 5.72 (2H, s); $\textsuperscript{13}$C NMR (75 MHz, MeOD) $\delta$ 23.1, 47.0; MS (ESI+) $m/z$ 87 (M+1); FT-IR $\nu$(N-H) 3269 cm$^{-1}$.

Scheme 6-8. Synthesis of hexahydropyridazine (HHPZ).
7 Summary and Recommendations

7.1 Summary of Results

An in-depth study into the structure-activity relationship on the reaction between heterocyclic amines and CO$_2$ has been performed. Using in situ ATR FT-IR spectroscopy the chemical reactions between CO$_2$ and the heterocyclic amines were characterised. The chemical species formed in the reaction were identified using the infrared absorbance of characteristic functional groups, such as carboxylate and amino groups.

The effect of structure on CO$_2$/amine reactivity was assessed according to a correlation between the infrared active ionic reaction products (carbamate, bicarbonate and protonated amine) and cumulative CO$_2$ absorption; CO$_2$ absorption capacity; initial rate of CO$_2$ absorption; and a correlation between the atomic properties of the amine and carbamate derivative with the infrared spectral data, CO$_2$ absorption capacity and initial absorption rate. Computational studies using B3LYP / 6-31+G** and MP2 / 6-31+G** were performed to investigated the atomic properties of the amines and carbamate derivative. The N-COO$^-$ carbamate bond and resonance structure of the carboxylate moiety were analysed. Gas-phase harmonic frequency and intensity calculations were also used to guide in the assignment of the infrared carbamate vibrational modes.

A correlation between cumulative CO$_2$ absorption and infrared carbamate and bicarbonate absorbance enabled the observation of carbamate hydrolysis in the amine / CO$_2$ / H$_2$O systems. This was then used to determine the effect of structure on the hydrolytic lability of the carbamate derivatives.

Two series of heterocyclic amines were investigated, including monoamines and diamines. The monoamines investigated included piperidine and a series of commercially available functionalised piperidine derivatives, e.g. those with methyl-, hydroxyl- and hydroxyalkyl-substituents. The diamines investigated included novel hexahydropyrimidine (HHPY), methyl
hexahydropyrimidines (MHHPY and DMHHPY) and hexahydropyridazine (HHPZ); piperazine (PZ), and 2,6- and 2,5- dimethylpiperazines (2,6-DMPZ and 2,5-DMPZ).

Overall the results obtained highlighted the increased reactivity of heterocyclic amines compared to conventional amines MEA, DEA and AMP, particularly with regards to the Cα-substituted amines 2-MP, MHHPY and 2,5-DMPZ. The calculated atomic properties suggested that this was an artefact of an increase in the exposed area of the amino nitrogen for reaction with CO₂ increasing the amine’s nucleophilicity. This allows for increased initial absorption rates compared to acyclic amines.

For the monoamines, the formation of the carbamate derivatives of the 3 and 4-hydroxyl, 3 and 4-hydroxymethyl, and 4-hydroxyethyl substituted piperidines were kinetically less favourable than the carbamate derivatives of piperidine and the 3 and 4-methyl substituted piperidines. These amines did however exhibit similar absorption capacities, with the exception of the 3 and 4-hydroxypiperidines. This was attributed to a difference in the hydrolytic lability of the carbamate species.

Carbamate hydrolysis was observed in the piperidine and the 3 and 4-methyl and hydroxylalkyl piperidine / CO₂ / H₂O systems with increasing CO₂ absorption. The hydroxyl substitution in the 3 and 4-hydroxypiperidines increased carbamate stability. Carbamate hydrolysis in these systems was observed to a much lesser extent than that of the piperidine and 3- and 4- methyl and hydroxylalkyl piperidine systems. Increased carbamate stability was also observed with the acyclic amines MEA and DEA. These amines share a structural similarity with MEA and DEA that being a hydroxyl group 2-3 carbon atoms removed from the amino nitrogen. The presence of an oxygen atom directly bonded to the nitrogen atom in the tertiary amine N-hydroxypiperidine completely hindered CO₂ absorption via the base-catalysis mechanism, as opposed to the methyl or hydroxyethyl substitution.

The 2-alkyl and hydroxyalkyl substituted piperidines favoured bicarbonate formation in the reaction with CO₂. The ability of these amines to form a carbamate in the initial stages of CO₂ absorption was established. Theoretical results for the 2-alkyl and hydroxyalkyl substituted piperidines suggest that a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area on the nitrogen atom both played a role in destabilising the carbamate derivative and increasing its susceptibility to hydrolysis. The contribution of each is dependent on the type and size of the substituent present. The structure of the carbamate derivatives of these amines revealed shorter N-COO⁻ bond lengths and a less delocalised electron distribution in the carboxylate moiety.
For the diamines, the PZ structural modifications had a significant impact on CO\textsubscript{2} / amine reactivity and carbamate lability. PZ displayed both the highest CO\textsubscript{2} absorption capacity and initial absorption rate. PZ forms a hydrolysis resistant carbamate as well as a dicarbamate. This behaviour was unique to PZ. Hydrolysis of the carbamate derivative of HHPY was observed. HHPY displayed similar CO\textsubscript{2} absorption characteristics to PZ, but with a higher propensity for bicarbonate formation. The introduction of \( \alpha \)-methyl substituents increased the propensity towards carbamate hydrolysis and bicarbonate formation. Additionally \( \alpha \)-methyl substitution decreased initial absorption rates in the 2,6-DMPZ and 2,5-DMPZ analogues of PZ. Increasing the number of methyl group’s \( \alpha \) to the NH also increased the rate of bicarbonate formation. Despite forming predominately bicarbonate, the initial absorption rate of MHHPY was much higher than that obtained for the corresponding \( \alpha \)-dimethyl substituted primary amine AMP and comparable with MEA and DEA. HHPZ was found to be relatively non-reactive towards CO\textsubscript{2}. Theoretical analysis for the \( \text{C}_\alpha \)-substituted diamines revealed a shorter N-COO\textsuperscript{-} carbamate bond length and a significant shift in electron distribution of the carboxylate moiety.

The blended DAP / DMHHPY exhibited an enhanced absorption capacity and rate. A similar enhancement was also observed for an AMP / PZ and AMP / piperidine blended system. The greatest enhancement was observed for AMP / PZ. This was attributed to the diamine structure and hydrolysis resistant carbamate derivative of PZ.

Capture absorbents that form more bicarbonate are economically desirable from the viewpoint that it is more cost-effective to re-release the CO\textsubscript{2} in the stripping stage of the PCC process. On the other hand amines that exhibit enhanced CO\textsubscript{2} absorption rates are also economically desirable from the viewpoint that a smaller absorption column is required to capture CO\textsubscript{2}. The AMP / PZ and DMHHPY / DAP blended amine systems offer a compromise between the two. However, it has also been demonstrated that the same compromise can be reached using sole CO\textsubscript{2} capture absorbents, such as piperidine or HHPY. These amines react rapidly with CO\textsubscript{2} to form a labile carbamate species that is readily hydrolysed to bicarbonate with increasing levels of CO\textsubscript{2} absorbed.

### 7.2 The Next Step

The structure-activity relationship study performed in this work has focused on speciation and carbamate lability; measured absorption capacities and rates; and calculated amine / carbamate atomic properties. Other factors that will play a role in CO\textsubscript{2} / amine capture chemistry include the absorbents viscosity, surface tension and surfactant properties.
The surface-active properties of amine molecules will determine how they align at the surface of the gas / liquid interface during the absorption process. This alignment was highly dependent on molecular structure and will affect absorbent properties such as viscosity and surface tension. These physicochemical properties impact on the amine / CO\textsubscript{2} interaction at the gas-liquid interface and thus amine / CO\textsubscript{2} reactivity. Incorporating these properties into the structure-activity relationship study would further improve our understanding of the amine and carbamate properties that confer enhanced CO\textsubscript{2} absorption characteristics. This would be particularly valuable where a clear trend in results was not identified in this study.

In this study the carbamate derivatives of the 3 and 4-hydroxyl and hydroxyalkyl piperidines were found to be kinetically less favourable than the carbamate derivatives of piperidine and the 3 and 4-methyl piperidines. This could not be clearly explained in terms of the calculated atomic properties for these amines and their carbamate derivatives. Investigating the surface-active properties of these amines would provide a means of further defining the amine / CO\textsubscript{2} interaction and hence the difference in reactivity.

A clear relationship between carbamate lability and atomic properties including the N-COO\textsuperscript{-} carbamate bond length and resonance structure of the carboxylate moiety was identified for C\textalpha-substituted amines. Increased carbamate lability was associated with a shorter N-COO\textsuperscript{-} bond length and a less delocalised electron distribution in the carboxylate moiety. This relationship was not as clearly defined for the 3 and 4-substituted piperidines. For instance, the hydroxyl substituted piperidines (3-HP and 4-HP) were found to form a carbamate less susceptible to hydrolysis than that of the alkyl and hydroxyalkyl substituted piperidines. This could not be clearly explained in terms of the calculated atomic properties. Neutron and X-ray scattering methods would allow the direct observation of carbamate structure and arrangement in the bulk aqueous phase of an amine / CO\textsubscript{2} / H\textsubscript{2}O system. This insight would allow further delineation of the effect of structure on carbamate lability.

Incorporation of the surface active properties of amines and the direct observation of carbamate structure into a structure-activity relationship study provides an opportunity to obtain a greater understanding of the fundamental chemistry involved the CO\textsubscript{2} absorption process. This is essential if further progress is to be made towards the development of more cost effective absorbents for post combustion CO\textsubscript{2} capture.
8 References


42. Littel R. J., Versteeg G. F. and Van Swaaij W. P. M. Kinetics of CO₂ with Primary and Secondary Amines in Aqueous Solutions—I. Zwitterion Deprotonation Kinetics


119. Mettler-Toledo AutoChem Inc. iC IR v.2.0.150.2, 2005. ReactIR Reaction Analysis Software. United States of America,


8. References


167. Nakayama T. 1992. *Hexahydopyridazine Derivatives, Used as Herbicide Intermediates - Prepared by Reacting 1,4-Dihalobutane with 1,2-Hydrazinedicarboxylate or 1,2-Di(arylcarbonyl)hydrazine and Base*. Patent EP519083-A.


Appendix

Journal Articles


Book Chapter


Conference Proceedings: Poster and Paper


An FTIR Spectroscopic Study on the Effect of Molecular Structural Variations on the CO₂ Absorption Characteristics of Heterocyclic Amines

Kelly Robinson,[a, b] Adam McCluskey,[b] and Moetaz I. Attalla*[a]

Herein, the reaction between CO₂ and piperidine, as well as commercially available functionalised piperidine derivatives, for example, those with methyl-, hydroxyl- and hydroxyalkyl substituents, has been investigated. The chemical reactions between CO₂ and the functionalised piperidines were followed in situ by using attenuated total reflectance (ATR) FTIR spectroscopy. The effect of structural variations on CO₂ absorption was assessed in relation to the ionic reaction products identifiable by IR spectroscopy, that is, carbamate versus bicarbonate absorbance. CO₂ absorption capacity and the mass-transfer coefficient at zero loading. On absorption of CO₂, the formation of the carbamate derivatives of the 3- and 4-hydroxymethyl-, 3- and 4-hydroxyethyl-substituted piperidines were found to be kinetically less favourable than the carbamate derivatives of piperidine and the 3- and 4-methyl-substituted piperidines. As the CO₂ loading of piperidine and the 3- and 4-methyl- and hydroxyalkyl-substituted piperidines exceeded 0.5 moles of CO₂ per mole of amine, the hydrolysis of the carbamate derivative of these amines was observed in the IR spectra collected. From the subset of amines analysed, the 2-alkyl- and 2-hydroxyalkyl-substituted piperidines were found to favour bicarbonate formation in the reaction with CO₂. Based on IR spectral data, the ability of these amines to form the carbamate derivatives was also established. Computational calculations at the B3LYP/6-31 + G** and MP2/6-31 + G** levels of theory were also performed to investigate the electronic/steric effects of the substituents on the reactivity (CO₂ capture performance) of different amines, as well as their carbamate structures. The theoretical results obtained for the 2-alkyl- and 2-hydroxyalkyl-substituted piperidines suggest that a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area of the nitrogen atom play a role in destabilising the carbamate derivative and increasing its susceptibility to hydrolysis. A theoretical investigation into the structure of the carbamate derivatives of these amines revealed shorter N–C bond lengths and a less-delocalised electron distribution in the carbonate moiety.

1. Introduction

Aqueous, amine-based, post-combustion capture (PCC) of CO₂ generated from coal-fired power stations has been identified as a crucial part of the global solution to climate change. The process involves separating CO₂ from other gases by reactive chemical absorption and re-releasing CO₂ from the absorbent by heating (solvent regeneration) in a two-step sequence. The technology is industrially proven for absorbents such as 30 wt% aqueous solutions of monoethanolamine (MEA) and diethanolamine (DEA), and has been used for decades to remove CO₂ from gas streams in small-scale commercial processes, such as natural-gas processing and ammonia production.[1]

The major challenge leading up to the deployment of aqueous, amine-based PCC on a large scale is adapting the existing technology to suit typical flue-gas conditions from a coal-fired power plant (low CO₂ partial pressures, typically ±1 bar, and a high volume of gas to be treated). The economics and feasibility of the process is largely dependent on the absorbent system, in particular, the capacity to absorb CO₂, how fast it can absorb CO₂ (rate) and the energy required (heat supplied) to re-release the CO₂ and regenerate the absorbent.[2] Lower capital and operational costs are associated with higher absorption capacities and absorption rates (i.e., smaller absorption columns are required) and smaller energy requirements. At present, a high energy and cost penalty is associated with large-scale application of the technology, with an expected 21% reduction in the efficiency of a coal-fired power plant when using current industry-standard technology.[3] One approach to reduce the energy requirements and cost of the process is through the development of more cost-effective and superior-performance amines.

Over the past few years there has been significant progress in the design and operation of CO₂-capture pilot plants with numerous research groups (e.g., Mitsubishi Heavy Industries (MHI), CSIRO and CO2CRC) establishing power-station-based pilot plants worldwide.[4] With recent advances in technology and the move towards demonstration-scale PCC plants, there is an increasing need to develop highly efficient absorbents.

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that are tailored for PCC. At present, MEA is the most extensively studied amine-based absorbent and is relatively well characterised with respect to its interaction with CO$_2$. For this reason, it has become the benchmark to which novel amines are compared. Currently, a select few proprietary formulations are also available from international commercial suppliers, such as Fluor[$^5$] BASF[$^6$] and MHI,[$^7$] for which they claim improved performance characteristics compared with MEA.

When CO$_2$ reacts with amines in aqueous solutions, carbamate, bicarbonate and protonated amine are generated. Briefly, primary (R$^1$NH$_3$) and secondary (R$^1$R$^2$NH) amines typically react with CO$_2$ in an aqueous environment to form a carbamate derivative, R$^1$R$^2$NHCOO$^-$, as shown in Scheme 1. This is a two-step mechanism that proceeds by the formation of the intermediate carbamic acid (a carboxylic acid derivative) followed by rapid deprotonation to the carbamate species (a carboxylic acid derivative) following the 2:1 stoichiometry of the reaction, and a larger input of energy is required for regeneration.$^{[8]}$ On the other hand, primary amines with one or more alkyl substituent at the $\alpha$-carbon ("sterically hindered"

\[ \text{R}_1^1 \text{N-H} + \text{B} + \text{CO}_2 \rightarrow \text{R}_1^1 \text{N-COO}^- + \text{BH}^+ \]

\[ \text{(} + \text{H}_2\text{O}) \]

\[ \text{R}_1^1 \text{N-H} + \text{HCO}_3^- \]

\[ \text{Scheme 1. Reaction mechanism for carbamate formation from the reaction of CO}_2 \text{ with primary (R}_1^1\text{R}_2^1\text{NH, in which R}_1 = \text{H} \text{ and secondary (R}_1^1\text{R}_2^1\text{NH) amines.} \]

slower reaction rates, higher absorption capacities and require less energy for regeneration.$^{[11, 12, 14, 17]}$

Previous studies have shown that a relationship exists between the structure of the amines and the CO$_2$ absorption characteristics.$^{[12, 16, 18, 19]}$ The molecular structure of conventional absorbents, such as primary (MEA) and secondary (DEA) amines, enable the formation of stable carbamate derivatives (Scheme 2). On the other hand, primary amines with one or more alkyl substituent at the $\alpha$-carbon ("sterically hindered"

\[ \text{H}_2\text{N-COO}^- \]

\[ \text{HO-} \text{NH} \text{OH} \]

\[ \text{HO-} \text{N-OH} \]

\[ \text{Scheme 2. The structure of a) primary amine MEA and MEA carbamate ([2-hydroxyethyl]carbamate); b) secondary amine DEA and its carbamate derivative [bis(2-hydroxyethyl)carbamate]; c) dimethyl-substituted primary amine AMP (or sterically hindered amine) and its unstable carbamate derivative [1-hydroxy-2-methyl-2-propylcarbamate]; d) cyclic diamine piperazine and its monocarbamate derivatives (piperazine-1-carboxylate and piperazine-1,4-dicarboxylate, respectively) and e) cyclic amine piperidine and piperazine 1,4-dicarboxylate.} \]

amines in industry parlance), such as 2-amino-2-methyl-1-propanol (AMP) (Scheme 2), are characterised as forming carbamates with low stability and bicarbonate as the major product of CO$_2$ absorption. Based on $^{13}$C NMR spectroscopy data, Chakraborty et al. first reported that the carbamate of AMP was formed to a much lesser extent than the carbamate of its unsubstituted counterpart MEA.$^{[18]}$ The aforementioned carbamate stability had been and remains to be assessed solely in relation to the degree of carbamate versus bicarbonate formation.$^{[14, 18]}$ The increased bicarbonate formation exhibited by C$_n$-substituted amines allowed for higher CO$_2$ loadings than that attainable with the unsubstituted counterparts.$^{[11, 16, 14]}$

The effect of the substituents on carbamate stability can manifest itself through either steric constraints on the amino nitrogen$^{[18]}$ and/or by inducing a change in the electronic envi-
environment of the amino nitrogen. However, current explanations for the variation in activity tend to focus solely on the concept of steric constraints, that is, with increasing steric crowding around the amino nitrogen there is a subsequent increase in bicarbonate formation, and hence, a decrease in carbamate stability. Both modifications affect amine reactivity towards $\text{CO}_2$ either by inducing a kinetic constraint along the carbamate reaction pathway (similar to that of tertiary amines) or by reducing the nucleophilicity of the amino nitrogen towards $\text{CO}_2$ and subsequently, by increasing the susceptibility of the resultant carbamate derivative to hydrolysis. Based on molecular-orbital arguments and computational calculations, Chakraborty et al. have reported that the dimethyl $\alpha$-substituent in AMP reduced the negative charge at the nitrogen donor site by 3.4% compared with the unhindered counterpart MEA. Furthermore, Chakraborty et al. went on to propose that this change in the electronic environment of the amino nitrogen reduced the basic strength of the amine, which weakened the bonding interaction with $\text{CO}_2$ and thus, generated an unstable carbamate derivative that was inherently more susceptible to hydrolysis. There have been no further studies expanding on these findings, particularly with respect to the steric/electronic effect of substituents larger than the methyl functional group.

Recently, heterocyclic amines, such as piperazine and piperidine (Scheme 2), have attracted considerable attention due to their increased activity for $\text{CO}_2$ absorption. Piperazine, in particular, has been found to exhibit significantly enhanced $\text{CO}_2$ absorption rates (53 000 m$^3$kmol$^{-1}$s$^{-1}$), along with an increased absorption capacity, compared with other primary and secondary amines, such as MEA (7000 m$^3$kmol$^{-1}$s$^{-1}$) and DEA (1200 m$^3$kmol$^{-1}$s$^{-1}$). This increased reactivity towards $\text{CO}_2$ has been attributed to the cyclic diamine structure of piperazine. The second amine moiety offers the potential for enhanced $\text{CO}_2$ absorption capacity either in the form of a second reactive site for carbamate formation or proton acceptance in the catalysis of bicarbonate formation, or in modifying enhancing the reactivity of the first amine site.

However, the low aqueous solubility of piperazine [1.7 mol$L^{-1}$ (146 g$L^{-1}$ at 20°C)] and piperazine carbamate [1.3 mol$L^{-1}$ (170 g$L^{-1}$ before precipitation)] limits its use as a sole $\text{CO}_2$ capture sorbent. Rather, piperazine is commonly used in catalytic quantities as an absorption accelerator in aqueous solutions of sterically hindered or tertiary amines. In contrast, piperidine, a heterocyclic secondary amine, does not suffer the same limitations and has improved aqueous solubility.

We believe that studying the reaction between $\text{CO}_2$ and piperidine, as well as commercially available functionalised piperidine derivatives, such as those with methyl, hydroxyl and hydroxalkyl substituents, provides valuable insights into the effect of molecular structural variation on $\text{CO}_2$/amine reactivity of cyclic amines and their enhanced activity compared with conventional primary and secondary amines. Herein, we report our findings.

2. Results and Discussion

To characterise the effects of molecular structural variation on $\text{CO}_2$/amine reactivity, the $\text{CO}_2$ absorption characteristics of a series of functionalised piperidines were investigated. Scheme 3 provides the structures of the subset of amines analysed. The chemical reactions between $\text{CO}_2$ and the functionalised piperidines were followed in situ by using attenuated total reflectance (ATR) FTIR spectroscopy. This novel technique allows the convenient and rapid analysis of chemical species to be carried out in an aqueous environment. The effect of structural variations on $\text{CO}_2$ absorption were assessed in relation to the ionic reaction products identifiable by IR spectroscopy, that is, carbamate versus bicarbonate absorbance, $\text{CO}_2$ absorption capacity—defined as the moles of $\text{CO}_2$ absorbed per mole of amine in solution—and the mass-transfer coefficient at zero loading, that is, the initial rate of $\text{CO}_2$ absorption.

![Scheme 3. Structures of the subset of functionalised piperidines examined herein.](image-url)
Computational calculations were also performed to investigate the electronic/steric effects of the alkyl, hydroxy and hydroxalkyl substituents on the reactivity (CO₂ capture performance) of different amines, as well as their carbamate structures.

2.1. IR Spectral Analysis

For the subset of amines analysed, a diamond-tipped ATR probe optically coupled to an FTIR spectrometer was used to monitor the reaction species that evolved in solution as CO₂ was absorbed. The chemical species formed in the reaction were identified by using the IR absorptions of characteristic functional groups reported in the literature (detailed in Section 2.1.1).

Briefly, a typical absorption experiment involved bubbling a 13% (v/v) CO₂ in nitrogen gas stream through an aqueous solution of amine (3 mol L⁻¹) in a glass reaction vessel. The difference between the CO₂ concentration in the reactor gas in- and outflows (measured by a Horiba VA 3000 CO₂ analyser) was used to determine the amount of CO₂ absorbed by the solution of amine (moles of CO₂ per mole of amine). Each experiment was run until the CO₂ concentration (in %) of the gas outflow returned to its original value (13%), that is, a maximum CO₂ loading was achieved. Depending on the amine, a typical run lasted between 45 and 90 min. The ATR probe was immersed in the aqueous solution of amine for the duration of the experiment and in situ IR measurements were obtained simultaneously with the CO₂ absorption measurements. The FTIR spectrometer was set to continuously collect spectra over the spectral range of 4000-650 cm⁻¹. Prior to analysis of the amine/CO₂/H₂O spectra, the baseline was adjusted to zero (for full details, see the Experimental Section).

2.1.1. Piperidine

Figure 1 presents a partial profile of the sequential IR spectra, in the 1800–900 cm⁻¹ region, collected during a typical CO₂ absorption experiment with an aqueous solution of piperidine (3 mol L⁻¹). Five major FTIR signals evolve with CO₂ absorption, and hence, can be related to the vibrational modes of the potential ionic reaction products, including piperidine carbamate (NCOO⁻), piperidine–H⁺ and bicarbonate (HCO₃⁻). Piperidine, which is a secondary amine, should typically react with CO₂ in solution to form a carbamate derivative. A specific assignment of the spectral signals that emerged is detailed below.

The most striking feature in the original aqueous piperidine spectrum and subsequent spectra is the broad absorbance band arising at 1643 cm⁻¹. This band is present in the spectrum of pure water and has been assigned to the O–H bending mode of water.[27, 28]

Three main signals have been assigned to the vibrational modes of piperidine–COO⁻, as shown in Figure 1. The O–COO⁻ stretching vibration (vN–COO⁻) is at 1283 cm⁻¹ and the asymmetric (v,COO⁻) and symmetric (v,COO⁻) stretching vibrations of the carboxylate moiety are at 1514 and 1434 cm⁻¹, respectively. Although the COO⁻ species is a carboxylic acid derivative, it does not give rise to the typical strong carbonyl (C=O) absorbance band at around 1700 cm⁻¹. The electron distribution of the COO⁻ group of the deprotonated carboxylic acid diffuses across both C=O bonds equally to stabilise the carboxylate moiety. The two oxygen atoms become coupled, giving rise two absorbance bands, an asymmetric and symmetric COO⁻ stretch, at lower frequencies than those of ν= C=O of carboxylic acids.[28]

Geometry optimisation of the piperidine–COO⁻ species at the B3LYP/6-31+G** and MP2/6-31+G** levels of theory revealed both C=O bond lengths were almost identical: rN–O/C=O = 1.258 and 1.264 Å, respectively, along with partial negative charges on both oxygen atoms. The ν,COO⁻ and ν,COO⁻ bands of carboxylates generally give rise to two absorbance bands in the 1650–1540 and 1450–1360 cm⁻¹ regions, depending on the molecular constituents.[28]

The absorbance band at 1477 cm⁻¹ has been assigned to the NH₂ bending mode of piperidine–H⁺. To confirm this assignment, spectral data was collected during the gradual acidification of the original piperidine solution (3 mol L⁻¹) by using concentrated HCl. A small signal evolved at around 1477 cm⁻¹ on protonation of the amine functionality.

As expected, an almost identical relationship existed between IR absorbance and cumulative CO₂ absorption (Figure 2) for the signals assigned to both piperidine–COO⁻ and piperidine–H⁺. The absorbance was observed to increase at the rate of carbamate formation at the reaction onset and decrease after a loading of 0.5 moles of CO₂ per mole of amine. The absorbance in high CO₂ loadings may be attributed to the sequential onset of a new reaction pathway, such as the hydrolysis of the NCOO⁻ derivative to HCO₃⁻. The relationship identified above can be distinguished from that observed for the absorbance band that evolves at 1354 cm⁻¹, which showed a corresponding increase in absorbance after a loading of 0.5 moles of CO₂ per mole of amine. This band has been assigned to νC=O of HCO₃⁻, which was in good agreement with literature values for aqueous HCO₃⁻.[27, 29] There are two possible reaction pathways that can lead to the formation of HCO₃⁻ in an aqueous amine environment: through the hydrolysis of the NCOO⁻ derivative or through the direct nucleophilic attack.
of OH⁻ on dissolved CO₂. The IR spectral data (Figure 2) are illustrative of the first of these two pathways, with the simultaneous decline in NCOO⁻ absorbance and increase in HCO₃⁻ absorbance.

