An Equilibrium Study of Carbamate Formation Relevant to Post Combustion Capture of CO₂

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy at the School of Environmental and Life Sciences, Chemistry University of Newcastle by

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April, 2012

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Author’s Declaration

I hereby certify that the work embodied in this thesis is the result of original research and has not been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due references has been made in the text.

Signature & Date

Debra Fernandes
Thesis by publication

Acknowledgement of Authorship

I hereby certify that this thesis is in a form of series of published papers of which I am the lead/co-author. I have included as part of the thesis a written statement from each co-author, endorsed by the Faculty of Science and Information Technology, Assistant Dean (Research Training), attesting to my contribution to the publications/scholarly work.

Signature & Date

Debra Fernandes
Acknowledgements

There have been so many people who have helped me through all these years for making my PhD experience a memorable one. Naming every individual is a tough task; however I would like to thank a few people who have been the key influence in this journey.

It is difficult to overstate my gratitude to my Ph.D. supervisors: Professor Marcel Maeder and Dr Robert Burns for their tremendous guidance, sound advice, encouragement and support through my project. This has been an invaluable contribution to my life and to my learning, without them I would have been lost in the tide of amines and CO₂ absorption data.

Further thanks go to Prof. Geoffrey Lawrance, Dr. Ian van Altena, Dr. Monica Rossignoli, Dr. Nichola McCann, Dr. Xiaoguang Wang and Dr. Graeme Puxty for all their encouragement and endless wealth of knowledge and ideas, technical support, proof reading and advice in nuclear magnetic resonance spectroscopy.

I also wish to thank the laboratory personal and the administration staff of the Department of Chemistry for their generous helping hand, words of encouragement and support throughout my project.

Particular thanks must also go to all my fellow postgraduates; Duong, Yaser, Will, Kylie, Hanadi, Hanki, Wahyu, Purnama, Dianna, Mohamed, Ahmed, Anang, and Azrin with whom I have shared great life experiences in the labs as well as outdoors, in particular, the bbq’s, and also thanks for putting up with my occasional whinging. I wish you all the best in your thesis.

Massive thanks goes to Sheena (sissy), Benju (benzooo), Rebecca (Bec), Duong (Duongy/Dong), Jade (Jedo), Gajj (Gajjy/Pavam), Ahmed, Sahi, James (Bear), Sandy, Ghufran (Ghufrina), Arslan (Azozobaba), Vinal, Hussain, Hassan, Yaser (Easer) and Diego for your contribution and influence in my life particularly; for putting up with my occasional tantrums, traumas, acting to be great listeners, cooking, parties, calling and
texting me a million times just to check on my wellbeing, driving me for shopping and workplace. I thank all of you for the wonderful times and memories, which are locked in my mind forever and will be for always no matter where my life journey will take me. ‘Each friend represents a world in us, a world possibly not born until they arrive, and it is only by this meeting that a new world is born’.

I wish you all a happy and prosperous life

I would also like to thank the University Of Newcastle, Australia and the Tom Farrell Institute for giving me an opportunity to peruse my dreams and for all the financial support throughout my PhD. Without this support I would have never embarked on this journey of a life time filled with great experience and a wonderful outcome.

I have been very fortunate to have been given the opportunity of travelling in Australia and Europe for conferences and in particular, undertaking a project at the University of Barcelona, Spain under the supervision of Prof. Manuel Martinez. I would like to thank him for his kindness, hospitality, encouragement and particularly for being calm, positive and patient especially when the instrument decided not to work 😊

Finally, I thank the Lord God Almighty for the strength and all the blessings, especially for the blessing of a wonderful family. My dad-Rubiano, mom-Succorina, brother-Darryl and sister-Deslyna have been the greatest support in my entire life and through this rocky road journey of PhD. Your faith and constant encouragement has helped me peruse my dream. Love you always!!!
Dedication

This thesis is dedicated to my family
Publications and Conferences resulting from my project


Papers in preparation

8) Fernandes, D., Conway, W., Wang, X., Burns, R., Lawrance, G., Puxty, G., Maeder, M., The activity of the diamine “piperazine” and the formation of carbamate(s) from the reaction(s) with CO$_2$(aq) in aqueous solution at 25.0 °C for post combustion capture processes. 2012, (Draft in preparation).


Conference Oral-Presentations

1) Debra Fernandes – Interaction of piperazine with CO$_2$(aq) in post combustion capture, International Conference on Carbon Reduction Technologies, Poland, September 2011.