2.1.2. Effect of N-Methyl, Hydroxyl and Hydroxyalkyl Substituents

N-Methylpiperidine (1-MP), N-hydroxypiperidine (1-HP) and N-hydroxyethylpiperidine (1-PE) are tertiary amines and cannot react directly with CO₂ to form a NCOO⁻ derivative due to the absence of hydrogen atoms bonded directly to the nitrogen atom. Instead tertiary amines form bicarbonate through a base-catalysed pathway. For this reason, their activity was compared with the set of secondary amines analysed. However, the IR spectra collected for these amines was used as a standard for bicarbonate formation in the amine/CO₂/H₂O system. Figure 3a shows the IR spectra for an aqueous solution of 1-PE (3 mol L⁻¹) as CO₂ is absorbed into solution, with the characteristic broad bicarbonate absorbance band evolving at 1350–1360 cm⁻¹. Further confirmation of this assignment is provided in Figure 3b, which shows the evolution of this broad absorbance band at 1354 cm⁻¹ in the IR spectra of an aqueous solution of piperidine (3 mol L⁻¹) with the gradual addition of ammonium bicarbonate.

2.1.3. Effect of 2-Methyl and 2-Hydroxyalkyl Substituents

The spectral data collected for 2-methylpiperidine (2-MP), 2-(hydroxy)methylpiperidine (2-PM) and 2-(2-hydroxyethyl)piperidine (2-PE)/CO₂/H₂O systems differ significantly from that of the piperidine/CO₂/H₂O system. The spectra, however, were very similar to those of the tertiary amines 1-MP and 1-PE with the evolution of the characteristic broad absorbance band at around 1354 cm⁻¹, which was indicative of HCO₃⁻ formation. Figure 4 illustrates this similarity by presenting a partial profile of the sequential IR spectra collected during typical CO₂ absorption experiments with aqueous solutions (3 mol L⁻¹) of 2-MP (Figure 4a) and 2-PM (Figure 4b).

A common misconception for amines with one or more substituents at the α-carbon (e.g., AMP), or in this study 2-methyl-, 2-hydroxymethyl- and 2-hydroxyethyl-substituted piperidines, is the notion that they are sterically hindered and unable to form the carbamate species. Recently Ismael et al. theoretically investigated the mechanism of carbamate formation by the absorption of CO₂ in AMP by using DFT calculations. They suggested that it was kinetically unfavourable for AMP to form a carbamate in the reaction with CO₂. Rather, the reaction proceeds directly to bicarbonate formation through an OH⁻ catalysis mechanism, similar to that of tertiary amines. To date, there has been no direct observation of the carbamate derivative of sterically hindered amines, with the exception of a very recent theoretical and experimental study undertaken by Jackson et al.[10] In this study, direct observation of the carbamate derivatives of the C₅-substituted amines AMP and tris(hydroxymethyl)aminomethane (THAM) were made. The work will be presented in a forthcoming publication.[10]

In an attempt to observe the carbamate derivatives of 2-MP, 2-PM and 2-PE by using in situ ATR FTIR spectroscopy, spectral analysis was performed...
data were collected during CO$_2$ absorption experiments with solutions of amine/hexanol. In the absence of water, HCO$_3^-$ formation through the CO$_2$ or NCOO$^{-}$/CO$_3^-$ hydrolysis pathway should be suppressed. To confirm this inhibition of HCO$_3^-$ formation, spectral data were collected during CO$_2$ irradiation of a solution of tertiary amine (1-PE)/hexanol. The spectra presented in Figure 5a show there were no spectral changes in the 1800–900 cm$^{-1}$ region, as expected with a 1-PE/CO$_2$/H$_2$O system (Figure 3a). The 1-PE/hexanol solution did not absorb any CO$_2$ due to the inhibition of HCO$_3^-$ formation. For comparison and to establish the formation of NCOO$^{-}$ derivatives in a non-aqueous environment, spectral data were also collected for a solution of piperidine/CO$_2$/hexanol. The piperidine/hexanol solution absorbed CO$_2$ to an upper limit of 0.5 moles of CO$_2$ per mole of amine. The spectra presented in Figure 5b show the evolution of carbamic acid/carbamate absorbance bands, including $\nu_{C=O}$ (1640), $\nu_{as\ COO^{-}}$ (1540), $\nu_{s\ COO^{-}}$ (1425) and $\nu_{N-COO^{-}}$ (1279 cm$^{-1}$).

In the absence of water, 2-MP, 2-PM and 2-PE were found to absorb a small amount of CO$_2$, unlike tertiary amine 1-PE. The IR spectral profiles, presented in Figures 6a and 6b for 2-PE/CO$_2$/hexanol and 2-MP/CO$_2$/hexanol systems, respectively, show the evolution of the same absorbance bands [$\nu_{C=O}$ (1639 and 1638), $\nu_{as\ COO^{-}}$ (1536), $\nu_{s\ COO^{-}}$ (1416 and 1417), $\nu_{N-COO^{-}}$ (1276 and 1278 cm$^{-1}$)], although somewhat weaker, as those observed for the piperidine/CO$_2$/hexanol system.

Figure 4. IR spectra of aqueous solutions (3 mol L$^{-1}$) of a) 2-MP and b) 2-PM as CO$_2$ is absorbed. Both sets of spectra show the evolution of the characteristic broad HCO$_3^-$ absorbance band at 1354 cm$^{-1}$.

Figure 5. The IR spectra collected as CO$_2$ was bubbled through solutions in a) 1-PE/hexanol and b) piperidine/hexanol.

Figure 6. The IR spectra collected as CO$_2$ was bubbled through a) 2-PE/hexanol solution and b) 2-MP/hexanol solution.
Because the intensity of these absorbance bands is weak, further clarification of the existence of these anions was established based on negative-ion electrospray ionisation mass spectrometry (ESI-MS) data.\textsuperscript{[31]}

Aqueous solutions of 2-MP, 2-PM and 2-PE (130–150 $\mu$g mL\textsuperscript{-1}) with NaHCO\textsubscript{3} (50–70 $\mu$g mL\textsuperscript{-1}) were analysed using a Waters Acquity HPLC-MS system. The carbamate derivatives of 2-MP (m/z 141.9), 2-PM (m/z 158.0) and 2-PE (m/z 172.0) were observed in the negative-ion ESI-MS broad-scan spectrum. A dissociation peak corresponding to the mass loss of CO\textsubscript{2} (m/z 44) was also evident in the multiple collision-induced dissociation (CID) spectrum of the 2-MP carbamate parent ion.\textsuperscript{[31]} However, in the case of the 2-PM and 2-PE carbamate parent ions, a dissociation signal corresponding to the mass loss of m/z 46 was evident in the CID spectra. The carbamate derivatives of 2-PM and 2-PE both have exchangeable hydrogen atoms on the hydroxyl group of the alkyl side chain that is within close proximity of the carboxylate moiety, similar to that of the anions of $\alpha$-hydroxy carboxylic acids. These anions are known to dissociate with a mass loss of m/z 46, corresponding to the loss of formic acid.\textsuperscript{[32]}

2.1.4. Effect of 3- and 4-Methyl, Hydroxyl and Hydroxyalkyl Substituents

The IR spectral profiles obtained for the 3- and 4-MP, 3- and 4-HP, 3- and 4-PM, and 4-PE/CO\textsubscript{2}/H\textsubscript{2}O systems illustrate a high degree of similarity with that of the piperidine/CO\textsubscript{2}/H\textsubscript{2}O system, in terms of signal positioning and the relationship between absorbance and cumulative CO\textsubscript{2} absorption, as shown in Figure 7. Figure 7a presents a partial profile of the sequential IR spectra collected during a typical CO\textsubscript{2} absorption experiment with an aqueous solution of 3-HP (3 mol L\textsuperscript{-1}). Figure 7b illustrates the relationship between IR absorbance and cumulative CO\textsubscript{2} absorption for the signals assigned to both carbamate and HCO\textsubscript{3}\textsuperscript{-} formation. The difference in frequencies corresponding to the stretching vibrations of the NCOO\textsuperscript{-} derivatives of piperidine and the 3- and 4-substituted piperidines do not exceed 6 cm\textsuperscript{-1}.

2.2. Absorption Capacity and Absorption Rate

To quantify the effect of the alkyl, hydroxy and hydroxyalkyl substituents on the relative reactivity (CO\textsubscript{2} capture performance) of the amino nitrogen, the CO\textsubscript{2} absorption capacity ($C_\text{a}$) and initial absorption rate (mass transfer coefficient, $K_\text{g}$ at zero loading) was determined for each individual amine.

The CO\textsubscript{2} absorption capacity was measured simultaneously with the IR spectral data during a typical CO\textsubscript{2} absorption/FTIR experiment with an aqueous solution of amine (3 mol L\textsuperscript{-1}). A wetted-wall column (WWC) apparatus was used to analyse the absorption rate of CO\textsubscript{2} into aqueous solutions of amine (1 mol L\textsuperscript{-1}). The change in concentration from 3 to 1 mol L\textsuperscript{-1} between the two different experimental techniques arose from the large volume of solution (1 L) required for a WWC experimental run, and consequently, the availability of the amines. A typical CO\textsubscript{2} absorption/FTIR experiment required a solution volume of only 30 mL, which allowed higher concentrations to be tested. All experiments were carried out at 40 °C, which was the current standard operating temperature for the absorption step of the PCC process. For a more detailed account of the experimental setup for the WWC, see the Experimental Section.

To analyse the electronic/steric effects of the alkyl, hydroxy and hydroxyalkyl substituents on the reactivity (CO\textsubscript{2} capture performance) of the amino nitrogen, the computational software package Spartan’08\textsuperscript{[33]} was used to calculate and compare optimised geometries of the functionalised piperidines at both the B3LYP/6-31 + G** and MP2/6-31 + G** levels of theory (for computational details, see the Experimental Section).

The measured absorption capacity ($C_\text{a}$) and mass-transfer coefficient ($K_\text{g}$) for the subset of alkyl-, hydroxy- and hydroxyalkyl-substituted piperidines analysed in this study are presented in Table 1. The effect of the substituents on the electrostatic potential (ESP) partial charge on the amino nitrogen and the exposed area on the nitrogen atom for the optimised forms of the amines are also provided. For comparison of reactivity, the $C_\text{a}$ and $K_\text{g}$ values obtained for conventional amine-based sorbents MEA, DEA and dimethyl-substituted AMP have also been included.

For the subset of cyclic secondary amines, with the exception of 2-PE, a significant increase in the exposed area of the amino nitrogen was found when compared with that of the
conventional secondary amine DEA [3.53 (B3LYP) and 3.47 Å² (MP2)]. This could account for the higher initial absorption rates obtained for the cyclic amines, with an increase in exposure of the electron density of the reactive site increasing the amines nucleophilicity.

The similarity in the $C_A$ value of piperidine and those of the 3- and 4-alkyl- and hydroxyalkyl-substituted piperidines is consistent with the interpretation of the IR spectra. These amines react with CO$_2$ to form a relatively stable NCOO$^-$ derivative, which at higher CO$_2$ loadings begins to hydrolyse to form bicarbonate. The hydrolysis of the NCOO$^-$ species permits the CO$_2$ loading of these amines to exceed 0.5 moles of CO$_2$ per mole of amine, despite the consumption of 2 molecules of amine per molecule of CO$_2$ in the carbonate reaction pathway.

Methyl substitution in 3-MP and 4-MP had a relatively small effect on the electronic properties of the amino nitrogen or on the exposed area of the reactive site (amino nitrogen). This is reflected in the $K_j$ values obtained for these amines, which are almost identical to that of piperidine. A similar theoretical trend in electronic properties was observed for 3-PM, 4-PM and 4-PE. These amines, however, exhibited smaller $K_j$ values than the methyl-substituted counterparts. Across the subset of functionalised piperidines, both the MP2 and B3LYP calculated trends in the ESP charge on the amino nitrogen and the exposed area on the nitrogen atom are in good agreement.

Hydroxy-substituted 3-HP and 4-HP exhibited smaller $C_A$ values and $K_j$ values than those of piperidine. These amines still, however, exhibited higher initial absorption rates than Table 1 for 2-MP, 2-PM and 2-PE. The role of these substituents in significantly altering the reactivity of the amino nitrogen towards CO$_2$ and destabilising the NCOO$^-$ derivative seems to manifest itself through both electronic effects and by reducing the exposed surface area on the nitrogen atom (Table 1).

The methyl substitution in 2-MP significantly increased the negative ESP charge on the amino nitrogen relative to piperidine and the 3- and 4-substituted piperidine derivatives. This electronic influence on the reactive site was found to be far less pronounced in 2-PM and 2-PE. However, the hydroxyl alkyl side chain in these two amines was found to significantly reduce the exposed area on the nitrogen atom compared with the methyl side chain in 2-MP and the hydroxyethyl side chain in 3-PM, 4-PM, 3-PE and 4-PE.

In terms of $C_A$ and $K_j$ values, 2-PM stands out from the rest of the amines. While this amine has been identified in this study as forming predominantly HCO$_3^-$ on absorption of CO$_2$, it showed a significant improvement in the $K_j$ value compared with 2-PM and 2-PE. Although the 2-methyl substituent was found to have the largest electronic influence on the amino nitrogen, it exerted the smallest effect in terms of reducing the exposed area on the nitrogen atom. A plausible explanation for the increased $K_j$ value may be that the increased exposure of the amino nitrogen, relative to 2-PM and 2-PE, facilitates the initial uptake of CO$_2$ to form an unstable NCOO$^-$ derivative. The electronic effect exerted by the neighbouring methyl group facilitates the destabilisation of the NCOO$^-$ derivative, which is then readily hydrolysed to HCO$_3^-$.

In contrast, both 2-

![Table 1. Measured absorption capacity ($C_A$), at 40 °C with an amine concentration of 3 mol L$^{-1}$ and mass-transfer coefficient ($K_j$), at 40 °C, zero loading and an amine concentration of 1 mol L$^{-1}$, for aqueous solutions of the alkyl-, hydroxy- and hydroxyalkyl-substituted piperidines. For comparison, the reactivity of conventional absorbers, such as MEA, DEA and dimethyl-substituted AMP, have been included. Also provided are the atomic properties, including ESP charge on nitrogen and the exposed area on the nitrogen atom for all optimised amine structures.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A^{[a]}$</th>
<th>$K_j^{[b]}$</th>
<th>ESP charge on nitrogen</th>
<th>Exposed area on nitrogen [Å$^2$]</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B3LYP</td>
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**tertiary amines**

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**conventional absorbents**

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</tr>
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<td></td>
<td>AMP</td>
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<td>0.61</td>
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</tbody>
</table>

[a] Moles of CO$_2$ per mole of amine. [b] mol s$^{-1}$ cm$^{-2}$ Pa$^{-1}$ (× 10$^{-3}$). [c] Nm = not measured.

MEA and DEA, but with similar $C_A$ values. Similar to MEA and DEA, both 3-HP and 4-HP have a hydroxyl group two to three carbon atoms removed from the amino nitrogen. The presence of the hydroxyl substituent in 3-HP and 4-HP had little effect on the electronic properties of the amino nitrogen. The hydroxyl group in 3-HP was, however, found to reduce the exposed area of the nitrogen atom. It should also be noted that the presence of an oxygen atom directly bonded to the nitrogen atom in the tertiary amine 1-HP (Table 1) completely hindered CO$_2$ absorption, as opposed to methyl or hydroxyethyl substitution.

The tendency of 2-methyl- and 2-hydroxyalkyl-substituted piperidines to favour HCO$_3^-$ formation over NCOO$^-$ formation, as indicated by the IR spectral data, is reflected in the higher $C_A$ value and lower rate of absorption (lower $K_j$ value) reported in Table 1 for 2-MP, 2-PM and 2-PE. The role of these substituents in significantly altering the reactivity of the amino nitrogen towards CO$_2$ and destabilising the NCOO$^-$ derivative seems to manifest itself through both electronic effects and by reducing the exposed surface area on the nitrogen atom (Table 1).

The methyl substitution in 2-MP significantly increased the negative ESP charge on the amino nitrogen relative to piperidine and the 3- and 4-substituted piperidine derivatives. This electronic influence on the reactive site was found to be far less pronounced in 2-PM and 2-PE. However, the hydroxyl alkyl side chain in these two amines was found to significantly reduce the exposed area on the nitrogen atom compared with the methyl side chain in 2-MP and the hydroxyethyl side chain in 3-PM, 4-PM, 3-PE and 4-PE.

In terms of $C_A$ and $K_j$ values, 2-PM stands out from the rest of the amines. While this amine has been identified in this study as forming predominantly HCO$_3^-$ on absorption of CO$_2$, it showed a significant improvement in the $K_j$ value compared with 2-PM and 2-PE. Although the 2-methyl substituent was found to have the largest electronic influence on the amino nitrogen, it exerted the smallest effect in terms of reducing the exposed area on the nitrogen atom. A plausible explanation for the increased $K_j$ value may be that the increased exposure of the amino nitrogen, relative to 2-PM and 2-PE, facilitates the initial uptake of CO$_2$ to form an unstable NCOO$^-$ derivative. The electronic effect exerted by the neighbouring methyl group facilitates the destabilisation of the NCOO$^-$ derivative, which is then readily hydrolysed to HCO$_3^-$.
hydroxyl substituents in 2-PM and 2-PE were found to have the least effect on the electronic environment of the amino nitrogen, but substantially reduced the exposed area on the nitrogen atom. Table 1 shows 2-PM and 2-PE to have the smallest $K_c$ values.

2.3 Effect of Substituents on Carbamate Structure

To analyse the effect of the alkyl, hydroxyl and hydroxyalkyl substituents on the N–CO$^-$ bond formed in the carbamate derivatives of the substituted piperidines, as well as the resonance structure of the carboxylate moiety, a subset of low energy conformers for each carbamate derivative were optimised and compared at both the B3LYP/6-31+G** and MP2/6-31+G** levels of theory.

For the lowest-energy conformer of each carbamate derivative, Table 2 provides the calculated N–CO$^-$ ($r_{\text{N-CO}}$) bond lengths (Å), $r_{\text{C1-O1}}$/$r_{\text{C1-O2}}$ (Å) (see Scheme 4) and ESP partial negative charges on both oxygen atoms. The trends in results obtained at the two levels of theory were found to be in good agreement.

From Table 2, it can be seen that the lowest-energy conformers for the carbamate derivatives of 3-HP, 2-PM and 2-PE all exhibited intramolecular hydrogen bonding between the hydroxyl proton of the hydroxyl or hydroxyalkyl side chain and the carboxylate moiety. In the case of 3-hydroxypiperidine-1-carboxylate and 3-(hydroxymethyl)piperidine-1-carboxylate conformers, when compared with conformers with no hydrogen bonding present (provided in Table 2), the presence of intramolecular hydrogen bonding is shown to affect both the N–C bond length and resonance structure of the carboxylate moiety. It should be noted that the calculated conformers are gas-phase conformers and may not be dominant in solution. It should also be noted here, without going into detail, that solvation effects will influence the stability of the carbamate derivative, along with electronic/steric effects and intramolecular hydrogen bonding.

The theoretical investigation of the structural features of the different carbamate derivatives presented in Table 2 revealed the N–CO$^-$ bond to be single bond in character. However, the carbamate derivatives of the 2-methyl- and 2-hydroxyalkyl-substituted 2-HP, 2-PM and 2-PE were found to have a shorter N–C bond length than the carbamate derivatives of piperidin-1-carboxylate, 3- and 4-MP-, 3- and 4-PM-, and 4-PE-substituted piperidines.

The negative charge on the resonance structure of the carboxylate moiety in piperidine-1-carboxylate, 3-methylpiperidine-1-carboxylate, 4-methylpiperidine-1-carboxylate, 3-(hydroxymethyl)piperidine-1-carboxylate and 4-(hydroxymethyl)piperid-

<table>
<thead>
<tr>
<th>Carbamate derivative</th>
<th>$r_{\text{N-CO}}$ (Å)</th>
<th>$r_{\text{C1-O1}}$/$r_{\text{C1-O2}}$ (Å)</th>
<th>ESP charge on O1/O2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP</td>
<td>MP2</td>
<td>B3LYP</td>
</tr>
<tr>
<td>Piperidine-1-carboxylate</td>
<td>1.475</td>
<td>1.469</td>
<td>1.264/1.264</td>
</tr>
<tr>
<td>2-Methylpiperidine-1-carboxylate</td>
<td>1.469</td>
<td>1.464</td>
<td>1.266/1.265</td>
</tr>
<tr>
<td>2-(2-Hydroxyethyl)piperidine-1-carboxylate</td>
<td>1.457</td>
<td>1.469</td>
<td>1.264/1.264</td>
</tr>
<tr>
<td>3-Hydroxypiperidine-1-carboxylate</td>
<td>1.460$^{(a)}$</td>
<td>1.459$^{(a)}$</td>
<td>1.280/1.258$^{(a)}$</td>
</tr>
<tr>
<td>2-(Hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.486$^{(b)}$</td>
<td>1.482$^{(b)}$</td>
<td>1.261/1.261$^{(b)}$</td>
</tr>
<tr>
<td>3-(Hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.476</td>
<td>1.470</td>
<td>1.265/1.264</td>
</tr>
<tr>
<td>4-(Hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.459$^{(c)}$</td>
<td>1.450$^{(c)}$</td>
<td>1.277/1.259$^{(c)}$</td>
</tr>
<tr>
<td>4-(Hydroxymethyl)piperidine-1-carboxylate</td>
<td>1.450$^{(d)}$</td>
<td>1.449$^{(d)}$</td>
<td>1.280/1.260$^{(d)}$</td>
</tr>
<tr>
<td>4-(2-Hydroxyethyl)piperidine-1-carboxylate</td>
<td>1.477$^{(e)}$</td>
<td>1.467$^{(e)}$</td>
<td>1.265/1.263$^{(e)}$</td>
</tr>
<tr>
<td>4-(2-Hydroxyethyl)piperidine-1-carboxylate</td>
<td>1.475</td>
<td>1.471</td>
<td>1.265/1.264</td>
</tr>
<tr>
<td>2-(2-Hydroxyethyl)piperidine-1-carboxylate</td>
<td>1.444$^{(f)}$</td>
<td>1.440$^{(f)}$</td>
<td>1.280/1.259$^{(f)}$</td>
</tr>
</tbody>
</table>

[a] Conformer exhibits hydrogen bonding between the hydroxyl proton of the hydroxyl or hydroxyalkyl side chain and the carboxylate moiety. [b] Conformer with no hydrogen bonding present. [c] Calculated to be the lowest-energy conformer of [a] and [b]. [d] Out of the subset of low-energy conformers analysed, all exhibited hydrogen bonding.
idine-1-carboxylate), and 4-(2-hydroxyethyl)piperidine-1-carboxylate was also shown to be centred equally on the two oxygen atoms, with the calculated ESP partial negative charge on both oxygen atoms being identical, along with both C–O bond lengths ($r_{C1-O1}$ and $r_{C1-O2}$). In contrast, the electron distribution in the carboxylate moiety of 2-methylpiperidine-1-carboxylate, 2-(hydroxymethyl)piperidine-1-carboxylate and 2-(2-hydroxyethyl)piperidine-1-carboxylate was less delocalised across the two oxygen atoms. One oxygen atom was found to increase in negative charge, while the other decreased. The C–O bond length incorporating the more negatively charged oxygen atom was also found to increase in double-bond character, whereas the C–O bond length incorporating the less negatively charge oxygen atom became more single bond in character. In light of the IR spectral data, the increased $C_A$ values and lower $K_C$ values obtained for 2-MP, 2-PM and 2-PE, a shorter N–C bond length and shift in electron distribution of the carboxylate moiety seemed to reduce the stability of the carbamate derivative, and thus, its resilience to hydrolysis.

The theoretical results obtained in this study are illustrative of a trend at the B3LYP/6-31$+G^{**}$ and MP2/6-31$+G^{**}$ levels of theory. The values obtained depend on the computational model used and cannot be compared with other theories.

### 3. Conclusions

The chemical reactions between CO$_2$ and a subset of alkyl- hydroxy- and hydroxyalkyl-substituted piperidines have been successfully followed in situ by using ATR FTIR spectroscopy. The chemical species formed in the reaction were identified by using the IR absorption of characteristic functional groups. The effect of the structural variations on CO$_2$ absorption has been assessed in relation to the prevalent ionic reaction products identified, that is, carbamate versus bicarbonate, along with CO$_2$ absorption capacity (moles of CO$_2$ absorbed per mole of amine in solution) and initial absorption rate (mass transfer coefficient at zero loading). The results obtained highlighted the increased reactivity of cyclic amines compared with conventional amines MEA, DEA and AMP, particularly with regards to the α-substituted amines. On absorption of CO$_2$, the formation of the carbamate derivatives of the 3- and 4-hydroxy-, 3- and 4-hydroxymethyl-, and 4-hydroxyethyl-substituted piperidines was found to be kinetically less favourable than the carbamate derivatives of piperidine and the 3- and 4-methyl-substituted piperidines. These amines did, however, exhibit similar absorption capacities. During the CO$_2$ absorption/FTIR experiments, as the CO$_2$ loading of piperidine and the 3- and 4-methyl- and hydroxyalkyl-substituted piperidines exceeded 0.5 moles of CO$_2$ per mole of amine, the hydrolysis of the carbamate derivative of these amines was observed in the IR spectra collected. From the subset of amines analysed, the 2-alkyl- and 2-hydroxyalkyl-substituted piperidines were found to favour bicarbonate formation in the reaction with CO$_2$. Based on IR spectral data, the ability of these amines to form the carbamate derivative was also established. The theoretical results obtained for the 2-alkyl- and hydroxyalkyl-substituted piperidines suggest that a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area on the nitrogen atom play a role in destabilising the carbamate derivative and increasing its susceptibility to hydrolysis. The contribution of each is dependent on the type and size of the substituent present. Theoretical investigations into the structure of the carbamate derivatives of these amines revealed shorter N–C bond lengths and a less-delocalised electron distribution in the carboxylate moiety.

### Experimental Section

Absorption/FTIR Experiments: A simplified schematic of the absorption reactor apparatus used to analyse aqueous CO$_2$/amine reactivity is shown in Figure 8. A gas stream of 13% CO$_2$ (v/v) (>99.9% purity, BOC Australia) in N$_2$ (derived from cryogenic boil off) with a flow rate of 1.8 L min$^{-1}$ was bubbled through an aqueous solution of amine (3 mol L$^{-1}$) in a glass reactor vessel maintained at 40 °C by a temperature-controlled water bath (Techne). The CO$_2$ content of both the gas in- and outflows was measured using a Horiba VA 3000 CO$_2$ analyser. The difference between the CO$_2$ concentration of the reactor gas in- and outflows was used determine the amount of CO$_2$ absorbed by the amine solution. Each experiment was run until the measured CO$_2$ concentration in the outflow returned to the original value. A typical run lasted between 45 and 90 min. Solution volumes of 30 mL were used for all experiments, determined based on the quantity of amine available.

For the duration of each absorption experiment, an ATR diamond-tipped IR probe, coupled through a mirrored K6 conduit to an iC10 FTIR spectrometer (all supplied by Mettler-Toledo), was immersed in the aqueous solution of amine. In situ IR measurements were obtained simultaneously with the CO$_2$ absorption measurements, with the FTIR spectrometer set to continuously collect spectra for the duration of the absorption experiment over the spectral range of 4000–650 cm$^{-1}$. Each spectrum was recorded as the average of

![Figure 8. A simplified schematic of the CO$_2$ absorption reactor/FTIR system.](image-url)
256 scans over a sampling interval of 15 s with a resolution of 4 cm⁻¹. The amines investigated were purchased from Sigma Aldrich, Acros Organics and Tokyo Chemical Industry, with a purity of ≥98% and used without further purification.

Absorption Rate Experiments: A WWC was used to analyse the absorption rate of CO₂ into aqueous solutions of the functionalised piperidines, at a reaction temperature of 40 °C. The process involved counter-contacting a 1 mol L⁻¹ aqueous amine thin liquid film (flow rate: 220 mL min⁻¹), with a N₂/CO₂ gas stream (flow rate: 5 L min⁻¹) on the surface of a stainless-steel rod with a known surface area (effective height: 8.21 cm, diameter: 1.27 cm). The CO₂/N₂ composition (v/v) was varied to achieve CO₂ partial pressures in the range of 0–20 kPa. The difference between the CO₂ concentration of the reactor gas in- and outflows (measured by an Horiba VA-3000 CO₂ analyser), along with the known experimental parameters, including gas flow rate and contact area for reaction, were used to determine the flux and resultant kinetics (mass transfer coefficient, Kj). A schematic of the wetted wall reaction chamber (column) and overall design of the apparatus used in this study is shown in Figure 9.

Computational Details: The computational software package Spartan'08[20] was used to calculate and compare optimised geometries of the functionalised piperidines and their carbamate derivatives. First, molecular mechanics calculations using the MMFF94 force field and Monte-Carlo search algorithm was used to obtain a set of low-energy conformers for each amine and carbamate molecule. Each subset of low-energy conformers were then resubmitted as a geometry optimisation at the B3LYP/6-31 + G** and MP2/6-31 + G** levels of theory to obtain an equilibrium geometry corresponding to an energy minima. Vibrational analysis was performed for all optimised geometries to ensure that they corresponded to local minima, that is, there were no imaginary frequencies.

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Keywords: absorption · amines · carbon dioxide · heterocycles · IR spectroscopy

CO$_2$ Absorption of Heterocyclic Amines

An ATR-FTIR Study on the Effect of Molecular Structural Variations on the CO$_2$ Absorption Characteristics of Heterocyclic Amines, Part II

Kelly Robinson, Adam McCluskey, and Moetaz I. Attalla*

This paper reports on an ATR-FTIR spectroscopic investigation of the CO$_2$ absorption characteristics of a series of heterocyclic diamines: hexahydropyrimidine (HHPY), 2-methyl and 2,2-dimethylhexahydropyrimidine (MHHPY and DMHHPY), hexahydropyridazine (HHPZ), piperazine (PZ) and 2,5- and 2,6-dimethylpiperazine (2,6-DMPZ and 2,5-DMPZ). By using in situ ATR-FTIR the structure–activity relationship of the reaction between heterocyclic diamines and CO$_2$ is probed. PZ forms a hydrolysis-resistant carbamate derivative, while HHPY forms a more labile carbamate species with increased susceptibility to hydrolysis, particularly at higher CO$_2$ loadings (>0.5 mol CO$_2$/mol amine). HHPY exhibits similar reactivity toward CO$_2$ to PZ, but with improved aqueous solubility. The α-methyl-substituted MHHPY favours HCO$_3^-$ formation, while MHHPY exhibits comparable CO$_2$ absorption capacity to conventional amines MEA and DEA. MHHPY show improved reactivity compared to the conventional α-methyl-substituted primary amine 2-amino-2-methyl-1-propanol. DMHHPY is representative of blended amine systems, and its reactivity highlights the advantages of such systems. HHPZ is relatively unreactive towards CO$_2$. The CO$_2$ absorption capacity $C_a$ (mol CO$_2$/mol amine) and initial rates of absorption $R_0$ (mol CO$_2$/mol amine min$^{-1}$) for each reactive diamine are determined: PZ: $C_a=0.92$, $R_0=0.045$; 2,6-DMPZ: $C_a=0.86$, $R_0=0.025$; 2,5-DMPZ: $C_a=0.88$, $R_0=0.018$; HHPY: $C_a=0.85$, $R_0=0.032$; MHHPY: $C_a=0.86$, $R_0=0.018$; DMHHPY: $C_a=1.1$, $R_0=0.032$; and HHPZ: no reaction. Calculations at the B3LYP/6-31+G** and MP2/6-31+G** calculations show that the substitution patterns of the heterocyclic diamines affect carbamate stability, which influences hydrolysis rates.

1. Introduction

The dominant sources of anthropogenic CO$_2$ emission are fossil-fuel combustion and industrial processes.$^{[1,2]}$ Sequestration of this CO$_2$ is now a major target for reduction of atmospheric CO$_2$ levels. While it is clear that any significant long-term reduction in greenhouse gas emissions must involve changing our approach to energy production and consumption, technologies are required to reduce levels in the short term. Coal-fired power stations are the largest point-source emitters of CO$_2$ in Australia and worldwide.$^{[3]}$ The prospect of integrating post-combustion CO$_2$ capture (PCC) technology in both existing and new coal-fired power stations offers the potential to lower CO$_2$ emissions in the face of existing and predicted growth in the number of coal-fired power stations.$^{[4]}$

Currently, aqueous amine-based PCC is viewed as the most promising and near-ready technology for the reduction of CO$_2$ emissions from coal-fired power stations. PCC involves separating CO$_2$ from a flue gas stream by chemical absorption and releasing CO$_2$ from the absorbent by heating in a two-step process for subsequent storage or industrial use. PCC is industrially proven with absorbents such as aqueous monoethanolamine (MEA), used for decades for CO$_2$ removal from gas streams in small-scale commercial processes such as ammonia production and natural-gas processing.$^{[5,6]}$

Despite being an established technology, deployment of current industry-standard technology (30 wt% aqueous MEA) on a large scale applies a considerable efficiency penalty to the power generation process. Regeneration of PCC absorbent is energy-intensive$^{[7]}$ and will result in up to 25% reduction in the net efficiency of a coal-fired power plant.$^{[8,9]}$ Clearly, the absorption/regeneration characteristics of the amine-based PCC absorbent will influence the economic feasibility of this technology. One approach to reducing the energy requirements and cost of the PCC process is the development of more cost effective and better performing amines. There is considerable scope to develop absorbents that show higher CO$_2$ absorption, lower regeneration costs and greater chemical stability, particularly in the face of an increasing move towards demonstration-scale PCC plants.

The CO$_2$ absorption/desorption by aqueous amine-based absorbents has been, and continues to be, extensively studied in the search for improvements in PCC efficiency. The CO$_2$ absorption/desorption process is shown schematically in Figure 1. Typically, CO$_2$ reacts with aqueous amines to generate carba-
CO₂ absorption by aqueous amines is a reversible process, and the degree of reversibility is amine-dependent. Amines that form stable carbamates exhibit faster reaction rates, but a larger input of energy is required for absorbent regeneration. Conversely, amines that form more bicarbonate than carbamate exhibit slower reaction rates and require less energy for regeneration. Recent technological advances have allowed for the convenient and rapid analysis of these chemical species to be carried out in situ during the PCC absorption/desorption cycle by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. In particular, the ability of ATR-FTIR to distinguish carbamate from bicarbonate formation accelerates the screening of potential PCC amines. [10, 17]

We recently reported the application of ATR-FTIR in a model PCC absorbent system with substituted piperidines. [10] Herein we report on the in situ CO₂ absorption characteristics of a series of heterocyclic diamines (Figure 2): piperazine (PZ), 2,6-dimethyl- and 2,5-dimethylpiperazine (2,6-DMPZ and 2,5-DMPZ), hexahydropyrimidine (HHPY), 2-methylhexahydropyrimidine (MHHPY), 2,2-dimethylhexahydropyrimidine (DHHHPY) and hexahydropyridazine (HHPZ).

2. Results and Discussion

2.1. Infrared Spectral Analysis

The effect of structural variations on the CO₂ absorption characteristics of the heterocyclic diamines shown in Figure 2 were assessed in relation to the IR-identifiable products, that is, carbamate versus bicarbonate absorbance; CO₂ absorption capacity, defined as moles of CO₂ absorbed per mole of amine in solution (mol CO₂/mol amine); and the initial rate of CO₂ absorption (mol CO₂/mol amine min⁻¹). Full details of our experimental approach is given in the Experimental Section and also in our previous work. [10] Each experiment was conducted until equilibrium was established and a maximum CO₂ loading achieved. This was amine-dependent but typically required 45–
90 mins. Calculations were also performed to investigate the electronic/steric effects of the structural variations on the amine-carbamate derivatives.

2.1.1. Piperazine (PZ)

Our investigations commenced with parent heterocyclic diamine PZ (Figure 2). As can be seen from the partial (1750–950 cm\(^{-1}\)) FTIR spectrum collected during a typical CO\(_2\) absorption experiment with an aqueous PZ solution (1.5 mol L\(^{-1}\)), five major FTIR peaks evolve during CO\(_2\) absorption (Figure 3). The carbamate (NCOO\(^-\)) derivatives of heterocyclic monoamines have been identified as giving rise to several strong absorbance bands in the 1600–1260 cm\(^{-1}\) region, including the asymmetric (ν\(_{\text{as}}\)COO\(^-\) = 1600–1500 cm\(^{-1}\)) and symmetric (ν\(_{\text{s}}\)COO\(^-\) = 1450–1350 cm\(^{-1}\)) vibrations of the COO\(^-\) moiety and the N–COO\(^-\) stretching vibration (ν\(_{\text{N–COO}}\) = 1300–1260 cm\(^{-1}\)) of the NCOO\(^-\) derivative.\(^{[90]}\) The protonated amine (NH\(_3^+\)) generated on absorption of CO\(_2\) was found to give rise to an absorbance band in the 1479–1474 cm\(^{-1}\) region (NH\(_3^+\) bending mode). In an amine/CO\(_2\)/H\(_2\)O system, the bicarbonate (HCO\(_3^-\)) species was identified as giving rise to a broad peak in the 1360–1354 cm\(^{-1}\) region (ν\(_{\text{C–O}}\)).\(^{[90,17]}\) Assignment was based on the spectral data acquired for 1-methylpiperidine (tertiary amine)/CO\(_2\)/H\(_2\)O and 2-amino-2-methyl-1-propanol (AMP)/CO\(_2\)/H\(_2\)O systems. It is known that the absorption of CO\(_2\) by aqueous AMP (α-dimethyl-substituted MEA derivative) leads to the formation of mostly HCO\(_3^-\) with no significant NCOO\(^-\) formation.\(^{[14,18,19]}\) Herein these peaks can be related to the vibrational modes of the potential ionic reaction products, including PZ-carbamate (PZ-CCO\(^-\)), protonated PZ (PZ-H\(^+\)) and bicarbonate (HCO\(_3^-\)). PZ, being a secondary diamine, should react with CO\(_2\) in solution to form NCOO\(^-\), predominately in the form of a protonated PZ-CCO\(^-\) derivative ("H\(_2\)NR,R\(_3\)NCOO\(^-\)).\(^{[20,21]}\) One amine moiety acts as the absorption site for CO\(_2\), and the other as a proton acceptor. PZ has also been reported to form the dicarbamate ("OOC-PZ-CCO\(^-\)"), which was detected by \(^{1}H\) and \(^{13}C\) NMR spectroscopy, at CO\(_2\) loadings of 0.2–0.8 mol CO\(_2\)/mol amine.\(^{[20,21]}\)

The FTIR spectra for the PZ/CO\(_2\)/H\(_2\)O system closely resembles that we previously reported for the piperidine/CO\(_2\)/H\(_2\)O system, differing only in slight shifts in key IR stretching frequencies.\(^{[10]}\) At low levels of absorbed CO\(_2\) the PZ/CO\(_2\)/H\(_2\)O system exhibits the ν\(_{\text{νC–O}}\) (1524 cm\(^{-1}\)), ν\(_{\text{νC–O}}\) (1432 cm\(^{-1}\)) and ν\(_{\text{νC–O}}\) (1276 cm\(^{-1}\) and 1294 cm\(^{-1}\)) of the PZ-CCO\(^-\) derivative and the NH\(_3^+\) vibration of PZ-H\(^+\) (1470 cm\(^{-1}\)). These peaks shift to 1546, 1425 and 1289 cm\(^{-1}\), respectively, with increasing CO\(_2\) absorption levels (Figure 3). As anticipated, a near-linear relationship between cumulative CO\(_2\) absorption and IR peak intensity is observed for the spectral peaks assigned to ν\(_{\text{νC–O}}\) and PZ-H\(^+\). Increased peak absorbance is concomitant with the rate of NCOO\(^-\) formation at the reaction onset plateauing as a maximum CO\(_2\) loading of 0.92 mol CO\(_2\)/mol amine is approached (Figure 4). This near-linear relationship differs from that observed for the ν\(_{\text{νC–O}}\) bands at 1276 and 1294 cm\(^{-1}\). From the data presented in Figures 3 and 4 the primary ν\(_{\text{νC–O}}\) absorbance emerged at 1276 cm\(^{-1}\) and was the dominant peak, but only at CO\(_2\)/mol amine loadings of 0.4–0.5 mol CO\(_2\)/mol amine. At amine loadings greater than 0.5 mol CO\(_2\)/mol amine the ν\(_{\text{νC–O}}\) absorbance decreases correspondingly with a sharp increase in intensity of the absorbance band at 1294 cm\(^{-1}\) and a frequency shift to 1289 cm\(^{-1}\). This trend in ν\(_{\text{νC–O}}\) peak absorbance in the 1294–1276 cm\(^{-1}\) region is attributed to formation of "OOC-PZ-CCO\(^-\). The IR absorbance of PZ/CO\(_2\)/H\(_2\)O in this region differs from those of all other heterocyclic amine and diamine systems thus far reported, and the remaining subset of secondary heterocyclic amines analysed in this study (see below) displays only a single ν\(_{\text{νC–O}}\) absorbance band in the 1283–1272 cm\(^{-1}\) region.

As the IR stretching frequencies of PZ-dicarbamate had not been previously reported we turned to computational approaches to facilitate the assignment of key vibrational modes of PZ-CCO\(^-\), in particular ν\(_{\text{νC–O}}\). Calculations were performed at the B3LYP/6-31+G** and MP2/6-31+G** levels (gas phase, Spartan '08).\(^{[22]}\) The B3LYP/6-31+G** calculations assigned PZ-ν\(_{\text{νC–O}}\) to a single band at 1282 cm\(^{-1}\) (no scaling), while MP2/6-31+G**
positioned this band at 1284 cm\(^{-1}\) (no scaling), similar in shape, but not as broad, as that which initially emerges at 1276 cm\(^{-1}\) in Figure 3. For the ‘OOC-PZ-COO’ species B3LYP/6-31+G\(^{**}\) gave two sharp \(v_{\text{N-CO}}\) absorbances at 1297–1266 and 1348–1345 cm\(^{-1}\), which correlated well with MP2/6-31+G\(^{**}\) calculated positions of 1302–1274 cm\(^{-1}\) and 1364–1355 cm\(^{-1}\). These values correlate well with the experimentally observed peaks at values of 1266, 1276 and 1294 cm\(^{-1}\), with the latter two shifting to 1289 cm\(^{-1}\) with CO\(_2\) absorption. The B3LYP/6-31+G\(^{**}\) and MP2/6-31+G\(^{**}\) calculations confirm our peak assignments for the PZ-CO\(_2\) carbamate absorption species above.

The evolution of a weak broad absorbance band in the 1360–1350 cm\(^{-1}\) region of the PZ-CO\(_2\)/H\(_2\)O IR spectral profile (Figure 3) was assigned to \(v_{\text{C,O}}\) of HCO\(_3\)\(^{-}\). This absorbance band was far less prominent than that we observed for the piperidine/CO\(_2\)/H\(_2\)O system. Additionally, this absorbance in the PZ system does not follow the trend observed with the corresponding piperidine system; that is, the depletion of \(v_{\text{N-CO}}\) does not follow the trend observed with the carbonate band.

The effect of alkyl substituents on the CO\(_2\) absorbance bands were less intense and only a single \(v_{\text{CO2}}\) absorbance band evolves in the 1289–1276 cm\(^{-1}\) region, with 

\[
\begin{align*}
\text{2,6-DMPZ} & \quad \text{2,6-dimethylpiperazine} \\
\text{2,5-DMPZ} & \quad \text{2,5-dimethylpiperazine}
\end{align*}
\]

The IR spectral data collected for the 2,6-DMPZ/CO\(_2\)/H\(_2\)O and 2,5-DMPZ/CO\(_2\)/H\(_2\)O are shown in Figures 5 and 6, respectively. The subtle structural variations between 2,6-DMPZ and 2,5-DMPZ (Figure 2) are almost identical to those recorded for the equivalent PZ system. While the \(v_{\text{NCO2}}\) and \(v_{\text{CO2}}\) bands were less intense and only a single \(v_{\text{NCO2}}\) absorbance band evolves in the 1289–1276 cm\(^{-1}\) region, all major absorbances of the 2,6-DMPZ system are within 6 cm\(^{-1}\) of those of the PZ system: \(v_{\text{NCO2}}\) at 1526 cm\(^{-1}\); \(v_{\text{CO2}}\) at 1425 cm\(^{-1}\); \(v_{\text{NCO2}}\) at 1279 cm\(^{-1}\) for 2,6-DMPZ-CO\(_2\); NH\(_2\) bending of 2,6-DMPZ-H\(^{+}\) at 1464 cm\(^{-1}\); and HCO\(_3\)\(^{-}\) absorbance at 1354 cm\(^{-1}\). The \(v_{\text{NCO2}}\) and \(v_{\text{NCO2}}\) absorbances shift to 1550 and 1289 cm\(^{-1}\), respectively, with increasing CO\(_2\) absorption. The lack of a second \(v_{\text{NCO2}}\) absorbance is reflected in the relationship between absorbance and cumulative CO\(_2\) absorption (Figure 5).

Due to steric congestion arising from the two \(\alpha\)-CH\(_2\) moieties, initial CO\(_2\) absorption most likely occurred at the less hindered and more nucleophilic amine moiety, resulting in NCOO\(^{-}\) formation. This reduced nucleophilicity and hence reactivity towards CO\(_2\) hindered dicarbamate formation, correlating with the observation of a single \(v_{\text{NCO2}}\) peak in the IR spectrum. The reduced prevalence of dicarbamate formation resulted in increased hydrolysis and HCO\(_3\)\(^{-}\), as evidenced by rapid growth of the \(v_{\text{C,O}}\) band at 1354 cm\(^{-1}\) (Figure 5a, b). The \(\alpha\)-dimethylamine moiety acted catalytically, in a manner analogous to that reported for sterically hindered amines, to accelerate formation of HCO\(_3\)\(^{-}\).[10]

The subtle structural variations between 2,6-DMPZ and 2,5-DMPZ resulted in a significant change in the IR profile. In the case of the 2,5-DMPZ/CO\(_2\)/H\(_2\)O system the most dominant feature is HCO\(_3\)\(^{-}\) absorbance, as evidenced by the intense peak in...
the 1400–1300 cm\(^{-1}\) region. There is little evidence to support formation of a stable carbamate (Figure 6).\(^{10,17}\)

### 2.1.3. Hexahydropyrimidine (HHPY)

The HHPY/CO\(_2\)/H\(_2\)O system displayed some similarity with the PZ/CO\(_2\)/H\(_2\)O system in terms of signal positioning but with evidently weaker signals, due in part to the lower concentration of amine (HHPY) available for this study. Notwithstanding this, Figure 7 shows evolution of \(\nu_{\text{COO}}\) at 1570–1520 cm\(^{-1}\), \(\nu_{s\text{COO}}\) at 1427 cm\(^{-1}\), and \(\nu_{N\text{COO}}\) at 1293 cm\(^{-1}\) of HHPY-COO\(^-\); the NH\(^2\) + bending mode of HHPY-H\(^+\) at 1479 cm\(^{-1}\); and HCO\(_3\)\(^-\) absorbance at 1354 cm\(^{-1}\). The HCO\(_3\)\(^-\) absorbance band was more prominent than that observed for the PZ/CO\(_2\)/H\(_2\)O system, that is, HHPY forms a more labile NCOO\(^-\) derivative that is more susceptible to hydrolysis.

### 2.1.4. 2-Methylhexahydropyrimidine (MHHPY)

The IR spectrum of the MHHPY/CO\(_2\)/H\(_2\)O system is dominated by the broad HCO\(_3\)\(^-\) absorbance band in the 1400–1300 cm\(^{-1}\) region (Figure 8), which is characteristic of \(\alpha\)-substituted amines such as AMP.\(^{10,17}\) MHHPY is the methyl-substituted anologue of HHPY. Given the intensity of the HCO\(_3\)\(^-\) band in Figure 8, MHHPY was readily hydrolysed under the study conditions, with HCO\(_3\)\(^-\) formation dominating on absorption of CO\(_2\).

### 2.1.5. 2,2-Dimethylhexahydropyrimidine (DMHHPY)

Given the structural similarity between DMHHPY and MHHPY, we anticipated predominant HCO\(_3\)\(^-\) formation on CO\(_2\) absorption by DMHHPY. However the IR profile obtained for the DMHHPY/CO\(_2\)/H\(_2\)O system (Figure 9a) was significantly different to that obtained with MHHPY (Figure 8) and the HHPY and PZ systems (Figures 7 and 3, respectively). Here DMHHPY is acting more in keeping with a blended-amine PPC absorbent system. Close examination of the in-house synthesized DMHHPY revealed the presence of unconverted 1,3-diaminopropane (DAP) which had been unavoidably carried forward to the final product. Hence, the contamination of DMHHPY with DAP explains the observed blended-system-like IR profile (Figure 9a).

Re-examination of the IR spectrum of the DMHHPY/CO\(_2\)/H\(_2\)O system identified the NH bending mode of 1,3-diaminopropane at 1602 cm\(^{-1}\). While 1,3-diaminopropane \(\approx 37\%\), 1.91 g \((^1H\text{ NMR})\) was the minor component within the
DMHHPY (63%, 3.24 g)/CO\textsubscript{2}/H\textsubscript{2}O system, it formed predominantly the corresponding carbamate (DAP) on CO\textsubscript{2} absorption.

To allow potential deconvolution of the DAP and DMHHPY signals in the original DMHHPY/CO\textsubscript{2}/H\textsubscript{2}O IR profile, data were collected separately for a DAP/CO\textsubscript{2}/H\textsubscript{2}O system at a DAP concentration of 0.6 mol L\textsuperscript{-1} (Figure 9b). It is apparent that the original DMHHPY system is dominated by the reactivity of DAP (cf. Figure 9a, b). Both systems show evolution of \(\nu_{\text{COO}^-} (1565 \text{ cm}^{-1}, \text{respectively})\), \(\nu_{\text{vCOO}^-} (1440 \text{ cm}^{-1})\) and \(\nu_{\text{hCOO}^-} (1328 \text{ and } 1330 \text{ cm}^{-1}, \text{respectively})\) of the DAP-COO\textsuperscript{-} derivative and the NH\textsubscript{3}\textsuperscript{+} bending mode of protonated DAP (1492 cm\textsuperscript{-1}). For the blended DMHHPY/CO\textsubscript{2}/H\textsubscript{2}O system, weaker absorbance bands were also observed to emerge at 1385 and 1370–1350 cm\textsuperscript{-1} at CO\textsubscript{2} loadings above 1.0 mol CO\textsubscript{2}/mol amine. These new peaks are consistent with NCOO\textsuperscript{-} hydrolysis and HCO\textsubscript{3}\textsuperscript{-} formation. Carbamate hydrolysis was not observed for the pure DAP/CO\textsubscript{2}/H\textsubscript{2}O system.

In the initial DMHHPY/CO\textsubscript{2}/H\textsubscript{2}O system (Figure 9a) the DAP-COO\textsuperscript{-} absorbance bands dominate the IR spectrum. However in the DAP/CO\textsubscript{2}/H\textsubscript{2}O systems the carbamate absorbances are considerably weaker, the initial effect of which was thought to be that the DAP concentration on the DMHHPY system appears to be significantly higher than the 0.6 mol L\textsuperscript{-1} evident in Figure 9b. However, a similar difference in intensity between the carbamate absorbance bands of a blended AMP (2.4 mol L\textsuperscript{-1})/PZ (0.6 mol L\textsuperscript{-1}) system (Figure 10, further described below) versus an unblended PZ (0.6 mol L\textsuperscript{-1}) system was also observed (Figure 11). Carbamate absorbance in the unblended PZ system was found to be considerably weaker than that observed for the AMP/PZ blended system, despite equivalent PZ concentrations (6 mol L\textsuperscript{-1}). Based on the percentage concentrations determined by \textsuperscript{1}H NMR spectroscopy the ratio of DMHHPY to DAP in the blended system was 0.95/0.85 mol L\textsuperscript{-1} (total concentration 1.8 mol L\textsuperscript{-1}).

For comparative purposes an AMP/PZ blended amine system (2.4 mol L\textsuperscript{-1}/0.6 mol L\textsuperscript{-1}, respectively) was also investigated. Similarly to the blended DMHHPY absorbent, the AMP/PZ blend consists of an amine that forms predominantly HCO\textsubscript{3}\textsuperscript{-} on absorption of CO\textsubscript{2} (AMP, major constituent) and an amine that forms predominately NCOO\textsuperscript{-} (PZ, minor constituent). A similar trend in IR absorbance was observed in the spectral data collected for the AMP/PZ/CO\textsubscript{2}/H\textsubscript{2}O system (Figure 10) to that described above for the blended DMHHPY/CO\textsubscript{2}/H\textsubscript{2}O system. Despite PZ being the minor constituent of the amine blend, the PZ-carbamate absorbance bands dominated the IR spectral profile. Figure 10 shows the evolution of \(\nu_{\text{asCOO}^-} (1533 \text{ cm}^{-1})\), \(\nu_{\text{vCOO}^-} (1421 \text{ cm}^{-1})\) and \(\nu_{\text{hCOO}^-} (1276 \text{ cm}^{-1})\) and shifts to 1263 cm\textsuperscript{-1} of the PZ-COO\textsuperscript{-} derivative and the NH\textsubscript{3}\textsuperscript{+} vibration of PZ-H\textsuperscript{+} (1471 cm\textsuperscript{-1}). HCO\textsubscript{3}\textsuperscript{-} absorbance was seen to emerge in the 1386–1330 cm\textsuperscript{-1} region after a CO\textsubscript{2} loading of about 0.5 mol CO\textsubscript{2}/mol amine. For comparison Figure 11a and b present the IR spectral profile for an unblended AMP/CO\textsubscript{2}/H\textsubscript{2}O system (3 mol L\textsuperscript{-1}) and PZ/CO\textsubscript{2}/H\textsubscript{2}O system (0.6 mol L\textsuperscript{-1}), respectively. The HCO\textsubscript{3}\textsuperscript{-} absorbance band was more prominent in the IR spectra of the AMP/PZ/CO\textsubscript{2}/H\textsubscript{2}O system compared to that of the DMHHPY/CO\textsubscript{2}/H\textsubscript{2}O system. This was most likely due to the difference in amine concentrations, with the AMP/PZ blend having a total concentration of 3 mol L\textsuperscript{-1} and the DMHHPY/1,3-diaminopropane blend a total concentration of 1.5–1.8 mol L\textsuperscript{-1}.

![Figure 10. Partial IR spectral profile of an aqueous solution of an AMP/PZ blend (2.4/0.6 mol L\textsuperscript{-1}) respectively as CO\textsubscript{2} is absorbed to a maximum loading of 1.00 mol CO\textsubscript{2}/mol amine.](image-url)

![Figure 11. Partial IR spectral profile of an aqueous solution of a) unblended AMP (3 mol L\textsuperscript{-1}) and b) unblended PZ (0.6 mol L\textsuperscript{-1}) as CO\textsubscript{2} is absorbed to a maximum loading of 0.84 and 0.92 mol CO\textsubscript{2}/mol amine, respectively.](image-url)
2.1.6. Hexahydropyridazine

HHPZ absorbed no CO$_2$ during a typical CO$_2$ absorption/FTIR experiment. HHPZ is a hydrazine derivative that is reported to have a pK$_a$ value of 7.9,[23] which is much lower than that of PZ (9.73),[24] HHPY (9.75)[25] or 2,5-DMPZ (9.66).[26] The low basicity of HHPZ compared to the other diamines (pK$_a$ > 9.5) would significantly reduce the reactivity of the amine towards CO$_2$.

2.2. Absorption Capacity and Absorption Rate

Having established the role of our diamines to absorb CO$_2$, the initial absorption rate $R_a$ and absorption capacity $C_a$ were determined. The $R_a$ value was measured by a thermal gravimetric analysis (TGA) method, and $C_a$ was measured simultaneously with the IR spectral data (see Experimental Section). These data are presented in Table 1. For comparison, the reactivity of conventional absorbents such as MEA, DEA and AMP (a di-methyl-substituted MEA) are also included.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_a$ [mol CO$_2$/mol amine]</th>
<th>$R_a$ [mol CO$_2$/mol amine min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ</td>
<td>0.92</td>
<td>0.045</td>
</tr>
<tr>
<td>2,6-DMPZ</td>
<td>0.86</td>
<td>0.023</td>
</tr>
<tr>
<td>2,5-DMPZ</td>
<td>0.88</td>
<td>0.018</td>
</tr>
<tr>
<td>HHPY</td>
<td>0.85</td>
<td>0.032</td>
</tr>
<tr>
<td>MHPPY</td>
<td>0.86</td>
<td>0.018</td>
</tr>
<tr>
<td>DMHHPY</td>
<td>1.33</td>
<td>0.032</td>
</tr>
<tr>
<td>HHPZ</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MEA</td>
<td>0.56</td>
<td>0.027</td>
</tr>
<tr>
<td>DEA</td>
<td>0.60</td>
<td>0.015</td>
</tr>
<tr>
<td>AMP</td>
<td>0.84</td>
<td>0.006</td>
</tr>
</tbody>
</table>

[a] Mol CO$_2$/mol amine; data used to calculate $C_a$ were measured in the absorption reactor/FTIR system. [b] Mol CO$_2$/mol amine, min$^{-1}$; data used to calculate $R_a$ were measured by microscale TGA. Initial absorption rates were calculated by using linear regression to determine the slope of the absorption capacity curve. $R^2 > 0.995$. [c] A precipitate formed during CO$_2$ absorption/FTIR. [d] A precipitate formed during the CO$_2$ and N$_2$ runs of the TGA experiment. [e] A precipitate formed during the CO$_2$ run of the TGA experiment. This could be mainly due to the evaporation of water. [f] 3 mol L$^{-1}$ concentration analysed.

The current industry-standard PCC amine MEA returned $C_a$ = 0.56 mol CO$_2$/mol amine and $R_a$ = 0.027 mol CO$_2$/mol amine min$^{-1}$. From the data amassed for PZ, 2,6-DMPZ, HHPY and DMHHPY in Table 1, superior $C_a$ and $R_a$ values were observed for all these diamines relative to MEA. Superior $C_a$ values were also observed for 2,5-DMPZ and MHHPY, but with lower $R_a$ values. HHPZ did not react with CO$_2$ and DMHHPY was blended with DAP. Diamine $C_a$ values ranged from 0.85 (HHPY) to 0.92 (PZ) mol CO$_2$/mol amine and $R_a$ values from 0.018 (2,5-DMPZ) to 0.045 (PZ) mol CO$_2$/mol amine min$^{-1}$. While in absolute terms PZ was the standout pure diamine with the highest $C_a$ (0.92 mol CO$_2$/mol amine) and $R_a$ (0.045 mol CO$_2$/mol amine min$^{-1}$), $C_a$ and $R_a$ are not the sole factors to be considered in determining the most efficient PCC diamine absorbent; aqueous solubility and stability of the carbamate also play a role. HPPY displays higher water solubility than PZ, on the basis of observations when preparing 1.5 mol L$^{-1}$ amine solutions. HPPY was readily soluble at this concentration, as opposed to PZ, which required heating and stirring for dissolution. Additionally, HPPY displays high $C_a$ (0.85 mol CO$_2$/mol amine) and $R_a$ (0.032 mol CO$_2$/mol amine min$^{-1}$; Table 1) and showed clear evidence of formation of a hydrolysis-susceptible carbamate (see above and Figure 7).

The PZ analogues 2,6-DMPZ and 2,5-DMPZ displayed lower $R_a$ values of 0.025 and 0.018 mol CO$_2$/mol amine min$^{-1}$, respectively. As these analogues differ only in the number of methyl substituents (PZ has none) and their positioning, these data suggested that introduction of methyl moieties had an adverse effect on the initial rate of CO$_2$ absorption. 2,6-DMPZ has both methyl groups $\alpha$ to a single NH group, while 2,5-DMPZ has one methyl group $\alpha$ to each NH group. The measured $R_a$ values indicate that the effect of addition of $\alpha$-methyl groups is cumulative, with $R_a$ dropping from 0.032 (PZ) to 0.025 (2,6-DMPZ) to 0.018 mol CO$_2$/mol amine min$^{-1}$ (2,5-DMPZ). Concurrent with the reduction in $R_a$ was an increased prevalence towards HCO$_3^-$ formation for 2,5-DMPZ (see above and Figure 6). The reactivity of 2,6-DMPZ towards CO$_2$ was found to be similar to that of MEA, with the exception of a higher $C_a$ value. The propensity of 2,5-DMPZ for HCO$_3^-$ formation was similar to that observed with MHHPY (see above and Figure 8), which was reflected in the almost identical $C_a$ (0.88 and 0.86 mol CO$_2$/mol amine respectively) and $R_a$ (0.018 and 0.018 mol CO$_2$/mol amine min$^{-1}$, respectively) values obtained for these amines. The reactivity of 2,6-DMPZ towards CO$_2$ was found to be similar to that of MEA, with the exception of a higher $C_a$ value. 2,6-DMPZ was found to form predominantly carbamate on absorption of CO$_2$ (Figure 5), similar to HPPY (Figure 7). While the propensity for carbamate hydrolysis and subsequent HCO$_3^-$ formation is also similar to that observed with HPPY (cf. Figures 5 and 7), which was reflected in the almost identical $C_a$ (0.88 and 0.85 mol CO$_2$/mol amine, respectively) values, 2,6-DMPZ returned a lower $R_a$ value (0.025 and 0.032 mol CO$_2$/mol amine min$^{-1}$, respectively). Despite forming predominately HCO$_3^-$, the initial absorption rates obtained for both MHHPY and 2,5-DMPZ were much higher than that obtained for AMP and comparable to those of MEA and DEA (Table 1).

Of the amines examined, DMHHPY exhibited the highest $C_a$ (1.1 mol CO$_2$/mol amine) value and an $R_a$ value higher than that of MHHPY and comparable to that of HPPY. This is an artefact of the serendipitous blending with DAP, which contributes significantly to the observed CO$_2$ absorption capacity. Aqueous DAP has $C_a$ = 0.95 mol CO$_2$/mol amine. The bicarbonate-forming DMHHPY further promotes CO$_2$ absorption, resulting in $C_a$ > 1.0 mol CO$_2$/mol amine. The $\alpha$ amino groups of DAP contribute towards DMHHPY’s increased initial reaction rate compared to HPPY.
2.3. Effect of Structural Variations on Carbamate Structures

The effect of diamine structural variation on the ability to form stable carbamates was examined at the B3LYP/6-31+G** and MP2/6-31 +G** levels of theory. Geometry optimisations were initially performed on PZ, 2,6-DMPZ, 2,5-DMPZ, HHPY, MHHPY, DMHHPY and HHPZ. Table 2 lists selected atomic properties including electrostatic potential (ESP) partial charges on the amino nitrogen atoms and the exposed area on the nitrogen atoms for these diamines. The trends in results obtained at the two levels of theory were found to be in good agreement with one another.

Diamines can react with CO₂ in aqueous solution to form three possible forms of carbamate species: amine carbamate (HNR₂NCOO⁻), protonated amine carbamate (⁺H⁻HNR₂NCOO⁻) and dicarbamate. Of these three forms, 

\[ \text{+HNR}_2\text{NCOO}^- \] was expected to be the main reaction product, with one amino group acting as the binding site for CO₂ and the other as a proton acceptor. Geometry optimisations were next performed for the protonated amine-carbamate (⁺H⁻HNR₂NCOO⁻) and amine-carbamate (HNR₂NCOO⁻) species. For the lowest-energy conformer of each HNR₂NCOO⁻ and HNR₂NCOO⁻ derivative, Table 3 provides the calculated N-COO⁻ bond length \( r_{\text{N-C}}(\text{Å}) \), \( r_{\text{C1-O1/C1-O2}}(\text{Å}) \) (Figure 12) and ESP partial negative charges on both oxygen atoms as a measure of charge delocalisation.

As anticipated, methyl substitution significantly increased the partial negative charges on the amino groups of 2,6-DMPZ (N₁ = 0.718; N₂ = 0.752), 2,5-DMPZ (N₁ = 0.851; N₂ = 0.728) and HHPZ (N₁ = 0.584) and reduced the exposed area relative to PZ (N₁, N₂ = 0.584) and reduced the exposed area.

Table 3. Calculated N-COO⁻ bond lengths \( r_{\text{N-C}}(\text{Å}) \), \( r_{\text{C1-O1/C1-O2}}(\text{Å}) \) and ESP partial charge on both oxygen atoms for optimised geometries of the HNR₂NCOO⁻ and HNR₂NCOO⁻ derivatives of the subset of diamines analysed.

<table>
<thead>
<tr>
<th>Carbamate derivative</th>
<th>( r_{\text{N-C}}(\text{Å}) ) B3LYP</th>
<th>MP2</th>
<th>( r_{\text{C1-O1/C1-O2}}(\text{Å}) ) B3LYP</th>
<th>MP2</th>
<th>ESP charge on O1/O2 B3LYP</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺−PZ−carbamate</td>
<td>1.513</td>
<td>1.507</td>
<td>1.247/1.247</td>
<td>1.256/1.256</td>
<td>−0.690/−0.690</td>
<td>−0.681/−0.681</td>
</tr>
<tr>
<td>PZ−carbamate</td>
<td>1.471</td>
<td>1.477</td>
<td>1.257/1.257</td>
<td>1.264/1.264</td>
<td>−0.743/−0.743</td>
<td>−0.739/−0.739</td>
</tr>
<tr>
<td>H⁺−2,6-DMPZ−carbamate</td>
<td>1.508</td>
<td>1.505</td>
<td>1.248/1.249</td>
<td>1.256/1.256</td>
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<td>−0.680/−0.680</td>
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<tr>
<td>2,6-DMPZ−carbamate</td>
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<td>1.477</td>
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<td>1.264/1.264</td>
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<td>1.503</td>
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<td>1.259/1.253</td>
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<td>−0.702/−0.656</td>
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<tr>
<td>2,5-DMPZ−carbamate</td>
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<td>1.470</td>
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<td>1.266/1.264</td>
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<td>1.263/1.267</td>
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<td>H⁺−MHHPZ−carbamate</td>
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<td>1.417</td>
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<td>1.211/1.354d</td>
<td>−0.650/−0.772d</td>
<td>−0.640/−0.782d</td>
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<tr>
<td>MHHPZ−carbamate</td>
<td>1.463</td>
<td>1.469</td>
<td>1.258/1.260</td>
<td>1.264/1.266</td>
<td>−0.753/−0.770</td>
<td>−0.746/−0.759</td>
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<td>1.550</td>
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<td>1.243/1.253</td>
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<tr>
<td>MHHPZ−carbamate</td>
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<td>1.500</td>
<td>1.252/1.261</td>
<td>1.258/1.268</td>
<td>−0.758/−0.819</td>
<td>−0.743/−0.816</td>
</tr>
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<td>MHHPZ−carbamate</td>
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<td>1.221/1.353d</td>
<td>−0.575/−0.660d</td>
<td>−0.566/−0.670d</td>
</tr>
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<td>H⁺−HHPZ−carbamate</td>
<td>1.460</td>
<td>1.470</td>
<td>1.254/1.263</td>
<td>1.260/1.267</td>
<td>−0.741/−0.759</td>
<td>−0.736/−0.758</td>
</tr>
</tbody>
</table>
| [a] Isomer 1: R₂ = R₂ = CH₃ and R₁ = R₁ = H (Figure 12). [b] Isomer 2: R₂ = R₂ = CH₃ and R₁ = R₁ = H (Figure 12). [c] R₂ = R₂ = CH₃ and R₁ = R₁ = H (Figure 12). [d] Hydrogen bonding between O2 of the carbamate moiety and a proton of the NH⁺ group (Figure 12).
on the amino nitrogen atom of 2,6-DMPZ (N1 4.21 Å; N2 4.70 Å), 2,5-DMPZ (N1, N2 4.45 Å), MHHPY (N1 4.77 Å; N2 4.47 Å) and DMHHPY (N1 4.50 Å; N2 4.51 Å) relative to PZ (N1, N2 4.71 Å) at the 3BLYP level. These changes in electronic effects both have impact on the resonance structure of the carboxylate moiety and hence overall stability of the carba
date derivative (see below).

Studies herein (Figure 3 and 4) demonstrated that PZ forms a hydrolysis-resistant NCOO− derivative, and thus the optimised geometries of H−·PZ-COO− and PZ-COO− were used as the baseline against which the remaining amine NCOO− derivatives were compared. For both H−·PZ-COO− and PZ-COO−
resonance stabilisation of the carboxylate moiety is evident, with calculations showing identical charges on O1 and O2 as well as displaying identical rC−O values. The rC−O values of 1.247 and 1.257 Å reveal partial double-bond character for H−·PZ-
COO− and PZ-COO−, respectively (Table 3). The N−C−O bond length of both PZ-COO− species was of single-bond character (standard single-bond rC−N in PZ is 1.466 Å (3BLYP) and 1.465 Å (MP2)). H−·2,6-DMPZ-COO− and 2,6-DMPZ-COO− also exhibit this stable resonance structure, albeit with slightly shorter N−C−O bond lengths. These findings are in keeping with our IR studies on 2,6-DMPZ and PZ (Figure 5), which gave very similar outcomes, with the exception of the emergence of a small 
HCO− absorbance band. The protonated and unprotonated 2,6-DMPZ-COO− forms of isomer 2 (Figure 12), the minor reaction component, contributed to HCO− formation.

H−·HHPY-COO− displays lower levels of charge delocalisation across the two oxygen atoms. Changes in charge distribution and bond length were noted with rC−O1 = 1.227 Å and rC−O2 = 1.277 Å, which were mirrored in the change in electron density at O1 (−0.641) and O2 (−0.735) (3BLYP). The shift in electron distribution was much less pronounced in the HHPY-COO− species with an rC−O1 of 1.257 Å and a rC−O2 of 1.259 Å which was mirrored in the change in electron density at O1 (−0.762) and O2 (−0.767) (3BLYP). The N−C−O bond lengths of H−·HHPY-
COO− (1.507 Å) and HHPY-COO− (1.475 Å) are similar to that of the PZ-COO− species (1.471 Å). These findings are in keeping with our IR studies (Figure 7), in which HHPY was identified as forming a more labile NCOO− derivative that is more susceptible to hydrolysis than that of PZ. The lowest energy conformer obtained for H−·HHPY-COO−, as opposed to HHPY-COO− species, exhibited intramolecular hydrogen bonding between the COO− group and the NH3+ moiety. The low-energy conformers of H−·MHHPY-COO− and H−·HHPZ-COO− were also found to exhibit the same intramolecular hydrogen bonding. The reso
nance structure of the H−·MHHPY-COO− was less delocalised with rC−O1 = 1.211 Å and rC−O2 = 1.354 Å, which was mirrored in the changes in electron density at O1 (−0.650) and O2 (−0.772) (3BLYP). The N−C−O bond length of H−·MHHPY-
COO− was found to be much shorter (1.417 Å). The shift in electron distribution of the carboxylate resonance structure was again much less pronounced in the MHHPY-COO− species compared to the H−·MHHPY-COO− species. MHHPY-COO− has a shorter N−C−O bond length (1.463 Å) than PZ-COO− (1.471 Å) and HHPY-COO− (1.475 Å). MHHPY forms predominan
tly HCO− on absorption of CO2 as does 2,5-DMPZ. Both species display shorter N−COO− bonds and lower levels of reso
nance stabilisation.

In our IR studies DMHHPY was found to be representative of a blended amine system. Nonetheless, optimised geometries of the H−·DMHHPY-COO− and DMHHPY-COO− were still analysed, and both exhibited reduced resonance in the carboxylate moiety with rC−O1 = 1.235 Å and rC−O2 = 1.244 Å, which was mirrored in the changes in electron density at O1 (−0.653) and O2 (−0.699), and with rC−O1 = 1.252 Å and rC−O2 = 1.261 Å, which was mirrored in the changes in electron density at O1 (−0.758) and O2 (−0.819) (3BLYP), respectively. Given the structural similarity of DMHHPY and MHHPY, DMHHPY was expected to form predominantly HCO− on absorption of CO2.

Experimentally HHPZ was unreactive towards CO2. Calculations revealed H−·HHPZ-COO− to have a significantly shorter N−COO− bond length of 1.390 Å (significant double-bond character), as well as the largest displacement in electron distribu
tion of the carboxylate resonance structure with rC−O1 = 1.215 Å and rC−O2 = 1.350 Å, which was mirrored in the changes in elec
tron density at O1 (−0.575) and O2 (−0.660) (3BLYP). This was much less pronounced in the HHPZ-COO− species; nonethe
less, in a diamine system it is typical for one amino group to act as binding site for CO2 while the other is protonated. These data support our experimental observations.

3. Conclusions

A series of heterocyclic diamines (PZ, 2,6-DMPZ, 2,5-DMPZ, HHYP, MHHPY, DMHHPY and HHPZ) have been evaluated as potential PCC absorbents by in situ ATR-FTIR spectroscopy. Of these diamines, PZ displayed both the highest CO2 absorption capacity (C∞ = 0.92 mol CO2/mol amine) and highest initial absorption rate (R0 = 0.045 mol CO2/mol amine min−1). These values represent a significant enhancement over currently used amines such as MEA. PZ forms a hydrolysis-resistant car
bamate, as well as a dicarbamate. This behaviour is unique to PZ. Hydrolysis of the carbamate derivative of HHPY was ob
servable in the IR spectra collected during CO2 absorption. HHPY displayed similar CO2 absorption characteristics to PZ, but with a higher propensity for HCO− formation. The intro
duction of α-methyl substituents increased the propensity to wards carbamate hydrolysis and HCO− formation. Additionally α-methyl substitution decreased R0, with PZ analogues 2,6-
DMPZ and 2,5-DMPZ displaying lower R0 values of 0.025 and 0.018 mol CO2/mol amine min−1, respectively. Increasing the number of methyl groups α to the NH group also increases the rate of HCO− formation. Despite forming predominately HCO−, the R0 of MHHPY (0.018 mol CO2/mol amine min−1) was much higher than that of the corresponding α-dimethyl substituted 1° amine AMP (R0 = 0.006 mol CO2/mol amine min−1) and comparable with that of the industrially relevant MEA and DEA. The serendipitously blended DAP/DMHHPY ex
hibited the highest C∞ (1.1 mol CO2/mol amine) and excellent R0 (0.032 mol CO2/mol amine min−1). HHPZ was found to be relatively unreactive towards CO2. In all instances our calculations at the 3BLYP/6-31+G** and MP2/6-31+G** levels of theory supported our experimental observation. Finally, we
propose that HHPY offers the best compromise between high CO₂ absorption capacity, carbamate formation, hydrolysis to HCO₃⁻ and water solubility for future use in model, and potentially pilot-scale, PCC systems.

**Experimental Section**

**General:** All starting materials were purchased from Sigma Aldrich and used without further purification. Solvents were bulk and distilled prior to use. H and ¹³C NMR spectra were recorded on a Bruker Avance AMX 300 MHz spectrometer at 300.1315 and 75.4762 MHz, respectively. Chemical shifts δ are reported relative to internal standards. Mass spectra were recorded on a Shimadzu LCMS-2010 EV spectrometer and obtained by the ESI method. IR spectra were recorded by ATR-FTIR on a Mettler-Toledo ic10 FTIR: spectrometer.

**Preparation of Hexahydropyrimidine (HHPY):** Formaldehyde (37 wt% solution, 1.5 mol, 126 g) was added dropwise to an ice-cooled, stirred aliquot of anhydrous 1,3-diaminopropane (1 mol, 74.1 g) over 30 mins. The reaction mixture was then stirred for 24 h at room temperature and cooled in an ice bath, and NaOH was added (1 mol, 40 g). The organic layer was transferred to a Dean–Stark apparatus and azeotropically distilled with cyclohexane (100 mL). The cyclohexane was removed in vacuo and the residue fractionally distilled to afford 2,2-dimethylhexahydropyrimidine (17 g, 20%) as a clear oil (b.p. 56–59° C/25 mbar, lit. [28]: b.p. 57–60° C/25 mm Hg). ¹H NMR (300 MHz, CDCl₃): δ = 1.36 (2H, m), 1.96 (2H, brs), 2.82 (4H, t, J = 5.5 Hz), 3.63 ppm (2H, s); ¹³C NMR (75 MHz, CDCl₃): δ = 28.61, 45.65, 62.79 ppm; MS (ESI⁺): m/z 87 (M + 1); FTIR: ν₃ 3267 cm⁻¹.

**Preparation of 2-Methylhexahydropyrimidine (MHPHY):** Acetaldehyde (0.215 mol, 9.5 g) in diethyl ether (100 mL) was added dropwise to ice-cooled 1,3-diaminopropane (0.2 mol, 14.8 g). The reaction mixture was then stirred over K₂CO₃ (0.4 mol, 55.4 g) for 24 h at room temperature. The solvent was removed in vacuo and the residue fractionally distilled to afford 2-methylhexahydropyrimidine (17.5 g, 87%) as a clear oil (b.p. 56–59° C/30 mbar, lit. [28]: b.p. 60° C/30 mm Hg). ¹H NMR (300 MHz, CDCl₃): δ = 0.80 (3H, d, J = 6.0 Hz), 1.09 (2H, m), 2.48 (2H, m), 2.76 (4H, m), 3.25 ppm (1H, q, J = 6.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 22.75, 26.80, 45.41, 67.09 ppm; MS (ESI⁻): m/z 87 [M⁻] +1; FTIR: ν₃ 3266 cm⁻¹.

**Preparation of 2,2-Dimethylhexahydropyrimidine (DMHHPY):** A solution of acetone (0.215 mol, 12.5 g) in diethyl ether (100 mL) was added dropwise to ice-cooled 1,3-diaminopropane (0.2 mol, 14.83 g). The reaction mixture was then stirred over K₂CO₃ (0.4 mol, 55.4 g) for 24 h at room temperature. The solvent was removed in vacuo and the residue fractionally distilled to afford 2,2-dimethylhexahydropyrimidine (16.17 g, 71%) as a clear oil (b.p. 50–54°C/25 mbar, lit. [28]: b.p. 65°C/25 mm Hg). ¹H NMR (300 MHz, CDCl₃): δ = 0.90 (6H, s), 1.05 (2H, m), 1.45 (2H, s), 2.60 ppm (4H, t, J = 5.7 Hz); ¹³C NMR (75 MHz, CDCl₃): δ = 27.26, 36.87, 39.99, 63.31 ppm; MS (ESI⁻): m/z 115 [M⁻] +1; FTIR: ν₃ 3271, 1602 cm⁻¹.

**Preparation of Hexahydropyridazine (HPHZ):** Dibromobutane (0.1 mol, 21.6 g) was added dropwise to a stirred solution of diethylhydrazine dicarboxylate (0.1 mol, 17.6 g), K₂CO₃ (0.2 mol, 27.7 g) and acetonitrile (100 mL) at room temperature. The reaction mixture was then heated to reflux for 24 h, cooled and filtered. The solvent was removed in vacuo and the residue fractionally distilled to afford 1,2-dicarbethoxyhexahydropyridazine (18.5 g, 80%) as a clear oil (b.p. 110–114°C/2–3 mbar, lit. [29]: 106–114°C/3 mm Hg). ¹H NMR (300 MHz, CDCl₃): δ = 1.07 (6H, m), 1.49 (4H, s), 2.74 (4H, brs), 3.97 ppm (4H, m); ¹³C NMR (75 MHz, CDCl₃): δ = 14.36, 23.19, 44.76, 61.93, 155.15 ppm; MS (ESI⁻): m/z 231 [M⁻] +1; FTIR: ν₃ 1706 cm⁻¹.

1,2-Dicarbethoxyhexahydropyridazine (0.13 mol, 30.1 g) was added to a solution of NaOH (0.72 mol, 20.8 g), water (20 mL) and methanol (150 mL). The reaction mixture was then heated to reflux for 20 h, cooled and the precipitated inorganic salt removed by filtration. The filtrate was heated to reflux for a further 20 h, cooled, filtered and the solvent removed in vacuo. The residue was extract-
atives.[22] First, molecular mechanics calculations using the MMFF94 force field and Monte Carlo search algorithm were used to obtain a set of low-energy conformers for each amine and carbamate molecule. Each subset of low-energy conformers were then re-submitted as a geometry optimisation at the B3LYP/6-31+G** and MP2/6-31+G** levels to obtain an equilibrium geometry corresponding to an energy minimum (characterized by a gradient < 0.001). Vibrational analysis was performed for all optimised geometries to ensure that they correspond to local minima, that is, there are no imaginary frequencies.

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Chapter 1

The Effect Molecular Structural Variations Has on the CO₂ Absorption Characteristics of Heterocyclic Amines

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This chapter details the novel application of in-situ Attenuated Reflectance Fourier Transform Infrared (ATR FT-IR) spectroscopy to investigate the effect molecular structural variation has on the CO₂ absorption characteristics of heterocyclic amines. The reaction between CO₂ and a subset of structurally variant amines were analyzed including piperidine, as well as commercially available functionalized piperidine derivatives, for example, those with methyl-, hydroxyl- and hydroxyalkyl- substituents. This new technique uses an ATR probe optically coupled to an FT-IR spectrometer to monitor the reaction species evolving in solution as CO₂ is being absorbed into solution. The effect of molecular structural variations on CO₂ absorption was then assessed in relation to the IR identifiable ionic reaction products, CO₂ absorption capacity and the mass-transfer coefficient at zero loading.

Introduction

At present, aqueous amine-based PCC is viewed as the most promising and near ready technology for the reduction of CO₂ emissions from coal-fired power stations. The technology is industrially proven for absorbents such as aqueous monoethanolamine (MEA), and has been used for decades to remove CO₂ from gas streams in small-scale commercial processes such as ammonia production.
and natural gas processing (1, 2). Despite being an established technology, deployment of current industry standard technology (30 wt % aqueous MEA system) on a large scale would come at the expense of the efficiency of the power generation process. The absorbent regeneration stage of the PCC process is energy intensive (3) requiring a substantial input of heat to re-release the CO₂ and as such anything from a 25-30% reduction in the net efficiency of a coal-fired power plant is expected (4, 5). The reactivity of the amine-based absorbent towards CO₂, i.e. its CO₂ absorption capacity and absorption rate, will also largely determine the economics and feasibility of the process. One approach to reduce the energy requirements and cost of the process is through the development of more cost-effective and superior-performing amines.

The chemical reactions involved in CO₂ absorption/desorption by aqueous amine-based absorbents are continually being investigated to identify potential for and make improvements in efficiency. When CO₂ reacts with amines in an aqueous environment, carbamate, bicarbonate (HCO₃⁻) and protonated amine are generated. Briefly, primary (R₁NH₂) and secondary (R₁R₂NH) amines, such as MEA and diethanolamine (DEA), respectively, typically react with CO₂ in an aqueous environment to form a carbamate derivative, R₁R₂NCOO⁻ (a carboxylate moiety), as shown in Scheme 1. The 2:1 stoichiometry of the reaction limits the absorption capacity of primary and secondary amines to a theoretical upper limit of 0.5 moles of CO₂ per mole of amine. Generally this reaction pathway is kinetically and thermodynamically favoured for primary and secondary amines (6). The carbamate species may undergo hydrolysis to produce HCO₃⁻ and regenerate a free amine (7–9) (Scheme 1). A certain amount of carbamate hydrolysis is anticipated to occur with most amines (10), however it has yet to be observed, and given the chemical stability of the carbamate derivative of primary and secondary amines, it does not occur at a readily appreciable rate (7).

![Scheme 1. Reaction mechanism leading to carbamate formation for the reaction of CO₂ with primary (R₁R₂NH, where R₂=H) and secondary (R₁R₂NH) amines (27).](attachment:image)

Tertiary amines (R₁R₂R₃N) do not react directly with CO₂ to form the carbamate species, as in the case of primary and secondary amines. The lack of a free proton on the nitrogen atom of these amines inhibits carbamate formation (9, 11, 12). Instead, tertiary amines are thought to behave as a catalyst, facilitating
the hydrolysis of CO$_2$ to generate HCO$_3^-$ (base-catalyzed reaction pathway) (9, 11, 13).

The degree of carbamate versus HCO$_3^-$ formation will impact on the CO$_2$ absorption capacity, absorption rate and regeneration energy of amine-based absorbents. Amines that form a stable carbamate derivative tend to exhibit faster reaction rates (14), however their absorption capacity is limited (11) due to the 2:1 stoichiometry of the reaction, and a larger input of energy is required for regeneration (9). On the other hand, amines that form more HCO$_3^-$ than carbamate exhibit slower reaction rates, higher absorption capacities and require less energy for regeneration (9–11, 15). The HCO$_3^-$ reaction pathway is kinetically and thermodynamically less favourable than that of carbamate formation (6).

Amines and their ionic reaction products (carbamate, HCO$_3^-$ and protonated amine) absorb radiation in the mid-infrared frequency range. Fourier Transform Infrared (FT-IR) spectroscopy is therefore capable of detecting these absorbing species (16–19). Recent advances in Attenuated Total Reflectance (ATR) FT-IR spectroscopy have allowed for the convenient and rapid analysis of these chemical species to be carried out in-situ as CO$_2$ is absorbed into an aqueous amine solution. In-situ FT-IR analysis in particular is a valuable tool as it can provide an insight into the reaction mechanism and pathway that is difficult to otherwise observe and measurements can be achieved without disturbing the system. Having this insight into the reaction pathway allows us to identify certain structural features of amines that give rise to more favorable characteristics for the absorption of CO$_2$, making it possible to tailor amine structures for enhanced CO$_2$ absorption capacities and rates.

Recently, heterocyclic amines such as piperazine and piperidine have attracted considerable attention due to their increased activity for CO$_2$ absorption. Piperazine in particular has been found to exhibit significantly enhanced CO$_2$ absorption rates (53,000 m$^3$/kmol s), along with an increased absorption capacity, compared to other primary and secondary amines, such as MEA (7,000 m$^3$/kmol s) and DEA (1,200 m$^3$/kmol s) (20). This increased reactivity towards CO$_2$ has been attributed to the cyclic and diamine structure of piperazine (20). The second amine moiety offers the potential for enhanced CO$_2$ absorption capacity either in the form of a second reactive site for carbamate formation or proton acceptance, in the catalysis of bicarbonate formation or in modifying/enhancing the reactivity of the first amine site. However, the low aqueous solubility of piperazine (1.7 mol/ L (146 g/ L) at 20°C) (21) and piperazine carbamate (1.3 mol/ L (170 g/ L) before precipitation) (22) limits its use as a sole CO$_2$ capture absorbent (22). Rather, piperazine is commonly used in catalytic quantities as an absorption accelerator in aqueous solutions of sterically-hindered or tertiary amines (22–26). In contrast, piperidine, the monoamine analogue of piperazine, does not suffer the same limitations with improved aqueous solubility.

In light of this, ATR FT-IR spectroscopy has been applied to investigating the reaction between CO$_2$ and a subset of structurally variant heterocyclic amines. We believe studying the reaction between CO$_2$ and piperidine, as well as commercially available functionalized piperidine derivatives, e.g. those with methyl, hydroxyl and hydroxyalkyl substituents, will provide valuable insight into the effect molecular structural variation has on CO$_2$/amine reactivity.
of heterocyclic amines and their enhanced activity compared to conventional primary and secondary amines. This chapter herein reports our findings.

**Characterizing the Effect Molecular Structural Variation Has on CO\textsubscript{2}/Amine Reactivity**

To characterize the effects of molecular structural variation on CO\textsubscript{2}/amine reactivity, the CO\textsubscript{2} absorption characteristics of a series of functionalized piperidines were investigated. Figure 1 provides the structures of the subset of amines analyzed. The chemical reactions between CO\textsubscript{2} and the functionalized piperidines were followed in-situ using ATR FT-IR spectroscopy. The effect of the structural variations on CO\textsubscript{2} absorption was then assessed in relation to the:

- IR identifiable ionic reaction products i.e. carbamate versus HCO\textsubscript{3} absorbance, with time and CO\textsubscript{2} absorption.
- CO\textsubscript{2} absorption capacity - moles of CO\textsubscript{2} absorbed per mole of amine in solution (mol CO\textsubscript{2}/mol amine), and
- mass transfer coefficient at zero loading - initial rate of CO\textsubscript{2} absorption.

The CO\textsubscript{2} absorption capacity was measured simultaneously with the IR spectral data during a typical CO\textsubscript{2} absorption/FT-IR experiment with an aqueous amine solution. Briefly, a typical absorption experiment involved bubbling a 13\% (v/v) CO\textsubscript{2} in nitrogen (N\textsubscript{2}) gas stream through an aqueous amine solution (3 mol/ L) situated in a glass reaction vessel. The difference between the CO\textsubscript{2} concentration of the reactor gas inflow and gas outflow (measured using a Horiba VA 3000 CO\textsubscript{2} analyzer) was used to determine the amount of CO\textsubscript{2} absorbed by the amine solution (mol CO\textsubscript{2}/mol amine). Each experiment was run until the percent CO\textsubscript{2} concentration of the gas outflow returned to its original value (13\%), i.e. chemical equilibrium had been reached and a maximum CO\textsubscript{2} loading was achieved. Depending on the amine a typical run lasted between 45-90 minutes. A diamond tip ATR probe, optically coupled to an FT-IR spectrometer (all supplied by Mettler Toledo), was immersed in the aqueous amine solution for the duration of the experiment and in-situ IR measurements were obtained simultaneously with the CO\textsubscript{2} absorption measurements. The FT-IR spectrometer was set to continuously collect spectra over the spectral range of 4000-650 cm\textsuperscript{-1}. Prior to analysis of the amine/CO\textsubscript{2}/H\textsubscript{2}O spectra, the baseline was adjusted to zero. For more details on the experimental technique see Robinson et al (27).

A wetted-wall column (WWC) apparatus was used to analyze the absorption rate of CO\textsubscript{2} into aqueous solutions of the functionalized piperidines (1 mol/ L). Briefly, the process involves counter-contacting a 1 mol/ L aqueous amine thin liquid film (170 ml/ min flow rate), with a N\textsubscript{2}/CO\textsubscript{2} gas stream (5 L/ min flow rate) on the surface of a stainless steel rod with a known surface area (effective height 8.21 cm, diameter 1.27 cm). The CO\textsubscript{2}/N\textsubscript{2} composition (v/v) was varied to achieve CO\textsubscript{2} partial pressures in the range of 0 to 20 kPa. The difference between the CO\textsubscript{2} concentration of the reactor gas inflow and gas outflow (measured using a Horiba VA-3000 CO\textsubscript{2} analyzer), along with the known experimental parameters
including gas flow rate and contact area for reaction, were used to determine the flux and mass transfer coefficient ($K_g$) at zero loading (27).

All experiments were carried out at 40°C, which is the current standard operating temperature for the absorption step of the PCC process.

![structures](image)

**Figure 1.** Structures of the subset of functionalized piperidines examined in this study.

### Infrared Spectral Analysis

The IR spectral window 1800-900 cm$^{-1}$ was focused on for monitoring the chemical species evolving in solution as CO$_2$ was being absorbed into solution. The region above 1800 cm$^{-1}$ and below 900 cm$^{-1}$ contained no valuable information. Above 1800 cm$^{-1}$ is the broad O-H stretch of water (3700 – 2500 cm$^{-1}$) and a ‘blind spot’ were the diamond sensor on the ATR probe absorbs IR radiation (2250 – 1950 cm$^{-1}$). Below 900 cm$^{-1}$ is the superimposition of a number of absorbing species in the system.
Piperidine

Figure 2 shows the IR spectral changes that occur in the 1800-900 cm\(^{-1}\) region as CO\(_2\) is absorbed by an aqueous piperidine (3 mol/ L) solution. Five major FT-IR peaks are shown to evolve with CO\(_2\) absorption in the 1800-900 cm\(^{-1}\) region and hence can be related to the vibrational modes of the potential ionic reaction products, including:

- piperidine-carbamate (piperidine-1-carboxylate) of the form R\(_1\)R\(_2\)NCOO\(^{-}\),
- protonated piperidine (piperidine-H\(^{+}\)), and
- bicarbonate (HCO\(_3\)^{-}).

![Figure 2. IR spectra of aqueous piperidine (3 mol/ L) as CO\(_2\) is absorbed to a maximum loading of 0.76 mol CO\(_2\)/mol amine, collected during a typical CO\(_2\) absorption/ FT-IR experiment (27). (see color insert)](image)

P Piperidine, being a secondary amine should typically react with CO\(_2\) in solution to form a carbamate derivative. Specific assignment of the spectral peaks that emerged is detailed below.

The broad peak at 1640 cm\(^{-1}\) present in the original aqueous piperidine spectra and subsequent spectra was also found to be present in the spectrum of pure water and has been assigned to the O-H bending mode of water (28, 29).

Three main peaks have been assigned to the vibrational modes of piperidine-1-carboxylate, as shown in Figure 2:
i. **1514 cm⁻¹** - asymmetric COO⁻ stretching vibration (**Vₘ₆COO⁻**)
ii. **1434 cm⁻¹** - symmetric COO⁻ stretching vibration (**VₛCOO⁻**)
iii. **1283 cm⁻¹** - N-COO⁻ stretching vibration (**VN-COO⁻**)

The carbamate species analyzed in this study are a deprotonated carboxylic acid derivative, or carboxylate (anionic), and do not give rise to the typical strong carbonyl (C=O) absorbance band expected to evolve at around 1700 cm⁻¹. The electron distribution of the negatively charged COO⁻ group in the deprotonated carboxylic acid becomes spread out across both C-O bonds equivalently to stabilize the carboxylate moiety (i.e. resonance stabilization). The two oxygen atoms become coupled, giving rise two absorbance bands, an asymmetric and symmetric COO⁻ stretch, at lower frequencies compared to that of the VC=O of carboxylic acids. The **Vₘ₆COO⁻** and **VₛCOO⁻** of carboxylates have been found to generally give rise to two absorbance bands in the 1650-1540 cm⁻¹ and 1450-1360 cm⁻¹ region, depending on the molecular constituents (29).

To guide in the assignment of the vibrational modes of piperidine-1-carboxylate, in particular VN-COO⁻; gas phase harmonic frequency (and intensity) calculations were performed for optimized geometries of the piperidine carbamate species (characterized by a gradient < 0.001), at both the B3LYP/6-31+G** and MP2/6-31+G** level of theory using ‘Spartan 08’ (30) software. Density functional theory (DFT) calculations (B3LYP) were employed as they are computationally economical and thus applicable to larger molecules such as that investigated in this study. DFT is also commonly used and has been reported to yield accurate geometries and reasonable vibration frequencies (31, 32). Ab initio calculations (MP2) were also performed for comparative purposes.

VN-COO⁻ was predicted to give rise to a sharp intense band at 1289 cm⁻¹ (B3LYP, no scaling) and 1287 cm⁻¹ (MP2, no scaling), similar in shape to that emerging at 1283 cm⁻¹ in Figure 2. The theoretical results were in good agreement with the experimental results with regards to VN-COO⁻, despite the exclusion of anharmonic effects and solvent corrections in the calculations, confirming our assignment of the 1283 cm⁻¹ absorbance band. With regards to the **Vₘ₆COO⁻** and **VₛCOO⁻**, the calculations were unable to match the assigned vibrational frequencies of the carboxylate moiety, predicting the frequency of **Vₘ₆COO⁻** at 1694 cm⁻¹ (very intense) and **VₛCOO⁻** at 1402 cm⁻¹ (very weak). Both the symmetric and asymmetric C-O stretching modes are appreciably affected by anharmonicity and solvation effects (33), as opposed to VN-COO⁻, which would account for the large differences between the experimental solution phase and calculated gas phase values. All calculated frequencies herein are reported with no scaling.

The absorbance band that appears at 1477 cm⁻¹ has been assigned to the NH₂⁺ bending mode of piperidine-H⁺. To confirm this assignment spectral data was collected during the gradual acidification of the original 3 mol/L piperidine solution using concentrated HCl acid (Figure 3). Figure 3 shows a small peak evolving at around 1477 cm⁻¹ on protonation of the amine functionality. The theoretical calculations predicted piperidine-H⁺ to have two NH₂⁺ bending modes, one at 1661 cm⁻¹ (B3LYP) or 1675 cm⁻¹ (MP2) (scissoring) and another at 1437 cm⁻¹ (B3LYP) or 1465 cm⁻¹ (MP2) (twisting). An absorbance band in the
1700-1620 cm\(^{-1}\) region \((8)\) was expected to evolve, however as can been seen from Figure 2, this region is obscured by the dominant broad water absorbance band at 1643 cm\(^{-1}\). The calculated \(\text{NH}_2^+\) bending mode at 1437 cm\(^{-1}\) (B3LYP) or 1465 cm\(^{-1}\) (MP2), depending on the level of theory, is in reasonably good agreement with the experimental value of 1477 cm\(^{-1}\).

![Graph showing IR spectra](image)

**Figure 3.** IR spectra of a 3 mol/L aqueous piperidine solution before and after acidification with concentrated HCl. (see color insert)

Figure 4 shows that an almost identical relationship exists between IR peak absorbance and cumulative CO\(_2\) absorption for the spectral peaks assigned to both piperidine-1-carboxylate (VN-COO\(^-\), \(V_{\text{as}}\text{COO}^+\) and \(V_{\text{s}}\text{COO}^+\)) and piperidine-H\(^+\). Peak absorbance is observed to increase at the rate of carbamate formation at the reaction onset and decrease after a loading of about 0.5 mol CO\(_2/\) mol amine. This decrease in peak absorbance was not only observable in the peak absorbance versus cumulative CO\(_2\) absorption curve presented in Figure 4, but it was also clearly evident in the raw sequential IR spectral data presented in Figure 2. This change in peak absorbance at high CO\(_2\) loadings (> 0.5 mol CO\(_2/\) mol amine) may be attributed to the sequential onset of a new reaction pathway such as the hydrolysis of the carbamate derivative to HCO\(_3^-\). The relationship identified above, with regards to the absorbance bands assigned to both piperidine-1-carboxylate and piperidine-H\(^+\), can be distinguished from that observed for the broad absorbance band that evolves at 1354 cm\(^{-1}\), which shows a corresponding increase in peak absorbance after a loading of about 0.5 mol CO\(_2/\) mol amine. This band has been assigned to the \(V_{\text{s}}\text{C-O}^+\) of HCO\(_3^-\), which is in good agreement with literature values for aqueous HCO\(_3^-\) \((16, 28)\). Falk and Miller \((16)\) investigated the IR spectrum of CO\(_2\) in aqueous solution, reporting carbonate (CO\(_3^{2-}\)) and HCO\(_3^-\) to give rise to bands at around 1385 cm\(^{-1}\) and 1360 cm\(^{-1}\).
cm\(^{-1}\), respectively. The IR absorbance of HCO\(_3\)\(^-\) in an aqueous amine/CO\(_2\) system was established by separate experiments that are detailed below.

![Graph](image)

**Figure 4.** The relationship between the cumulative CO\(_2\) absorption of aqueous piperidine (3 mol/L) and IR peak absorbance for the bands assigned to the vibrational modes of piperidine-1-carboxylate, piperidine-H\(^+\) and HCO\(_3\)\(^-\) (27). (see color insert)

There are two possible reaction pathways that can lead to the formation of HCO\(_3\)\(^-\) in an aqueous amine environment i.e. via the

i. hydrolysis of the carbamate species (equation 1 and 2, where base ‘B’ is a second amine molecule or molecule of water) or

ii. direct nucleophilic attack of OH\(^-\) on dissolved CO\(_2\) (base-catalyzed reaction pathway, typical of tertiary amines) (equation 3 and 4).

\[
\begin{align*}
\text{R}_1\text{R}_2\text{NH} + \text{CO}_2 + \text{B} & \rightleftharpoons \text{R}_1\text{R}_2\text{NCOO}^- + \text{BH}^+ \\
\text{R}_1\text{R}_2\text{NCOO}^- + \text{H}_2\text{O} & \rightleftharpoons \text{R}_1\text{R}_2\text{NH} + \text{HCO}_3^- \\
\text{R}_1\text{R}_2\text{R}_3\text{N} + \text{H}_2\text{O} & \rightleftharpoons \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ + \text{OH}^- \\
\text{OH}^- + \text{CO}_2 & \rightleftharpoons \text{HCO}_3^-
\end{align*}
\]

The IR spectral data presented in Figure 2 and 4, for the aqueous piperidine/CO\(_2\) system, is illustrative of the first of these two pathways (equation 1 and 2) with the simultaneous decline in absorbance of the V\(_{\text{COO}^-}\), V\(_{\text{C}=\text{O}}\) and VN-COO\(^-\) of piperidine-1-carboxylate and increase in HCO\(_3\)\(^-\) absorbance.
To demonstrate further that the trend in peak absorbance identified above is indicative of a carbamate derivative undergoing hydrolysis, IR spectral data was collected during a typical CO₂ absorption experiment with aqueous piperazine (PZ) (1.5 mol/ L). PZ is the diamine analogue of piperidine and is believed to form a stable carbamate derivative, as well as a dicarbamate species (20, 34).

Piperazine

The IR spectral profile presented in Figure 5 for the aqueous PZ/ CO₂ system closely resembles that of the monoamine analogue piperidine (Figure 2), with regards to peak positioning (PZ frequencies are slightly shifted). The aqueous PZ/ CO₂ system (Figure 5) exhibits the V₃₆COO⁻ (1524 cm⁻¹ and shifts to 1546 cm⁻¹ as CO₂ is absorbed), V₅₆COO⁻ (1425 cm⁻¹) and VN-COO⁻ (1276 cm⁻¹ and shifts to 1289 cm⁻¹) of the PZ-carbamate derivative (1-piperazinium-4-carboxylate (H-HNR₁R₂NCOO⁻) or piperazine-1-carboxylate (HNR₁R₂NCOO⁻)); and the NH₂⁺ vibration of the PZ-H⁺ species (1470 cm⁻¹, including piperazinium, piperazine-1,4-diium and 1-piperazinium-4-carboxylate).

![IR spectra of aqueous PZ (1.5 mol/ L) as CO₂ is absorbed to a maximum loading of 0.92 mol CO₂/ mol amine, collected during a typical CO₂ absorption/FT-IR experiment. (see color insert)](image)

As expected, an almost identical relationship exists between IR peak absorbance and cumulative CO₂ absorption (Figure 6) for the spectral peaks assigned to the V₃₆COO⁻ and V₅₆COO⁻ of the PZ-carbamate species and PZ-H⁺. Peak absorbance is observed to increase at the rate of carbamate formation at
the reaction onset and level off as a maximum CO₂ loading of 0.92 mol CO₂/ mol amine is approached. However, this trend can be differentiated from that observed for the VN-COO⁻ absorbance bands that evolve at 1276 cm⁻¹ and 1294 cm⁻¹ (Figure 5). Figures 5 and 6 show the peak emerging at 1276 cm⁻¹ to be the dominant absorbance band, increasing with initial CO₂ absorption up to a loading of about 0.4 - 0.5 mol CO₂/ mol amine at which point it ceases to increase in intensity, and a corresponding sharp increase in intensity of the absorbance band at 1294 cm⁻¹ is observed, along with a shift in frequency to 1289 cm⁻¹. The emergence of the intense VN-COO⁻ absorbance band at 1289 cm⁻¹ may be attributed to the formation of PZ-dicarbamate (OOC-PZ-COO⁻). This trend in peak absorbance was not observed for the heterocyclic monoamine piperidine (Figure 2) or for the remaining subset of secondary heterocyclic amines analyzed in this study.

![Graph](image-url)

**Figure 6.** The relationship between the cumulative CO₂ absorption of aqueous PZ (1.5 mol/ L) and IR peak absorbance for the bands assigned to the vibrational modes of the PZ-carbamate species, PZ-H⁺ and HCO₃⁻. (see color insert)

The weak broad absorbance band beginning to emerge in the 1350-1360 cm⁻¹ region of the aqueous PZ/CO₂ IR spectral profile (Figure 5) may be assigned to the V₅C-O of HCO₃⁻. This absorbance band is far less prominent than that observed for the aqueous piperidine/CO₂ system (Figure 2) and does not illustrate the same trend in peak absorbance, i.e. the simultaneous decline in V₅COO⁻, V₅COO⁻ and VN-COO⁻ and increase in HCO₃⁻ absorbance bands, at high CO₂ loadings (> 0.5 mol CO₂/ mol amine) (Figure 5 and 6). Based on the IR spectral data presented in Figure 5 and 6, PZ forms a stable carbamate derivative that does not undergo hydrolysis as readily as the piperidine-carbamate derivative.
Tertiary amines, such as the N-methyl, -hydroxyl and -hydroxyalkyl substituted piperidines (1-MP, 1-HP and 1-PE, respectively) analyzed in this study, form HCO$_3^-$ on absorption of CO$_2$. The lack of a free proton on the nitrogen atom of these amines inhibits carbamate formation. For this reason their activity will not be compared to the subset of secondary amines being analyzed. However, the IR spectra collected for these amines will be used as a standard for HCO$_3^-$ formation in an aqueous amine/CO$_2$ system. Furthermore, the results obtained for these amines illustrate the effect different N-substituents have on CO$_2$ absorption via the base-catalyzed reaction pathway.

The IR spectral profile presented in Figure 7 for aqueous 1-PE (3 mol/L) shows the evolution of a characteristic broad HCO$_3^-$ absorbance band in the 1350-1360 cm$^{-1}$ region, with CO$_2$ absorption. Further confirmation of this assignment is provided in Figure 8, which shows the evolution of a similar broad absorbance band in the 1360-1350 cm$^{-1}$ region with the gradual addition of ammonium bicarbonate to an aqueous piperidine (3 mol/L) solution. The same broad absorbance band was also observed in the IR spectral data collected for the aqueous 1-MP/CO$_2$ system. 1-HP was an exception, the IR spectral data collected for this amine showed no spectral changes for the duration of the experiment. The tertiary amine 1-HP did not absorb any CO$_2$, as opposed to 1-MP and 1-PE. It seems that the hydroxyl substituent directly bonded to the amino nitrogen in 1-HP, as opposed to the alkyl or hydroxyalkyl substituent in 1-PM and 1-PE, respectively, inhibits a tertiary amine’s role as a catalyst in the base-catalyzed hydrolysis of CO$_2$ to generate HCO$_3^-$.

![Graph](image_url)

**Figure 7.** IR spectral profile obtained for aqueous 1-PE (3 mol/L), collected during a typical CO$_2$ absorption/FT-IR experiment (27). (see color insert)
Figure 8. IR spectra of an aqueous piperidine solution (3mol/ L) with the gradual addition of ammonium bicarbonate (27). (see color insert)

Effect of 2-Methyl and -Hydroxyalkyl Substituents

The 2-MP, 2-PM and 2-PE compounds analyzed in this study, all share a common structural feature, that being either an alkyl or hydroxyalkyl substituent on the carbon alpha (Cα) to the amino nitrogen. The IR spectral data collected for these amines differ significantly from that obtained for the aqueous piperidine system. Their spectra however, are very similar to that of the tertiary amines 1-MP and 1-PE (though much more intense), with the evolution of the characteristic broad absorbance band in the 1360-1350 cm⁻¹ region, indicative of HCO₃⁻ formation. Figure 6 illustrates this similarity, presenting sequential IR spectral data collected during a typical CO₂ absorption/ FT-IR experiment with aqueous solutions (3 mol/ L) of 2-MP (Figure 9) and 2-PE (Figure 10).

A common misconception for amines with one or more substituents at the α-carbon (e.g. conventional absorbent 2-amino-2-methyl-1-propanol (AMP)), or in this study the 2-methyl (2-MP), 2-hydroxymethyl (2-PM) and 2-hydroxyethyl (2-PE) substituted piperidines, is the notion that they are sterically-hindered and unable to form the carbamate species. Recently, a theoretical study undertaken by Ismael et al (35) suggested that the carbamate reaction pathway is kinetically unfavorable for these amines, rather the reaction proceeds directly to HCO₃⁻ formation via a base-catalyzed reaction mechanism, similar to that of tertiary amines. However, in an even more recent theoretical and experimental study undertaken by Jackson et al. (36), direct observation of the carbamate derivatives of the Cα-substituted amines AMP and tris(hydroxymethyl)amino methane (THAM) were made based on negative-ion electrospray ionization
mass spectrometry (ESI-MS) data and the reaction of these amines with sodium bicarbonate (NaHCO₃) to form a carbamate species in an aqueous environment.

Figure 9. IR spectra of aqueous 2-MP (3 mol/ L) as CO₂ is absorbed to a maximum loading of 0.93 mol CO₂/mol amine, collected during a typical CO₂ absorption/ FT-IR experiment (27). (see color insert)

Figure 10. IR spectra of aqueous 2-PE (3 mol/ L) as CO₂ is absorbed to a maximum loading of 0.87 mol CO₂/mol amine, collected during a typical CO₂ absorption/ FT-IR experiment (27). (see color insert)
In an attempt to observe the carbamate derivatives of 2-MP, 2-PM and 2-PE in real time as a result of the reaction with gaseous CO₂ (at low partial pressures i.e. 13 % CO₂ (v/v) in N₂ @ 1 atm) and using in-situ ATR FT-IR spectroscopy, spectral data was collected during CO₂ absorption experiments with amine/hexanol solutions. In a non-aqueous environment, HCO₃⁻ formation via the CO₂ or carbamate hydrolysis pathway should be suppressed. To confirm this inhibition of HCO₃⁻ formation, spectral data was collected during a typical CO₂ absorption with a tertiary amine (1-PE)/hexanol solution. Figure 11a shows there to be no spectral changes in the 1800-900 cm⁻¹ region, for the duration of the experiment (run time = 20 mins), as would be expected with an aqueous 1-PE/CO₂ system (Figure 7). The 1-PE/hexanol solution did not absorb any CO₂ due to the inhibition of HCO₃⁻ formation. For comparison and to establish the formation of carbamate species in a non-aqueous environment, spectral data was also collected during a typical CO₂ absorption experiment with a piperidine/hexanol solution. The piperidine/hexanol solution absorbed CO₂ to an upper limit of 0.5 mol CO₂/mol amine, as opposed to the upper limit of 0.76 mol CO₂/mol amine obtained for the aqueous piperidine solution (Figure 2). The spectra presented in Figure 11b shows the evolution of piperidine-1-carboxylate and piperidine-H⁺ absorbance bands including VₐsCOO⁻ (1540 cm⁻¹), Vₐ COO⁻ (1425 cm⁻¹) and VN-COO⁻ (1279 cm⁻¹); and one of the NH₃⁺ bending modes (scissoring) at 1643 cm⁻¹ (this mode was not observed in the piperidine/CO₂/H₂O system due to the broad H₂O absorbance band in this region). The NH₃⁺ bending mode (wagging) identified as being responsible for the evolution of the absorbance band at 1477 cm⁻¹ in the IR spectral data collected for the aqueous piperidine/CO₂ system is not observable in the spectral data presented in Figure 11b for the piperidine/CO₂/hexanol system. This is due to the coinciding strong absorbance of the original piperidine/hexanol solution in this region.

The Ca-substituted piperidines, including 2-MP, 2-PM and 2-PE, were found to absorb a small amount of CO₂ in a non-aqueous environment, as opposed to the tertiary amine 1-PE. This in itself is indicative of these amines being able to form a carbamate species, one that it is inherently susceptible to hydrolysis in an aqueous environment and subsequently HCO₃⁻ formation. The IR spectral profiles presented in Figure 12a and b for the 2-PE and 2-PM/CO₂/hexanol solutions, shows the evolution of the same absorbance bands as that observed for the piperidine/CO₂/hexanol system, although somewhat weaker, including the NH₂⁺ bending mode of protonated 2-PE and 2-MP (1639 and 1638 cm⁻¹, respectively); and the VₐsCOO⁻ (1536 cm⁻¹), Vₐ COO⁻ (1416 and1417 cm⁻¹) and VN-COO⁻ (1276 and 1278 cm⁻¹) of 2-(2-hydroxyethyl)piperidine-1-carboxylate and 2-methylpiperidine-1-carboxylate, respectively (carbamate derivatives of 2-PE and 2-PM, respectively). Because the intensity of these absorbance bands is weak, further clarification of the existence of these elusive anions was established based on ESI-MS data (37) and the method utilized by Jackson et al. in their detection of carbamate anions (36).
Figure 11. The IR spectra collected as CO₂ was bubbled through a) a 1-PE/hexanol solution (3 mol/L) and b) a piperidine/hexanol solution (3 mol/L) (27). (see color insert)
Figure 12. The IR spectra collected as CO₂ was bubbled through **a)** a 2-PE/hexanol solution (3 mol/ L) and **b)** a 2-MP/hexanol solution (3 mol/ L) (27). (see color insert)
Table 1. Comparison of the frequencies assigned to \( V_{as}COO^- \), \( V_sCOO^- \), \( VN-COO^- \) and \( NH_2^+ \) for piperidine and the 3- and 4- methyl, hydroxyl and hydroxyalkyl substituted piperidines.

<table>
<thead>
<tr>
<th>Amine/CO(_2)/H(_2)O System</th>
<th>Infrared Vibrational Modes and Frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( V_{as}COO^- )</td>
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<tr>
<td>piperidine</td>
<td>1514</td>
</tr>
<tr>
<td>3-MP</td>
<td>1519</td>
</tr>
<tr>
<td>4-MP</td>
<td>1519</td>
</tr>
<tr>
<td>3-HP</td>
<td>1521</td>
</tr>
<tr>
<td>4-HP</td>
<td>1521</td>
</tr>
<tr>
<td>3-PM</td>
<td>1516</td>
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<tr>
<td>4-PM</td>
<td>1516</td>
</tr>
<tr>
<td>4-PE</td>
<td>1520</td>
</tr>
</tbody>
</table>

Briefly, the method involved the addition of NaHCO\(_3\) (50-70 \( \mu \)g/ ml) to aqueous solutions of 2-MP, 2-PM and 2-PE (130-150 \( \mu \)g/ ml), followed by analysis in a Waters Acquity HPLC-MS system. The carbamate derivatives of 2-MP (m/z = 141.9), 2-PM (m/z = 158.0) and 2-PE (m/z = 172.0) were observable in the negative ion ESI-MS broad scan spectrum. A dissociation peak corresponding to the mass loss of CO\(_2\) (m/z = 44) was also evident in the multiple collision-induced dissociation (CID) spectrum of the 2-MP-carbamate parent ion (2-methylpiperidine-1-carboxylate) (37). However, in the case of the 2-PM and 2-PE carbamate parent ions (2-(hydroxymethyl)piperidine-1-carboxylate and 2-(2-hydroxyethyl)piperidine-1-carboxylate, respectively), a dissociation peak corresponding to the mass loss of m/z = 46 was evident in their CID spectrum. A mass loss of m/z = 46 was also observed by Jackson et al. (36) in the CID spectrum they obtained for the carbamate derivative of secondary amine DEA. The carbamate derivatives of 2-PM and 2-PE, as well as DEA, both have exchangeable hydrogens on the hydroxyl group of the alkyl side chain that is within close proximity of the carboxylate moiety, similar to that of the anions of \( \alpha \)-hydroxy carboxylic acids. These anions are known to dissociate by eliminating a mass loss of m/z = 46, corresponding to the loss of formic acid (38).

**Effect of 3- and 4-Methyl, Hydroxyl and Hydroxyalkyl Substituents**

The IR spectral data collected for aqueous solutions of the 3- and 4- alkyl (3-MP and 4-MP), hydroxyl (3-HP and 4-HP) and hydroxyalkyl (3-PM, 4-PM and 4-PE) substituted piperidines illustrate a high degree of similarity with that of aqueous piperidine on absorption of CO\(_2\), in terms of peak positioning and the relationship between peak absorbance and cumulative CO\(_2\) absorption for the spectral peaks assigned to carbamate, protonated amine and HCO\(_3^-\) formation.
Table 1 provides a brief summary of the frequencies assigned to the carbamate vibrational modes $V_{as}$COO$^-$, $V_{s}$COO$^-$, and VN-COO$^-$, as well as the protonated amine (NH$_2^+$) vibrational mode, for the 3- and 4- substituted piperidines. For comparison the vibrational frequencies of piperidine-1-carboxylate and piperidine-H$^+$ have also been included. From Table 1 it can be seen that the difference in frequencies corresponding to the vibrational modes of protonated amine and the carbamate derivatives of piperidine and the 3- and 4-substituted piperidines, do not exceed 7 cm$^{-1}$. There are a few differences in the IR spectral data collected, particularly with regards HCO$_3^-$ formation and carbamate hydrolysis in the aqueous 3-HP and 4-HP/CO$_2$ systems, which are discussed below.

With regards to the 3- and 4- methyl and hydroxyalkyl substituted piperidines, Figures 13-15 highlight the similarity in the spectral data collected for these amines, presenting a) a partial profile of the sequential IR spectral data collected for aqueous 3-MP (3 mol/ L), 3-PM (3 mol/ L) and 4-PE (3 mol/ L), respectively; and b) the corresponding relationship between peak absorbance and cumulative CO$_2$ absorption for the spectral peaks assigned to carbamate, protonated amine and HCO$_3^-$ formation. The IR spectral data obtained for 4-MP and 4-PM have not been included as they closely resemble that of the IR spectral data presented in Figures 13-15.

Both the sequential IR spectral data and the peak absorbance versus cumulative CO$_2$ absorption curve, presented in Figures 13-15 for 3-MP, 3-PM and 4-PE, respectively, clearly illustrate the hydrolysis of the carbamate species (3-methylpiperidine-1-carboxylate, 3-(hydroxymethyl)piperidine-1-carboxylate and 4-(2-hydroxyethyl)piperidine-1-carboxylate, respectively) at high CO$_2$ loadings (> 0.5 mol CO$_2$/ mol amine) to generate HCO$_3^-$.

With regards to the 3- and 4- hydroxyl substituted piperidines (3-HP and 4-HP) hydrolysis of the carbamate species (3-hydroxypiperidine-1-carboxylate and 4-hydroxypropiperidine-1-carboxylate, respectively) was not as evident in the IR spectral data collected for these amines, compared to piperidine, 3-MP, 4-MP, 3-PM, 4-PM and 4-PE. Figure 16 presents a) a partial profile of the sequential IR spectral data collected for aqueous 3-HP (3 mol/ L); and b) the relationship between peak absorbance and cumulative CO$_2$ absorption for the spectral peaks assigned to 3-hydroxypiperidine-1-carboxylate, 3-hydroxypropiperidine-H$^+$ and HCO$_3^-$ formation. From Figure 16a it can be seen that the evolution of the broad HCO$_3^-$ absorbance band in the 1360-1350 cm$^{-1}$ is not as prominent as that observed to evolve in the IR spectra collected for piperidine (Figure 2), or the 3- and 4- methyl and hydroxyalkyl substituted piperidines (Figures 13-15). The absorbance of the original aqueous 3-HP solution in this region, contributes to the intensity of the absorbance band seen to evolve, as well as the odd shape of this band compared to previously assigned HCO$_3^-$ absorbance bands. The peak absorbance versus cumulative CO$_2$ absorption curve presented in Figure 16b also does not show to the same extent the decline in intensity of the carbamate absorbance bands as that observed for piperidine or the other 3- and 4- substituted piperidines. Further evidence with regards to the carbamate derivatives of 3-HP and 4-HP being less susceptible to hydrolysis is discussed below in terms of their absorption capacity.
Figure 13. **a)** IR spectra of aqueous 3-MP (3 mol/L) as CO$_2$ is absorbed to a maximum loading of 0.75 mol CO$_2$/mol amine, collected during a typical CO$_2$ absorption/FT-IR experiment; and **b)** the relationship between the cumulative CO$_2$ absorption of 3-MP and IR peak absorbance for the bands assigned to 3-methylpiperidine-1-carboxylate, 3-methylpiperidine-H$^+$ and HCO$_3$- (see color insert)
Figure 14. **a)** IR spectra of aqueous 3-PM (3 mol/ L) as CO₂ is absorbed to a maximum loading of 0.74 mol CO₂/mol amine, collected during a typical CO₂ absorption/ FT-IR experiment; and **b)** the relationship between the cumulative CO₂ absorption of 3-PM and infrared peak absorbance for the bands assigned to 3-(hydroxymethyl)piperidine-1-carboxylate, 3-(hydroxymethyl)piperidine-H⁺ and HCO₃⁻. (see color insert)
Figure 15. **a)** IR spectra of aqueous 4-PE (3 mol/L) as CO$_2$ is absorbed to a maximum loading of 0.74 mol CO$_2$/mol amine, collected during a typical CO$_2$ absorption/FT-IR experiment; and **b)** the relationship between the cumulative CO$_2$ absorption of 4-PE and infrared peak absorbance for the bands assigned to 4-(2-hydroxyethyl)piperidine-1-carboxylate, 4-(2-hydroxymethyl)piperidine-H$^+$ and HCO$_3^-$.

(see color insert)
Figure 16. a) IR spectra of aqueous 3-HP (3 mol/L) as CO₂ is absorbed to a maximum loading of 0.61 mol CO₂/mol amine, collected during a typical CO₂ absorption/FT-IR experiment; and b) the relationship between the cumulative CO₂ absorption of 3-HP and IR peak absorbance for the bands assigned to 3-hydroxypiperidine-1-carboxylate, 3-hydroxypiperidine-H⁺ and HCO₃⁻. (see color insert)
Absorption Capacity and Absorption Rate

To quantify the effect of the alkyl, hydroxy and hydroxyalkyl substituents on the relative reactivity of the amino nitrogen, the CO₂ absorption capacity (Cₐ) and initial absorption rate (mass transfer coefficient (K_g) at zero loading) was determined for each individual amine.

The measured absorption capacity (Cₐ) and mass transfer coefficient (K_g) for the subset of alkyl, hydroxyl and hydroxyalkyl substituted piperidines analyzed in this study are presented in Table 2. For comparison of reactivity, the Cₐ and K_g values obtained for conventional amine-based absorbents MEA, DEA and AMP (di-methyl substituted analogue of MEA) have been included in Table 2.

The Cₐ and K_g results presented in Table 2 highlight the significant increase in reactivity of cyclic secondary amines compared to conventional straight chain aliphatic primary and secondary amines MEA and DEA, respectively. Particularly noteworthy is the increase in initial absorption rates of the α-substituted cyclic amines 2-MP, 2-PM and 2-PE compared to that of the α -substituted aliphatic amine AMP, given the similarity in structure (i.e. they are considered sterically-hindered). The K_g values obtained for 2-MP, 2-PM and 2-PE are even comparable/ higher compared to that of MEA.

The 3- and 4- alkyl and hydroxyalkyl substituted piperidines exhibited similar absorption capacities (0.74 - 0.76) to that of piperidine (0.76) (Table 1). This similarity in Cₐ values is consistent with the interpretation of the IR spectral data collected for these amines, that being they react with CO₂ to form a relatively stable carbamate derivative, which at higher CO₂ loadings (> 0.5 mol CO₂/ mol amine) begins to hydrolyze forming HCO₃⁻. The hydrolysis of the carbamate species permits the CO₂ loading of these amines to well exceed 0.5 mol CO₂/ mol amine, despite the 2:1 stoichiometry of the carbamate reaction pathway. However, on absorption of CO₂ the formation of the carbamate derivatives of the 3- and 4-hydroxymethyl substituted piperidines were found to be kinetically less favorable than the carbamate derivatives of piperidine and the 3 and 4-methyl substituted piperidines. In terms of K_g values or initial rates of CO₂ absorption, methyl substitution at the 3- and 4- position of the piperidine ring had a relatively small effect, as opposed to the 3- and 4- hydroxyalkyl substituents. As shown in Table 1, the K_g values obtained for 3-MP (3.73) and 4-PM (3.75) were comparable to that of piperidine (3.85), where as the values obtained for 3-PM (2.32) and 4-PM (1.86) were much smaller. The initial CO₂ absorption rate of 4-PE was not measured due to the availability of the amine.

Hydroxyl substitution in 3-HP (0.61, 2.24) and 4-HP (0.64, 2.28) lead to both reduced Cₐ and K_g values, respectively, compared to piperidine, as well as its methyl substituted analogues. The lower Cₐ values obtained for these amines is consistent with the interpretation of the IR spectral data, that being their carbamate derivatives are less susceptible to hydrolysis at higher CO₂ loadings compared to the carbamate derivatives of piperidine or the methyl and hydroxyalkyl substituted piperidines. These amines still however exhibited higher initial absorption rates than MEA and DEA, but with similar Cₐ values. Both 3-HP and 4-HP share a structural similarity with MEA and DEA that being a hydroxyl group 2-3 carbon removed from the amino nitrogen. It should also be noted that presence of an
Table 2. Measured absorption capacity ($C_A$) at 40°C and 3 mol/L amine concentrations; and mass transfer coefficient ($K_g$) at 40°C, zero loading and 1 mol/L amine concentrations, for aqueous solutions of the alkyl, hydroxyl and hydroxyalkyl substituted piperidines. For comparison the reactivity of conventional absorbents such as MEA, DEA and AMP have been included at the bottom of the table (27).

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A$ (mol CO$_2$/mol amine)</th>
<th>$K_g$ (mol/s.cm$^2$Pa) (x10$^{-10}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>piperidine</td>
<td>0.76</td>
<td>3.85</td>
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<tr>
<td>2-methylpiperidine (2-MP)</td>
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<tr>
<td>4-methylpiperidine (4-MP)</td>
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</tr>
<tr>
<td>3-hydroxy piperidine (3-HP)</td>
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<td>1.27</td>
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<td>Tertiary Amines</td>
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<td>N-methylpiperidine (1-MP)</td>
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<td>Nm$^a$</td>
</tr>
<tr>
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<td>Nm$^a$</td>
</tr>
<tr>
<td>N-(2-hydroxyethyl)piperidine (1-PE)</td>
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<td>Nm$^a$</td>
</tr>
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<td>Conventional Absorbents</td>
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<td>1.48</td>
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<tr>
<td>diethanolamine (DEA)</td>
<td>0.60</td>
<td>0.61</td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>0.84</td>
<td>0.61</td>
</tr>
</tbody>
</table>

$^a$ Nm= Not measured

Oxygen atom directly bonded to the nitrogen atom in the tertiary amine 1-HP (Table 2) completely hindered CO$_2$ absorption, as opposed to the methyl or hydroxyethyl substitution in 1-MP and 1-PE. The IR data collected for 1-HP showed no spectral changes in the 1800-900 cm$^{-1}$ region, where as the IR data collected for 1-MP and 1-PE showed the evolution of HCO$_3^-$.

The tendency of the 2-methyl and 2-hydroxyalkyl substituted piperidines to favor HCO$_3^-$ formation over carbamate formation, as indicated by the IR spectral data, is reflected in the higher $C_A$ and lower $K_g$ values reported in Table 2, for 2-MP, 2-PM and 2-PE.
In terms of $C_A$ and $K_g$ values 2-MP (0.93, 2.38, respectively) stands out from the rest of the amines. Whilst the amine has been identified in this study as forming predominantly $\text{HCO}_3^-$ on absorption of CO$_2$, it showed a significant improvement in the $K_g$ value, as well as $C_A$ value, compared to 2-PM (0.85, 1.07) and 2-PE (0.87, 1.27). This may be accounted for by the less bulky methyl substituent on the Cu of 2-MP, compared to the hydroxymethyl or hydroxyethyl substituent in 2-PM and 2-PE, respectively. Based on the IR spectral data the ability of these amines to form a carbamate derivative, inherently susceptible to hydrolysis, was established. A plausible explanation for the difference in reactivity may be that the increased exposure of the amino nitrogen in 2-MP, compared to 2-PM and 2-PE, facilitates the initial uptake of CO$_2$ to form an unstable carbamate derivative. The electronic effect exerted by the neighboring methyl group (electron donating) (27) facilitates the destabilization of the carbamate derivative, which is then readily hydrolyzed to $\text{HCO}_3^-$. The electronic and/or steric effect of the substituents present on the $\alpha$-carbon of these amines play a large role in destabilizing the carbamate derivative and increasing its susceptibility to hydrolysis (27).

References

The Effect of Molecular Structural Variations has on the CO₂ Absorption Characteristics of Heterocyclic Amines

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² Chemistry, School of Environmental & Life Sciences, The University of Newcastle, Callaghan

Introduction
The chemical reactions involved in CO₂ absorption by aqueous amine absorbers are being investigated in order to optimise chemical efficiency of the post combustion CO₂ capture process. We believe studying the reaction between CO₂ and piperidine (a cyclic 2° amine), as well as commercially available functionalised piperidine derivatives, e.g. those with methyl-, hydroxyl- and hydroxyalkyl- substituents, will provide valuable insight into the effect of molecular structural variation on CO₂/amine reactivity of cyclic amines and their enhanced activity compared to conventional straight chain aliphatic 1° and 2° amines, as employed, e.g., as monoethanolamine (MEA). To characterise the effects of molecular structural variation on CO₂/amine reactivity, the chemical reactions between CO₂ and the subset of functionalised piperidines were followed in situ using ATR FT-IR spectroscopy. The effect of structural variations on CO₂ absorption was assessed in relation to the IR identifiable ionic reaction products i.e. carbamate (COO⁻) versus bicarbonate (HCO₃⁻) absorbance (Fig. 1 and 2, respectively); CO₂ absorption capacity (Cₐ) and the mass transfer coefficient (kₓ) at zero loading (initial absorption rate) (Table 1). To analyse the electrostatic effects of the different substituents on the relative reactivity (capture performance) of the amino nitrogen, the computational software package ‘Spartan 08’ was used to calculate and compare the electrostatic potential (ESP) partial charge on the amino nitrogen and exposed area (Å²) on the nitrogen atom for optimised geometries of the functionalised piperidines at both the B3LYP/6-31G* and MP2/6-31G* level of theory (Table 1).

Infrared Spectral Analyses
Infrared Spectral Profile of a Piperidine/CO₂/H₂O System
- Five major FT-IR peaks are shown to evolve with CO₂ absorption (Fig. 1a, b) and hence can be related to the vibrational modes of the potential ionic reaction products including piperidine-COO⁻, piperidine-H⁺ and HCO₃⁻.
- 1514 cm⁻¹; 1434 cm⁻¹ symmetric and asymmetric stretching vibration of piperidine-COO⁻ (a carboxylate moiety).
- 1477 cm⁻¹ NH₃ bending mode of piperidine-H⁺.
- 1236 cm⁻¹ N-COO stretching vibration of the COO⁻ derivative.
- 1354 cm⁻¹ Symmetric C-O stretching vibration of HCO₃⁻.

- The IR spectral profiles obtained for the 3- and 4- methyl, hydroxyl and hydroxyalkyl substituted piperidines/CO₂/H₂O systems illustrated a high degree of similarity with that of the piperidine/CO₂/H₂O system, in terms of peak positioning and the relationship between peak absorbance and cumulative CO₂ absorption (Fig. 1b).

- As the CO₂ loading of piperidine and the 3- and 4- substituted piperidines exceeded 0.5 mol CO₂/mol amine, hydrolysis of their COO⁻ derivatives was also observable in the IR spectra collected. Fig. 1b shows peak absorbance to increase at the rate of 5.0 mol CO₂/mol amine.

Effect of the 2-alkyl and -hydroxylalkyl Substituents
- From the subset of amines analysed the 2- methyl and -hydroxylalkyl substituted piperidines were found to favour HCO₃⁻ formation on absorption of CO₂ (Fig. 2).

Absorption Capacity and Initial Absorption Rate
- The similarity in the Cₓ of piperidine and the 3- and 4- methyl and hydroxyl substituted piperidines is consistent with the interpretation of the IR spectra (Fig. 1a, b). These amines react with CO₂ to form a relatively stable COO⁻ derivative, which at higher CO₂ loadings begins to hydrolise forming HCO₃⁻. The hydrolis of the COO⁻ species permits the CO₂ loading of these amines to exceed 0.5 mol CO₂/mol amine. Formation of the COO⁻ derivatives of the 3- and 4- hydroxyl and hydroxyalkyl substituted piperidines were found however to be kinetically less favourable than that of piperidine and the 3- and 4- hydroxyalkylpiperidines.
- The tendency of 2- methyl and hydroxyalkyl substituted piperidines to favour HCO₃⁻ formation over COO⁻ formation, as indicated by the IR spectral data (Fig. 2), is reflected in the higher Cₓ and smaller Kₓ values reported in Table 1. Despite these amines forming predominantly HCO₃⁻, they were found to exhibit Kₓ values comparable to that of MEA and DEA. 2-methyipiperidine in particular was found to exhibit a significantly higher initial absorption rate. Although the 2-methyl substituent was found to have the largest electronic influence on the amino nitrogen, it exerted the smallest effect in terms of reducing the exposed area on the nitrogen atom (Table 1). In contrast, the 2-hydroxyalkylpiperidines were found to have the smallest effect on the electronic environment of the amino nitrogen but substantially reduced the exposed area on the nitrogen atom, these amines were found to have the smallest Kₓ values compared to 2-methylpiperidine.
- The theoretical results presented in Table 1, show that for the 2- substituted piperidines a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area on the nitrogen atom will play a role in destabilising the COO⁻ derivative and increasing its susceptibility to hydrolis.

Table 1: Measured Cₓ at 40°C and Kₓ at 40°C and zero loading for the subset of functionalised piperidines. For comparison the reactivity of conventional amines MEA, DEA and AMP has also been included at the bottom of the table. Also provided are the theoretical results obtained for the ESP charge on nitrogen and the exposed area (Å²) on the nitrogen atom for all optimised amine structures. * stands for not measured.

<table>
<thead>
<tr>
<th>Amine</th>
<th>0.5 mol CO₂/mol amine</th>
<th>1.0 mol CO₂/mol amine</th>
<th>2.0 mol CO₂/mol amine</th>
<th>3.0 mol CO₂/mol amine</th>
<th>ESP Charge on Nitrogen (e)</th>
<th>ESP Charge on Nitrogen (Å²)</th>
<th>Exposed Aromatic Nitrogens (Å²)</th>
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<td>Piperidine</td>
<td>0.75</td>
<td>1.25</td>
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<td>1.85</td>
<td>-0.030</td>
<td>6.70</td>
<td>6.46</td>
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<td>0.93</td>
<td>2.36</td>
<td>3.86</td>
<td>5.84</td>
<td>-0.036</td>
<td>6.46</td>
<td>6.46</td>
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<tr>
<td>4-Methylpiperidine (4-MP)</td>
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<td>3.85</td>
<td>6.96</td>
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<td>-0.030</td>
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References
3. The effect of molecular structural variation on CO₂/amine reactivity of cyclic amines and their enhanced activity compared to conventional straight chain aliphatic 1° and 2° amines, as employed, e.g., as monoethanolamine (MEA).
The effect molecular structural variations has on the CO\textsubscript{2} absorption characteristics of heterocyclic amines

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Abstract

\textit{In-situ} ATR FT-IR spectroscopy has been used to investigate the reaction between CO\textsubscript{2} and piperidine, as well as commercially available functionalised piperidine derivatives, e.g., those with methyl-, hydroxyl-, and hydroxyalkyl- substituents. The effect of the substituent’s on CO\textsubscript{2} absorption has been assessed in relation to the prevalent IR identifiable ionic reaction products, along with CO\textsubscript{2} absorption capacity and initial absorption rate. The results obtained highlight the enhanced reactivity of cyclic 2° amines compared to conventional 1° and 2° amines, MEA and DEA respectively. Formation of the COO\textsuperscript{-} derivatives of the 3- and 4- hydroxyl and hydroxyalkyl substituted piperidines were found to be kinetically less favourable than that of piperidine and the 3 and 4 –methyl substituted piperdines. As the CO\textsubscript{2} loading of piperidine and the 3- and 4- substituted piperidines exceeded 0.5 mol CO\textsubscript{2}/mol amine, hydrolysis of their COO\textsuperscript{-} derivative was observable in the IR spectral profiles. From the subset of amines analysed the 2-alkyl and 2-hydroxyalkyl substituted piperidines were found to favour HCO\textsubscript{3} formation. Despite forming predominantly HCO\textsubscript{3} these amines also exhibited initial absorption rates comparable to that of MEA and DEA, 2-MP in particular was found to exhibit a significantly higher initial absorption rate. Computational calculations at the B3LYP/6-31+G** and MP2/6-31+G** level of theory revealed that for the 2-alkyl and hydroxyalkyl substituted piperidines a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area on the nitrogen atom will play a role in destabilising the COO\textsuperscript{-} derivative and increasing its susceptibility to hydrolysis.

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Keywords: CO\textsubscript{2}; heterocyclic; amine; reactivity; infrared.

1. Introduction

Aqueous amine-based post combustion capture (PCC) of CO\textsubscript{2} generated from coal-fired power stations has been identified as a crucial part of the global solution to climate change. The process involves separating CO\textsubscript{2} from other gases by reactive chemical absorption and re-releasing CO\textsubscript{2}...
from the absorbent by heating in a two-step process. The technology is industrially proven for absorbents such as monoethanolamine (MEA), and has been used for decades to remove CO₂ from gas streams in commercial processes such as natural gas processing [1].

The major challenge leading up to the deployment of aqueous amine-based PCC on a large scale is adapting the existing technology to suit typical flue gas conditions from a coal-fired power plant. At present a high energy and cost penalty is associated with large scale application of the technology [2]. One approach to reducing the energy requirements and cost of the process is through the development of more cost effective and superior performing amines.

It is well established in the scientific literature on amine-based absorbents for PCC that a definite relationship exists between the structure of amines and their CO₂ absorption characteristics [3-6]. The molecular structure of conventional primary (1°) and secondary (2°) absorbents, such as MEA and diethanolamine (DEA) respectively, enable the formation of stable carbamate derivatives (COO⁻). On the other hand, 1° amines with one or more alkyl substituent’s at the α-carbon (“sterically-hindered” amines in industry parlance), such as 2-amino-2-methyl-1-propanol (AMP), are characterised as forming COO⁻ derivatives of low stability with bicarbonate (HCO₃⁻) being the major product of CO₂ absorption. The effect of the substituents on COO⁻ stability can manifest itself through either steric constraints on the amino nitrogen [3] and/or by inducing a change in the electronic environment of the amino nitrogen [6]. Current explanations for the variation in activity, however, tend to focus solely on the concept of steric constraints i.e. with increasing steric crowding around the amino nitrogen there is a subsequent increase in HCO₃⁻ formation and hence decrease in COO⁻ stability. Both modifications will affect amine reactivity towards CO₂. The resultant destabilisation of the COO⁻ species (and associated increase in HCO₃⁻ formation) allows for higher CO₂ loadings and lower absorbent regeneration energies when comparing sterically-hindered amines to their non-hindered counterparts.

Recently, heterocyclic amines such as piperazine and piperidine have received considerable attention due to their increased activity for CO₂ absorption. Piperazine in particular has been found to exhibit significantly higher CO₂ absorption rates compared to other 1° and 2° amines [7]. This increased reactivity towards CO₂ has been attributed to the cyclic and diamine structure of piperazine [7]. The second amine moiety offers the potential for enhanced CO₂ absorption capacity either in the form of a second reactive site for COO⁻ formation or proton acceptance, in the catalysis of HCO₃⁻ formation or in modifying/enhancing the reactivity of the first amine site. However, the low solubility of piperazine (1.7 mol/L at 20°C [8, 9]) and piperazine-COO⁻ (1.3 mol/L [8]) limits its use as a sole CO₂ capture sorbent [8]. In contrast, piperidine a heterocyclic 2° amine does not suffer the same limitations with improved aqueous solubility.

We believe studying the reaction between CO₂ and piperidine, as well as commercially available functionalised piperidine derivatives, e.g. those with methyl-, hydroxyl- and hydroxyalkyl-substituents, will provide valuable insight into the effect of molecular structural variation on CO₂/amine reactivity of cyclic amines and their enhanced activity compared to conventional 1° and 2° amines. Herein we report our findings.

2. Experimental

To characterise the effects of molecular structural variation on CO₂/amine reactivity, the chemical reactions between CO₂ and the subset of functionalised piperidines were followed in-situ using Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) spectroscopy. The effect of the substituents on CO₂ absorption was then assessed in relation to the prevalent ionic reaction products identified, i.e., COO⁻ versus HCO₃⁻, along with CO₂ absorption capacity and mass transfer coefficient at zero loading (initial absorption rate).

Absorption/FT-IR Experiments

A simplified schematic of the absorption reactor apparatus, used to analyse aqueous CO₂/amine reactivity, is shown in Fig. 1. A gas stream of 13% CO₂ (v/v) (>99.9% purity, BOC Australia) in N₂
(derived from cryogenic boil-off) with a flow rate of 1.8 L/min was bubbled through a 3 mol/L aqueous amine solution, maintained at 40°C. The difference between the CO₂ concentration of the reactor gas inflow and gas outflow (measured with a Horiba VA-3000 CO₂ analyser) was used to determine the amount of CO₂ absorbed by the amine solution.

For the duration of each absorption experiment an ATR diamond tipped IR probe, coupled via a mirrored K6 conduit to an ic10 FT-IR spectrometer (all supplied by Mettler-Toledo), was immersed in the aqueous amine solution. In-situ IR measurements were obtained simultaneously with the CO₂ absorption measurements, with the FT-IR spectrometer set to continuously collect spectra for the duration of the absorption experiment over the spectral range of 4000-650 cm⁻¹. Each spectrum was recorded as the average of 256 scans over a sampling interval of fifteen seconds with a resolution of 4 cm⁻¹. The amines investigated were purchased from Sigma Aldrich, Acros Organics and Tokyo Chemical Industry, with a purity of ≥ 98% and used without further purification.

Figure 1. Simplified schematic of the CO₂ absorption reactor/FT-IR system.

Absorption Rate Experiments

A wetted-wall column (WWC) was used to analyse the initial absorption rate of CO₂ into aqueous solutions of the functionalised piperidines, at a reaction temperature of 40°C. The process involved counter-contacting a 1 mol/L aqueous amine thin liquid film (220 ml/min flow rate), with a N₂/CO₂ gas stream (5 L/min flow rate) on the surface of a stainless steel rod with a known surface area (effective height 8.21 cm, diameter 1.27 cm). The CO₂/N₂ composition (v/v) was varied to achieve CO₂ partial pressures in the range of 0 to 20 kPa. The difference between the CO₂ concentration of the reactor gas inflow and gas outflow (measured by an Horiba VA-3000 CO₂ analyser), along with the known experimental parameters including gas flow rate and contact area for reaction, were used to determine the flux and mass transfer coefficient at zero loading.

3. Results and Discussion

Infrared Spectral Analysis

Piperidine

Fig. 2 shows the sequential IR spectra, in the 1800-900 cm⁻¹ region, collected during a typical CO₂ absorption experiment with a 3 mol/L aqueous piperidine solution. Five major FT-IR peaks are shown to evolve with CO₂ absorption and hence can be related to the vibrational modes of the potential ionic reaction products including piperidine-COO⁻ (carboxylate derivative), piperidine-H⁺ and bicarbonate (HCO₃⁻). Based on the IR absorption of characteristic functional groups specific assignment of the spectral peaks that emerged is detailed below.

Three main peaks have been assigned to the vibrational modes of piperidine-COO⁻ (Fig. 2). The N-COO⁻ stretching vibration (ν₁(COO⁻)) at 1283 cm⁻¹ and the asymmetric and symmetric stretching vibrations (ν₂(COO⁻) and ν₃(COO⁻)) of the carboxylate moiety at 1514 cm⁻¹ and 1434 cm⁻¹ respectively.

The ν₁(COO⁻) and ν₃(COO⁻) of carboxylates have been found to generally give rise to two absorbance bands in the 1650-1540 cm⁻¹ and 1450-1360 cm⁻¹ region [10].
Relative Infrared Absorbance

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7

Wavenumber (cm⁻¹)

900 1000 1100 1200 1300 1400 1500 1600 1700 1800

0 mol CO₂/mol amine
0.20 mol CO₂/mol amine
0.50 mol CO₂/mol amine
0.60 mol CO₂/mol amine
0.76 mol CO₂/mol amine

Figure 2. Infrared spectra of aqueous piperidine as CO₂ is absorbed to a loading of 0.76 mol CO₂/mol amine

The absorbance band that appears at 1477 cm⁻¹ has been assigned to the NH₂⁺ bending mode of piperidine-H⁺. To confirm this assignment spectral data was collected during the gradual acidification of the original 3 mol/L piperidine solution using concentrated HCl acid. A small peak of the same profile evolved at around 1477 cm⁻¹ on protonation of the amine functionality.

As expected, an almost identical relationship exists between IR absorbance and cumulative CO₂ absorption (Fig. 3) for the spectral peaks assigned to both piperidine-COO⁻ and piperidine-H⁺. Peak absorbance is observed to increase at the rate of COO⁻ formation at the reaction onset and decrease after a loading of 0.5 mol CO₂/mol amine. The decrease in peak absorbance at high CO₂ loadings may be attributed to the sequential onset of a new reaction pathway such as the hydrolysis of the COO⁻ derivative to HCO₃⁻. The relationship identified above can be distinguished from that observed for the absorbance band that evolves at 1354 cm⁻¹, which shows a corresponding increase in peak absorbance after a loading of 0.5 mol CO₂/mol amine. This band has been assigned to the ν₅-C=O of HCO₃⁻, which is in good agreement with literature values for aqueous HCO₃⁻ [11, 12]. There are two possible reaction pathways that can lead to the formation of HCO₃⁻ in an aqueous amine environment i.e. via the hydrolysis of the COO⁻ derivative or via the direct nucleophilic attack of OH⁻ on dissolved CO₂. The IR spectral data (Fig. 2 and 3) is illustrative of the first of these two pathways, with the simultaneous decline in COO⁻ absorbance and increase in HCO₃⁻ absorbance.

Effect of N –Methyl, –Hydroxy and –Hydroxyalkyl Substituents

N-methylpiperidine (1-MP), N-hydroxypiperidine (1-HP) and N-hydroxyethylpiperidine (1-PE) are tertiary (3°) amines and cannot react directly with CO₂ to form a COO⁻ derivative, due to the absence of hydrogen atoms bonded directly to the nitrogen atom. Instead 3° amines form HCO₃⁻ via a base-catalysed pathway. For this reason their activity will not be compared to the set of 2° amines being analysed. The IR spectra collected for these amines, however, will be used as a standard for HCO₃⁻ formation in an amine/CO₂/H₂O system. Fig. 4a shows the spectral profile for a 3 mol/L aqueous 1-PE system, as CO₂ is being absorbed into solution, with the characteristic broad HCO₃⁻ absorbance band evolving at 1350-1360 cm⁻¹. Further confirmation of this assignment is provided in Fig. 4b, which shows the evolution of this broad absorbance band at 1354 cm⁻¹ in the IR spectra of aqueous 3 mol/L piperidine with the gradual addition of ammonium bicarbonate.

Effect of 2 –Methyl and –Hydroxyalkyl Substituents

The spectral data collected for 2-methylpiperidine (2-MP), 2-hydroxymethylpiperidine (2-PM) and 2-(2-hydroxyethyl)piperidine (2-PE) /CO₂/H₂O systems differ significantly from that of the piperidine/CO₂/H₂O system. Their spectra, however, are very similar to that of the 3° amines 1-MP
Figure 3. The relationship between the cumulative CO$_2$ absorption into aqueous piperidine and IR peak absorbance.

Figure 4. a) Infrared spectra of aqueous 3mol/L 1-PE as CO$_2$ as CO$_2$ is absorbed; b) the infrared spectra of an aqueous 3 mol/L piperidine solution with gradual addition of ammonium bicarbonate.

and 1-PE (Fig. 4a) with the evolution of the characteristic broad absorbance band at around 1354 cm$^{-1}$, indicative of HCO$_3^-$ formation. Fig. 5 illustrates this similarity, presenting a partial profile of the sequential infrared spectra collected during typical CO$_2$ absorption experiments with 3 mol/L aqueous solutions of 2-MP (Fig. 5a) and 2-PM (Fig. 5b).

Effect of 3- and 4- Methyl, Hydroxy and Hydroxyalkyl Substituents

The infrared spectral profiles obtained for 3- and 4- methylpiperidine (3-MP and 4-MP), 3- and 4- hydroxy piperidine (3-HP and 4-HP), 3- and 4- hydroxymethylpiperidine (3-PM and 4-PM) and 4-(2-hydroxyethyl)piperidine (4-PE) /CO$_2$/H$_2$O systems illustrate a high degree of similarity with that of the piperidine/CO$_2$/H$_2$O system, in terms of peak positioning and the relationship between peak absorbance and cumulative CO$_2$ absorption. As the CO$_2$ loading of these amines exceeded 0.5 mol CO$_2$/ mol amine, hydrolysis of their carbamate derivatives was also observable in the infrared spectra collected. The difference in frequencies corresponding to the stretching vibrations of the COO$^-$ derivatives of piperidine and the 3- and 4- substituted piperidines do not exceed 6 cm$^{-1}$.

Absorption Capacity and Absorption Rate

To quantify the effect of the alkyl-, hydroxyl- and hydroxylalkyl- substituents on the relative reactivity of the amino nitrogen, the CO$_2$ absorption capacity ($C_A$) and mass transfer coefficient at zero loading (i.e., initial absorption rate, $K_G$) were determined for each individual amine (Table 1). For comparison of reactivity, the $C_A$ and $K_G$ values obtained for conventional amine-based absorbents MEA, DEA and di-methyl substituted AMP have been included in Table 1.
To analyse the electronic/steric effects of the different substituents on the relative reactivity of the amino nitrogen (capture performance), the computational software package ‘Spartan 08’ [13] was used to calculate and compare optimised geometries of the functionalised piperidines at both the B3LYP/6-31+G** and MP2/6-31+G** level of theory. The effect of the substituents on the calculated electrostatic potential (ESP) partial charge on the amino nitrogen, and the exposed area on the nitrogen atom for the optimised forms of the amines, are also provided in Table 1.

The $C_A$ and $K_G$ results presented in Table 1 highlight the significant increase in reactivity of cyclic 2° amines compared to conventional straight chain aliphatic 1° and 2° amines MEA and DEA respectively. Particularly noteworthy is the increase in initial absorption rate of the $\alpha$-substituted cyclic amines 2-MP, 2-PM and 2-PE compared to that of the $\alpha$-substituted aliphatic 1° amine AMP, given the similarity in structure (i.e. they are considered sterically-hindered).

The similarity in the $C_A$ of piperidine and the 3- and 4- alkyl and hydroxyalkyl substituted piperidines is consistent with the interpretation of the infrared spectra. These amines react with CO$_2$ to form a relatively stable COO$^-$ derivative, which at higher CO$_2$ loadings begins to hydrolyse forming bicarbonate. The hydrolysis of the COO$^-$ species permits the CO$_2$ loading of these amines to exceed 0.5 mol CO$_2$/mol amine, despite the consumption of two molecules of amine per molecule of CO$_2$ in the carbamate reaction pathway.

Methyl substitution in 3-MP and 4-MP had a relatively small effect on the electronic properties of the amino nitrogen or on the exposed area of the reactive site (amino nitrogen). This is reflected in the $K_G$ values obtained for these amines, which are almost identical to that of piperidine. A similar theoretical trend in electronic properties was observed for the 3- and 4- hydroxylalkyl substituted amines 3-PM, 4-PM and 4-PE. These amines however exhibited smaller $K_G$ values compared to their methyl substituted counterparts. Across the subset of functionalised piperidines, both the MP2 and B3LYP calculated trends in the ESP charge on the amino nitrogen and the exposed area on the nitrogen atom are in good agreement of one and other.

Both the hydroxyl substituted 3-HP and 4-HP exhibited smaller $C_A$ values as well as $K_G$ values compared to piperidine. These amines, however, still exhibited higher initial absorption rates than MEA and DEA, but with similar $C_A$ values. Both 3-HP and 4-HP share a structural similarity with MEA and DEA; that being a hydroxy group 2 to 3 carbon removed from the amino nitrogen. The presence of the hydroxyl substituent in 3-HP and 4-HP was found to have little effect on the electronic properties of the amino nitrogen. The hydroxyl group in 3-HP was, however, found to reduce the exposed area of the nitrogen atom. It should also be noted that presence of an oxygen atom directly bonded to the nitrogen atom in the tertiary amine N-hydroxypiperidine (Table 1) completely hindered CO$_2$ absorption, as opposed to the N-methyl or hydroxyethyl substitution.

The tendency of 2- methyl and hydroxyalkyl substituted piperidines to favour HCO$_3^-$ formation over COO$^-$ formation, as indicated by the IR spectral data, is reflected in the higher $C_A$ and $K_G$ values reported in Table 1, for 2-MP, 2-PM and 2-PE. The role of these substituents in

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**Figure 5.** IR spectral profile for an aqueous 3 mol/L solution of a) 2-MP and b) 2-PE as CO$_2$ is absorbed.
Table 1. Measured absorption capacity ($C_A$) at 40°C and mass transfer coefficient ($K_G$) at 40°C and zero loading for the subset of functionalised piperidines. The reactivity of conventional absorbents such as MEA, DEA and AMP has also been included at the bottom of the table. Also provided are the theoretical results obtained for the ESP charge on nitrogen and the exposed area on the nitrogen atom for all optimised amine structures.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A$ (mol CO$_2$/mol amine)</th>
<th>$K_G$ (mol/s.cm$^2$.Pa $\times 10^{-10}$)</th>
<th>ESP Charge on Nitrogen</th>
<th>Exposed Area on Nitrogen ($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MP2</td>
<td>B3LYP</td>
<td>MP2</td>
<td>B3LYP</td>
</tr>
<tr>
<td>piperidine</td>
<td>0.76</td>
<td>3.85</td>
<td>-0.671</td>
<td>-0.643</td>
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<tr>
<td>2-methylpiperidine (2-MP)</td>
<td>0.93</td>
<td>2.38</td>
<td>-0.869</td>
<td>-0.836</td>
</tr>
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<td>3-methylpiperidine (3-MP)</td>
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<td>3.73</td>
<td>-0.758</td>
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<tr>
<td>4-methylpiperidine (4-MP)</td>
<td>0.76</td>
<td>3.75</td>
<td>-0.682</td>
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</tr>
<tr>
<td>3-hydroxypiperidine (3-HP)</td>
<td>0.61</td>
<td>2.24</td>
<td>-0.671</td>
<td>-0.640</td>
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<tr>
<td>4-hydroxypiperidine (4-HP)</td>
<td>0.64</td>
<td>2.28</td>
<td>-0.670</td>
<td>-0.651</td>
</tr>
<tr>
<td>2-(hydroxymethyl)piperidine (2-PM)</td>
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<td>1.07</td>
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<td>3-(hydroxyethyl)piperidine (3-PM)</td>
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<td>2.32</td>
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<td>-0.720</td>
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<td>4-(hydroxyethyl)piperidine (4-PM)</td>
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<td>1.86</td>
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<td>2-(2-hydroxyethyl)piperidine (2-PE)</td>
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<td>1.27</td>
<td>-0.743</td>
<td>-0.729</td>
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<tr>
<td>4-(2-hydroxyethyl)piperidine (4-PE)</td>
<td>0.74</td>
<td>Nm*</td>
<td>-0.674</td>
<td>-0.659</td>
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<td>Tertiary Amines</td>
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<tr>
<td>N-methylpiperidine (1-MP)</td>
<td>0.31</td>
<td>Nm*</td>
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<td></td>
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<td>N-hydroxypiperidine (1-HP)</td>
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<td>Nm*</td>
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<tr>
<td>N-(2-hydroxyethyl)piperidine (1-PE)</td>
<td>0.27</td>
<td>Nm*</td>
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<td>Conventional Absorbents</td>
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<td>monoethanolamine (MEA)</td>
<td>0.56</td>
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<td>diethanolamine (DEA)</td>
<td>0.60</td>
<td>0.61</td>
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<tr>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>0.84</td>
<td>0.61</td>
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<td></td>
</tr>
</tbody>
</table>

* Nm= Not measured

significantly altering the reactivity of the amino nitrogen towards CO$_2$ and destabilising the COO$^-$ derivative seems to manifest itself through both electronic effects and by reducing the exposed surface area on the nitrogen atom.

The methyl substitution in 2-MP significantly increased the negative ESP charge on the amino nitrogen compared to piperidine and the 3- and 4- substituted piperidine derivatives. This electronic influence on the reactive site was found to be far less pronounced in 2-PM and 2-PE. However, the hydroxyalkyl side chain in these two amines was found to significantly reduce the exposed area on the nitrogen atom compared to the methyl side chain in 2-MP and the hydroxyalkyl side chain in 3-PM, 4-PM, 3-PE and 4-PE.

In terms of $C_A$ and $K_G$ values 2-MP stands out from the rest of the amines. Whilst the amine has been identified in this study as forming predominantly HCO$_3^-$ on absorption of CO$_2$, it showed a significant improvement in the $K_G$ value compared to 2-PM and 2-PE. Although the 2-methyl substituent was found to have the largest electronic influence on the amino nitrogen, it exerted the smallest effect in terms of reducing the exposed area on the nitrogen atom. A plausible explanation for the increased $K_G$ value may be that the increased exposure of the amino nitrogen, compared to 2-PM and 2-PE, facilitates the initial uptake of CO$_2$ to form an unstable COO$^-$ derivative. The electronic effect exerted by the neighbouring methyl group facilitates the destabilisation of the COO$^-$ derivative, which is then readily hydrolysed to HCO$_3^-$.

In contrast, both the 2-hydroxyalkyl substituents in 2-PM and 2-PE were found to have the smallest effect on the electronic environment of the amino nitrogen but substantially reduced the exposed area on the nitrogen atom. Both 2-PM and 2-PE were found to have the smallest $K_G$ values compared to 2-MP.

4. Conclusion

The chemical reactions between CO$_2$ and piperidine, as well as a subset of functionalised piperidines have been followed in-situ using ATR FT-IR spectroscopy. The effect of the structural
variations on CO$_2$ absorption has been assessed in relation to the prevalent IR identifiable ionic reaction products i.e. COO$^-$ versus HCO$_3^-$, along with CO$_2$ absorption capacity and initial absorption rate. Hydrolysis of the COO$^-$ derivative of piperidine and the substituted piperidines was observable in the IR spectra collected during CO$_2$ absorption. From the subset of amines analysed the 2-alkyl and 2-hydroxyalkyl substituted piperidines were found to favour HCO$_3^-$ formation in the reaction with CO$_2$. Despite forming predominantly HCO$_3^-$ these amines exhibited initial absorption rates comparable to that of MEA and DEA, 2-MP in particularly was found to exhibit a significantly higher initial absorption rate. The theoretical results obtained for the 2-alkyl and 2-hydroxyalkyl substituted piperidines suggest that a combination of both the electronic effect exerted by the substituent and a reduction in the exposed area on the nitrogen atom will play a role in destabilising the carbamate derivative and increasing its susceptibility to hydrolysis.

6. Acknowledgments

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7. References

THE EFFECT OF MOLECULAR STRUCTURAL VARIATIONS ON THE CO₂ ABSORPTION CHARACTERISTICS OF HETEROCYCLIC DIAMINES FOR AMINE-BASED POST COMBUSTION CO₂ CAPTURE

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ABSTRACT

The reaction between CO₂ and a subset of synthesised novel heterocyclic diamines, including hexahydroypyrimidine (HHPY), 2-methylhexahydroypyrimidine (MHHPY) and hexahydroypyridazine (HHPZ) have been investigated and compared to piperazine (PZ). The chemical reactions between CO₂ and the heterocyclic diamines were followed in-situ using ATR FT-IR spectroscopy. The effect of structural variations on CO₂ absorption was assessed in relation to the prevalent ionic reaction products identified (carbamate versus bicarbonate absorbance), CO₂ absorption capacity and initial absorption rate. HHPY was found to exhibit a similar reactivity toward CO₂ as PZ, with improved aqueous solubility. The α-methyl substituted MHHPY was found to favour HCO₃⁻ formation in the reaction with CO₂. Despite forming predominantly HCO₃⁻, MHHPY exhibited a comparable reactivity to that of the conventional amines MEA and DEA and improved reactivity when compared to the conventional α-methyl substituted primary amine AMP. HHPZ was found to be relatively non-reactive towards CO₂.

INTRODUCTION

At present, aqueous amine-based post-combustion capture (PCC) of CO₂ is viewed as the most promising and near ready technology for the reduction of CO₂ emissions from coal-fired power stations. The process involves separating CO₂ from a flue gas stream by reactive chemical absorption and re-releasing CO₂ from the absorbent by heating in a two-step process. The technology is industrially proven for absorbents such as monoethanolamine (MEA), and has been used for decades to remove CO₂ from gas mixtures in smaller scale commercial processes such as natural gas processing (Gielen et al., 2004). Despite being an established technology, there are many challenges that must be overcome before large scale implementation of the PCC process can be realised. One of these challenges involves addressing the large energy requirements and cost of the PCC process. One approach to reducing the energy requirements and cost of the process is through the development of more cost effective and superior performing amines (Robinson et al., 2011).

The chemical reactions involved in CO₂ absorption/desorption by aqueous amine-based absorbents are continually being investigated to identify potential for and make improvements in efficiency. When CO₂ reacts with amines in aqueous solution,
carbamate (NCOO\textsuperscript{-}), bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) and protonated amine are generated. Recent advances in FT-IR spectroscopy have allowed for the convenient and rapid analysis of these chemical species to be carried out in-situ as CO\textsubscript{2} is absorbed by an aqueous amine solution. In particular, the technique can distinguish NCOO\textsuperscript{-} from HCO\textsubscript{3}\textsuperscript{-} formation in the screening of potential amines (Robinson et al., 2009). The technique uses an attenuated total reflectance (ATR) probe optically coupled to an FT-IR spectrometer to monitor in-situ the reaction occurring. The knowledge derived from this technique allows the deduction and confirmation of the absorption reaction mechanisms. Having this insight into the reaction pathway allows us to identify certain structural features of amines that give rise to more favourable characteristics for the absorption of CO\textsubscript{2}, making it possible to tailor amine structures for enhanced absorption capacities and rates.

Recently, heterocyclic amines such as piperidine and piperazine (PZ) have received considerable attention due to their increased reactivity with CO\textsubscript{2} compared to conventional primary (1°) and secondary (2°) amines. In a recent study undertaken by Robinson et al. (2011), in-situ ATR FT-IR spectroscopy was applied to investigating the effect molecular structural variations has on the CO\textsubscript{2} absorption characteristics of piperidine, as well as commercially available functionalised piperidine derivatives: e.g. those with methyl-, hydroxyl- and hydroxyalkyl- substituents (Robinson et al., 2011). The study provided valuable insight into the effect of molecular structural variation on CO\textsubscript{2}/amine reactivity of heterocyclic amines and their enhanced activity compared to conventional 1° and 2° amines. This prompted us to further characterise the effects of molecular structural variation on CO\textsubscript{2}/amine reactivity, particularly with regards to heterocyclic diamines, such as PZ.

This paper reports on the ATR FT-IR spectroscopic investigation of the CO\textsubscript{2} absorption characteristics of a series of synthesised novel heterocyclic diamines, including hexahydropyrimidine and hexahydropyridazine derivatives. Similar to PZ, these amines are a six-membered ring compound containing two nitrogen atoms; however, they offer structural variance with regards to the position of the nitrogen atoms within the six-membered ring. The chemical reactions between CO\textsubscript{2} and the cyclic diamines were followed in-situ using ATR FT-IR spectroscopy. The effect of structural variations on CO\textsubscript{2} absorption was assessed in relation to the ionic reaction products identified (NCOO\textsuperscript{-} versus HCO\textsubscript{3}\textsuperscript{-} absorbance), CO\textsubscript{2} absorption capacity (mol CO\textsubscript{2}/mol amine) and initial absorption rate. The benefits of this work may lead to a greater cost saving in the implementation of the PCC process on a large scale.

**EXPERIMENTAL**

**Synthesis**

**General Experimental**

All starting materials were purchased from Sigma Aldrich and used without further purification. Solvents were bulk and distilled prior to use. All synthesised compounds were identified based on NMR (300 MHz (\textsuperscript{1}H) and 75 MHz (\textsuperscript{13}C), Bruker ‘Spectrospin 300’ spectrometer), MS (ESI, Shimadzu LCMS-2010 EV spectrometer) and IR (Mettler-Toledo ic10 ATR FT-IR spectrometer) data.

**Preparation (1) of Hexahydropyrimidine (HHPY)**

Formaldehyde (1.5 mol, 126 g of 37 wt % solution) was added, drop wise, to an ice-
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cooled and stirred aliquot of anhydrous 1,3-diaminopropane (1 mol, 74.1 g) over a period of 30 mins. The reaction mixture was further stirred for 24 hours, at 27°C, cooled on an ice-bath and NaOH pellets were added. The layers that formed were separated, with the upper layer being crude HHPY. Anhydrous HHPY was obtained on removal of water by azeotropic distillation with cyclohexane. The upper layer of crude HHPY was refluxed with 100 mL of cyclohexane under a Dean-Stark water separator. The cyclohexane was removed under reduced pressure at 40°C and the residue distilled affording anhydrous HHPY (17 g, 20%) as a clear oily fuming liquid (b.p. 57-60°C/27 mmbar, lit. b.p. 58-60°C/20 mmHg (Evans, 1967; Locke et al., 2007)).

**1H NMR (300 MHz, CDCl₃)** δ 1.36 (2H, m), 1.96 (2H, bs), 2.82 (4H, t, J = 5.5 Hz), 3.63 (2H, s); **13C NMR (75 MHz, CDCl₃)** δ 28.61, 45.65, 62.79; **MS (ESI+) m/z 87 (M+1); FT-IR ν(N-H) 3267 cm⁻¹.

**Preparation (2) of 2-Methylhexahydropyrimidine (MHHPY)**

A solution of acetaldehyde (0.215 mol, 9.5 g) in 100 mL diethyl ether was added, drop wise, to an ice-cooled and stirred aliquot of anhydrous 1,3-diaminopropane (0.2 mol, 14.8 g). The reaction mixture was then stirred over K₂CO₃ (0.4 mol, 55.4 g) for 24 hours, at 27°C, the solvent removed under reduced pressure at room temperature and the residue distilled affording MHHPY (17.5 g, 87%) as a clearly oily liquid (b.p. 56-59°C/30 mmbar, lit. b.p. 60°C/30 mmbar (Zelenin et al., 1998)).

**1H NMR (300 MHz, CDCl₃)** δ 0.80 (3H, d, J=6 Hz), 1.09 (2H, m), 2.48 (2H, m), 2.76 (4H, m), 3.25 (1H, q, J= 6 Hz); **13C NMR (75 MHz, CDCl₃)** δ 22.75, 26.80, 45.41, 67.09; **MS (ESI+) m/z 101 (M+1); FT-IR ν(N-H) 3266 cm⁻¹.

**Preparation (3) of Hexahydropyridazine (HHPZ)**

Dibromobutane (0.1 mol, 21.6 g) was added drop wise to a stirred solution of diethylhydrazine dicarboxylate (0.1 mol, 17.6 g), potassium carbonate (0.2 mol, 27.7 g) and acetonitrile (100 mL) at room temperature. The reaction mixture was then refluxed for 24 hours, let cool and filtered. The solvent was removed from the filtrate under reduced pressure at 40°C and the residue distilled affording 1,2-dicarbethoxyhexahydropyridazine (18.5 g, 80%) as a clear oily liquid (b.p. 110-114°C/2 mmbar, lit. b.p. 106-114°C/3 mmHg (Nakayama, 1992)).

**1H NMR (300 MHz, CDCl₃)** δ 1.07 (6H, m), 1.49 (4H, s), 2.74 (4H, bs), 3.97 (4H, m); **13C NMR (75 MHz, CDCl₃)** δ 14.36, 23.19, 44.76, 61.93, 155.15; **MS (ESI+) m/z 231 (M+1); FT-IR ν(C=O) 1706 cm⁻¹, no ν(N-H) at 3700-3500 cm⁻¹.

The obtained 1,2-dicarbethoxyhexahydropyridazine (0.13 mol, 30.1 g) was added to a solution of NaOH (0.72 mol, 20.8 g) in methanol (150 mL), refluxed for 20 hours, cooled and the precipitated inorganic salt removed by filtration. The filtrate was refluxed for a further 20 hours, cooled, filtered and the solvent removed under vacuum at 40°C. The residue was extracted well with dichloromethane, concentrated under vacuum at room temperature and distilled affording HHPZ (6.75 g, 60%) as a yellow oily liquid (b.p. 38-40°C/11 mmbar, lit. b.p. 38°C/8 mmHg (Sugiyama, 1995)).

**1H NMR (300 MHz, MeOD)** δ 2.39 (4H, m), 3.73 (4H, m), 5.72 (2H, s); **13C NMR (75 MHz, MeOD)** δ 22.06, 47.00; **MS (ESI+) m/z 87 (M+1); FT-IR ν(N-H) 3269 cm⁻¹.

**Micro-Scale Isothermal Gravimetric Analysis (IGA)**

A Setaram TG-DTA/DSC thermal gravimetric analyser was used to analyse aqueous CO₂/amine reactivity on a micro scale. In isothermal mode, at 40°C, the instrument measures the increase in mass of an aqueous amine solution (100 μL) when exposed to...
a gas stream of 15% CO\textsubscript{2} (v/v) (>99.9% purity, BOC Australia) in N\textsubscript{2} (derived from cryogenic boil-off) and ambient pressure. A gas flow rate of 30 mL/min was used for all experiments.

In order to determine total CO\textsubscript{2} uptake, two separate IGA experiments were performed for each amine. The first experimental run determined the mass loss due to evaporation when the test solution was exposed to a 100% N\textsubscript{2} gas stream. The second experimental run determined the mass increase of the test solution when exposed to CO\textsubscript{2} (15% CO\textsubscript{2} in N\textsubscript{2} gas stream) over the same length of time. Each experiment was performed on a fresh 100 µL aliquot of the test solution in a 100 µL alumina crucible (Setaram). From the data collected an absorption curve was then calculated for each amine by subtracting the mass at time \( t \) of the evaporation run from the mass at time \( t \) of the absorption run. Initial absorption rates could then be calculated by using linear regression to determine the slope of the absorption capacity curve.

**Absorption/FT-IR Experiments**

A simplified schematic of the absorption reactor apparatus, used to analyse aqueous amine/ CO\textsubscript{2} reactivity is shown in Fig. 1. A gas stream of 13% CO\textsubscript{2} (v/v) (>99.9% purity, BOC Australia) in N\textsubscript{2} (derived from cryogenic boil-off), with a flow rate of 1.8 L/min, was bubbled through a 1.5 mol/L aqueous amine solution (30 mL) in a glass reactor vessel maintained at 40°C by a water bath (Techne). The difference between the CO\textsubscript{2} concentration of the reactor gas inflow and gas outflow (measured with a Horiba VA-3000 CO\textsubscript{2} analyser) was used to determine the amount of CO\textsubscript{2} absorbed by the amine solution. Each experiment was run until the measured CO\textsubscript{2} concentration in the outflow returned to the original percentage value. A typical run lasted 30-45 mins.

For the duration of each absorption experiment, an ATR diamond tipped IR probe (Mettler-Toledo), coupled via a mirrored K6 conduit to an ic10 FT-IR spectrometer (Mettler-Toledo), was immersed in the aqueous amine solution. In-situ IR measurements were obtained simultaneously with the CO\textsubscript{2} absorption measurements, with the FT-IR spectrometer set to continuously collect spectra for the duration of the absorption experiment over the spectral range of 4000-650 cm\textsuperscript{-1}. Each spectrum was recorded as the average of 256 scans over a sampling interval of 15 secs with a resolution of 4 cm\textsuperscript{-1}. The amines investigated were synthesised according to the procedures detailed above, with the exception of commercially available PZ (Sigma Aldrich, purity ≥ 97%).
Fig. 1: A simplified schematic of the CO₂ absorption reactor/FT-IR system.

RESULTS AND DISCUSSION

Carbamate and Bicarbonate IR Absorbance Bands

The NCOO⁻ derivatives of heterocyclic monoamines, in particular piperidine, as well as alkyl-, hydroxyl- and hydroxyalkyl- substituted piperidine derivatives, have been identified as giving rise to several strong absorbance bands in the 1260-1600 cm⁻¹ region (Robinson et al., 2011) including: the symmetric (νₛCOO⁻, 1350-1450 cm⁻¹) and asymmetric (νₘₐₙ COO⁻, 1500-1600 cm⁻¹) vibrations of the COO⁻ moiety and the N-COO-stretching vibration (νN-COO⁻, 1260-1300 cm⁻¹) of the NCOO⁻ derivative (Fig. 2). The protonated amine generated on absorption of CO₂ was found to give rise to an absorbance band in the 1479-1474 cm⁻¹ region (NH₂⁺ bending mode) (Fig. 2).

In an amine/CO₂/H₂O system, the HCO₃⁻ species has been previously identified as giving rise to a broad absorbance band in the 1360-1354 cm⁻¹ region (νₛC-O) (Robinson et al., 2009). Assignment was based on the spectral data acquired for a 2-methyl-2-amino-1-propanol (AMP)/CO₂/H₂O system. It is well established in the scientific literature that the absorption of CO₂ by aqueous AMP (α-dimethyl substituted MEA derivative) leads to the formation of mostly HCO₃⁻ with no significant NCOO⁻ formation (Chakraborty et al., 1988; Sartori & Savage, 1983; Vaidya and Kenig, 2007).

The IR spectral data collected for the heterocyclic diamines PZ, HHPY, MHHPY and HHPZ analysed in this study were assessed according to the above NCOO⁻ and HCO₃⁻ peak assignments.

IR Spectral Analysis

Piperazine (PZ)

Fig. 2 presents a partial profile of the sequential IR spectra, in the 1800-900 cm⁻¹ region, collected during a typical CO₂ absorption experiment with a 1.5 mol/L aqueous PZ solution. Five major FT-IR peaks are shown to evolve with CO₂ absorption and hence can be related to the vibrational modes of the potential ionic reaction products including: PZ-carbamate (PZ-COO⁻), protonated PZ-COO⁻, and bicarbonate (HCO₃⁻). PZ, being a secondary diamine, should typically react with CO₂ in solution to form a NCOO⁻ derivative. One amine functionality will act as the binding site for CO₂, while the second amine functionality will accept the proton. PZ has also been reported to form dicarbamate (OOC-PZ-COO⁻) on absorption of CO₂ (Bishnoi and Rochelle, 2000). Specific assignment of the spectral peaks that emerged is detailed below.

The IR spectral profile presented in Fig. 2, for the PZ/CO₂/H₂O system, closely resembles that previously reported for the monoamine analogue piperidine/CO₂/H₂O system (Robinson et al, 2011), with regards to peak positioning (PZ frequencies are slightly shifted). The PZ/CO₂/H₂O system (Fig. 2) exhibits the νₘₐₙ COO⁻ (1425 cm⁻¹), νₕₙ COO⁻ (1524 cm⁻¹ and shifts to 1546 cm⁻¹ as CO₂ is absorbed) and νN-COO⁻ (1276 cm⁻¹ and shifts to 1289 cm⁻¹) of the PZ-COO⁻ derivative; and the NH₂⁺ vibration of PZ-H⁺ (1470 cm⁻¹).

As expected, an almost identical relationship exists between IR peak absorbance and cumulative CO₂ absorption (Fig. 3a) for the spectral peaks assigned to νₘₐₙ COO⁻, νₕₙ COO⁻ and PZ-H⁺. Peak absorbance is observed to increase at the rate of COO⁻
formation at the reaction onset and level off as a maximum CO$_2$ loading of 0.92 mol CO$_2$/mol amine is approached. The relationship identified above can be distinguished from that observed for the νN-COO$^-$ absorbance bands that evolve at 1276 cm$^{-1}$ and

1289 cm$^{-1}$ (Fig. 3a). Fig. 2 and 3a shows the peak emerging at 1276 cm$^{-1}$ to be the dominant absorbance band, increasing with initial CO$_2$ absorption up to a loading of about 0.4-0.5 mol CO$_2$/mol amine at which point it ceases to increase in intensity, and a corresponding sharp increase in intensity of the absorbance band at 1289 cm$^{-1}$ is observed. The emergence of the intense νN-COO$^-$ absorbance band at 1289 cm$^{-1}$ may be attributed to the formation of ‘OOC-PZ-COO$^-$. This trend in peak absorbance was not observed for the heterocyclic monoamine piperidine (Fig. 3b) or for the remaining subset of heterocyclic diamines analysed in this study. The IR spectral profiles obtained for these amines showed a single intense absorbance band in the 1283-1272 cm$^{-1}$ region for νN-COO$^-$(Fig. 4-5).

The evolution of a weak broad absorbance band in the 1350-1360 cm$^{-1}$ region may be assigned to the ν$_s$C=O of HCO$_3$$^-$. This absorbance band is far less prominent than that observed by Robinson et al. (2011), for the piperidine/CO$_2$/H$_2$O system, and does not illustrate the same trend in peak absorbance: i.e. the depletion of NCOO$^-$ absorbance bands and corresponding increase in the HCO$_3$$^-$ absorbance band after a CO$_2$ loading of about 0.5 mol CO$_2$/mol amine (Figure 3a and b). This trend in NCOO$^-$ and HCO$_3$$^-$ absorbance bands, observed for the piperidine/CO$_2$/H$_2$O system (Fig 3b) has been attributed to the hydrolysis of the piperidine-COO$^-$ derivative to HCO$_3$ at high CO$_2$ loadings (Robinson et al, 2011). The PZ/CO$_2$/H$_2$O system (Fig 3a) does not show the same simultaneous decline in ν$_s$COO$^-$, ν$_a$COO$^-$ and νN-COO$^-$ and increase in HCO$_3$$^-$ absorbance as that observed for piperidine. Based on the IR spectral data presented in Fig. 2 and 3a, for the PZ/CO$_2$/H$_2$O system, PZ forms a stable NCOO$^-$ derivative that does not undergo hydrolysis as readily as the piperidine-COO$^-$ derivative.

**Hexahydropyrimidine (HHPY)**

The IR spectral data collected for the HHPY/CO$_2$/H$_2$O system (Fig. 4) illustrates some similarity with that of the PZ/CO$_2$/H$_2$O system, in terms of signal positioning. Despite
the IR peak absorbance being somewhat weaker, the evolution of NCOO\textsuperscript{-} and HCO\textsubscript{3}\textsuperscript{-} absorbance bands are evident. The IR spectral data presented in Fig. 4 shows the evolution of the $\nu_{s}$COO\textsuperscript{-} at 1427 cm\textsuperscript{-1}; the $\nu_{as}$COO\textsuperscript{-} at 1570-1520 cm\textsuperscript{-1} (the signal for this absorbance band is very weak, making it difficult to accurately determine the frequency); the $\nu$N- COO\textsuperscript{-} at 1293 cm\textsuperscript{-1}, as a single strong absorbance band; the NH\textsubscript{2}\textsuperscript{+} bending mode of HHPY-H\textsuperscript{+} at 1479 cm\textsuperscript{-1}; and HCO\textsubscript{3}\textsuperscript{-} absorbance at 1354 cm\textsuperscript{-1}. The HCO\textsubscript{3}\textsuperscript{-} absorbance band is more prominent, than that observed for the PZ/CO\textsubscript{2}/H\textsubscript{2}O system, indicating that HHPY forms a less stable NCOO\textsuperscript{-} derivative that is more susceptible to hydrolysis.

To improve the quality of the IR spectral data collected for HHPY, the CO\textsubscript{2} absorption/FT-IR experiment needs to be run at a concentration higher than 1.5 mol/L. In this study the concentration was determined based on the quantity of amine available.

Fig. 3: The relationship between the cumulative CO\textsubscript{2} absorption and IR absorbance, for the bands assigned to the vibrational modes NCOO\textsuperscript{-} and HCO\textsubscript{3}\textsuperscript{-}, for aqueous solutions of a) PZ (1.5 mol/L) and b) piperidine (3 mol/L) (Robinson et al, 2011).

bending mode of HHPY-H\textsuperscript{+} at 1479 cm\textsuperscript{-1}; and HCO\textsubscript{3}\textsuperscript{-} absorbance at 1354 cm\textsuperscript{-1}. The HCO\textsubscript{3}\textsuperscript{-} absorbance band is more prominent, than that observed for the PZ/CO\textsubscript{2}/H\textsubscript{2}O system, indicating that HHPY forms a less stable NCOO\textsuperscript{-} derivative that is more susceptible to hydrolysis.

To improve the quality of the IR spectral data collected for HHPY, the CO\textsubscript{2} absorption/FT-IR experiment needs to be run at a concentration higher than 1.5 mol/L. In this study the concentration was determined based on the quantity of amine available.

Fig. 4: IR spectra of an aqueous solution of HHPY (1.5 mol/L) as CO\textsubscript{2} is absorbed to a maximum loading of 0.85 mol CO\textsubscript{2}/mol amine.
2-methylhexahydropyrimidine (MHHPY)

The IR spectral data collected for the MHHPY/CO$_2$/H$_2$O system (Fig. 5) differs from that observed for the PZ and HHPY/CO$_2$/H$_2$O systems. Fig. 6 shows the evolution of a dominant broad HCO$_3^-$ absorbance band in the 1350-1360 cm$^{-1}$ region, characteristic of $\alpha$-substituted amines such as AMP (Robinson et al., 2009; Robinson et al., 2011). MHHPY is the methyl-substituted analogue of HHPY. The infrared spectral data indicates that MHHPY forms predominantly HCO$_3^-$ in the absorption of CO$_2$.

The heterocyclic diamine HHPZ was found to absorb no CO$_2$ (Tab. 1) during a typical CO$_2$ absorption/FT-IR experiment. For this reason the IR spectral data collected will not be discussed.

**Absorption Capacity and Absorption Rate**

To quantify the effect of the structural variations on the relative reactivity of the amino nitrogen, the CO$_2$ absorption capacity ($C_A$) and initial absorption rate ($R_{IA}$) was determined for each individual amine (Tab. 1). $C_A$ was measured simultaneously with IR data during a typical CO$_2$ absorption experiment and $R_{IA}$ was measured using the micro scale TGA method. For comparison, the reactivity of conventional absorbents MEA, DEA and $\alpha$-dimethyl substituted AMP (methyl substituted analogue of MEA), have been included in Tab. 1.

Tab. 1 shows HHPY to exhibit $C_A$ and $R_{IA}$ values comparable with that of PZ. HHPY, however, offers the advantage of improved aqueous solubility compared to PZ, as well as the formation of a NCOO$^-$ derivative that is more susceptible to hydrolysis and the formation of HCO$_3^-$ (indicated by the IR spectral data). Amines that form more HCO$_3^-$ than NCOO$^-$ will exhibit slower reaction rates than those that form more NCOO$^-$; however, they require less energy for regeneration in the PCC process and hence have the potential to reduce overall costs.

Based on the IR spectral data, MHHPY ($\alpha$-methyl substituted analogue of HHPY) was found to form predominantly HCO$_3^-$ in the reaction with CO$_2$. Despite forming predominantly HCO$_3^-$, the initial absorption rate obtained for MHHPY was much higher than that obtained for the corresponding $\alpha$-dimethyl substituted 1° amine AMP and comparable to that of MEA and DEA.
The $C_A$ and $R_{IA}$ values obtained for HHPZ showed it to be relatively non-reactive towards CO$_2$.

The results presented in Tab. 1 highlights the increased reactivity of heterocyclic diamines, with the exception of HHPZ, compared with conventional amines MEA, DEA and AMP.

Tab. 1: Measured absorption capacity ($C_A$) and initial reaction rate, at 40°C and amine concentration of 1.5 mol/L for aqueous solutions of PZ, HHPY, MHHPY and HHPZ as well as conventional amines MEA, DEA and AMP.

<table>
<thead>
<tr>
<th>Amine</th>
<th>$C_A$[a]</th>
<th>$R_{IA}$[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piperazine (PZ)</td>
<td>0.92</td>
<td>0.045</td>
</tr>
<tr>
<td>Hexahydropyrimidine (HHPY)</td>
<td>0.85</td>
<td>0.032</td>
</tr>
<tr>
<td>2-methylhexahydropyrimidine (MHHPY)</td>
<td>0.86</td>
<td>0.018</td>
</tr>
<tr>
<td>Hexahydropyridazine (HHPZ)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Conventional Amine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monethanolamine (MEA)</td>
<td>0.56[c]</td>
<td>0.027</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>0.60[c]</td>
<td>0.015</td>
</tr>
<tr>
<td>AMP</td>
<td>0.84[c]</td>
<td>0.006</td>
</tr>
</tbody>
</table>

[a] mol CO$_2$/mol amine. Data used to calculate $C_A$ was measured simultaneously with the IR spectral data during a typical absorption/FT-IR experiment with an aqueous solution of amine (1.5 mol/L).

[b] mol CO$_2$/mol amine, min$^{-1}$. Data used to calculate $R_{IA}$ was measured on the micro-scale TGA. Initial absorption rates have been calculated by using linear regression to determine the slope of the absorption capacity curve. Correlation coefficients are 0.995 or better.

[c] (Robinson et al., 2011)

CONCLUSION

The chemical reactions between CO$_2$ and PZ, as well as a subset of synthesised novel heterocyclic diamines including HHPY, 2-MHHPY and HHPZ, have been followed in-situ using ATR FT-IR spectroscopy. The effect of the structural variations on CO$_2$ absorption has been assessed in relation to the prevalent IR identifiable ionic reaction products, i.e. COO$^-$ versus HCO$_3^-$, along with CO$_2$ absorption capacity and initial absorption rate. Based on the νN-COO$^-$ absorbance band, the formation of PZ-dicarbamate was observable in the IR spectra collected during CO$_2$ absorption. The formation of a HHPY or MHHPY dicarbamate ion was not evident in the IR spectra collected for these amines. The absorbance signal for HHPY and MHHPY amines was much weaker than that of PZ. To improve the quality of the IR spectral data collected for HHPY and MHHPY, the CO$_2$ absorption/FT-IR experiment needs to be run at a concentration higher than 1.5 mol/L. Despite the weaker signal, hydrolysis of the NCOO$^-$ derivative of HHPY was observable in the IR spectra collected during CO$_2$ absorption. NCOO$^-$ hydrolysis was not so evident in the IR spectra obtained for the PZ/CO$_2$/H$_2$O system. HHPY was also found to exhibit a similar reactivity toward CO$_2$ as PZ, with improved aqueous solubility. The α-methyl substituted MHHPY was found to form predominantly HCO$_3^-$ in the reaction with CO$_2$. Despite forming predominantly HCO$_3^-$, the initial absorption rate obtained for MHHPY was much higher than that obtained for the corresponding α-dimethyl substituted 1° amine AMP and comparable to that of MEA and DEA. HHPZ was found to be relatively non-reactive towards CO$_2$.  

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REFERENCES


Nakayama, T 1992, ‘Hexahydropyridazine derivatives, used as herbicide intermediates – prepared by reacting 1,4-dihalobutane with 1,2-hydrazinedicarboxylate or 1,2-di(arylcarbonyl)hydrazine and base’, EP519083-A.


BIOGRAPHY
Kelly Robinson is currently undertaking a PhD internship with CSIRO Energy Technology in conjunction with the University of Newcastle. Her research is a part of the Solvent Development Research Project for the CSIRO Post Combustion Capture program, with the aim to develop greater understanding of the chemistry involved in the absorption of CO$_2$ by aqueous amine absorbents.