2) Debra Fernandes – Amine Protonation and Implications for the Selection of Amines for PCC Applications, 9th Post Combustion Capture Day, CSIRO-Melbourne, December 2011
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<th>Description</th>
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<tr>
<td>AMP</td>
<td>2-amino-2methyl-1-propanol</td>
</tr>
<tr>
<td>AHPD</td>
<td>2-amino-2-hydroxymethyl-1-3-propandiol</td>
</tr>
<tr>
<td>BIS</td>
<td>2-amino-1,3-propandiol</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and sequestration</td>
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<tr>
<td>CFC’s</td>
<td>Chlorofluorocarbons</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>Carbonic acid</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>Carbonate</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>GHG’s</td>
<td>Greenhouse gases</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Hydrogen carbonate/Bicarbonate</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>MORP</td>
<td>Morpholine</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methyldiethanolamine</td>
</tr>
<tr>
<td>¹H NMR</td>
<td>Proton Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>PIPZ</td>
<td>Piperazine</td>
</tr>
<tr>
<td>PCC</td>
<td>Post-combustion capture</td>
</tr>
<tr>
<td>PIPD</td>
<td>Piperidine</td>
</tr>
<tr>
<td>PYRR</td>
<td>Pyrrolidine</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>pKₐ</td>
<td>Protonation constant</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethanolamine</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
</tr>
<tr>
<td>VLE</td>
<td>Vapour-liquid equilibrium</td>
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Abstract

The global community is currently facing a significant challenge in the form of climate change. The increasing emissions of greenhouse gases, especially carbon dioxide CO₂ is threatening the constitution of the Earth’s climate. This fosters the need for the removal of CO₂ from coal-fired power plants as it is the largest contributor to global CO₂ emissions.

One possible option for mitigating climate change is by CO₂ capture and sequestration (CCS), employing post-combustion capture of CO₂ (PCC). PCC is a mature technology for the capture of CO₂, as it is currently used in industry for gas-sweetening processes. The typical flue gas in power plants consists of about 80% N₂ and about 15% CO₂, with the remainder mainly unused O₂. For PCC purposes, separation of the two gases N₂ and CO₂ is important for compression, transportation and storage of CO₂. This can be achieved by reversible chemical absorption using amine-based solvents. Application of chemical absorption technology to power plants is not straightforward and poses several new challenges for chemists and chemical engineers, especially with the high cost associated with the process.

From a chemist’s point of view for PCC to be efficient the three main requirements are: 1) a fast reaction rate - this is the rate at which CO₂ interacts with the amine in aqueous solutions. For an ideal process the absorption of CO₂ has to be fast in order to minimise the size of the absorber column, 2) the stoichiometry of the amine-CO₂ interaction has to be 1:1 leading to a high loading capacity, and 3) the regeneration of the amine in the stripper column, the energy requirement of which is related to the protonation/deprotonation of the amine should be as low as possible, leading to a low cost and more efficient capture process.

A substantial number of studies on the interactions of amines and CO₂ have been published in the literature. However, most of the studies focus on the empirical functions but lack a mechanistic approach. As a consequence, the mechanism of the amine-CO₂ interaction is not clear. This thesis focuses on the molecular kinetics, the equilibria of carbamate formation in the reaction between amine and CO₂ in aqueous
solution, and the protonation constant of the amine. The amines investigated can be classified as primary, sterically-hindered primary, secondary, substituted-cyclic secondary and tertiary amines, with the aim of elucidating the possible effects of their chemical structures, electronic and steric effects, hydrogen bonding and substitution on the reaction rate of CO$_2$ absorption, carbamate stability and protonation/deprotonation of the amine.

As a result of this thesis we developed a complete reaction scheme in homogenous solution for the absorption of CO$_2$(aq) with H$_2$O/OH and amine. The reaction scheme is complicated and involves a number of kinetically observable reactions, defined by rate and equilibrium constants and protonation equilibria that are all coupled together. A detailed explanation of the scheme is given in all of the papers and also in the Introduction to this thesis.

The rate and equilibrium constants for a number of amines was investigated using stopped-flow spectrophotometry as this technique is capable of monitoring fast reactions occurring at the milliseconds time scale, while $^1$H NMR spectroscopy was used to monitor slower reactions. Monoethanolamine (MEA) and ammonia (NH$_3$) were investigated from 15 °C to 45 °C, analysis of the rate and equilibrium constants in terms of the Arrhenius, Eyring, and van’t Hoff relationships gave the relevant thermodynamic parameters. For sterically-hindered amines, substituted cyclic amines and piperazine a Brønsted correlation relating the protonation constant of the amines to the carbamic acid formation rate and equilibrium constants at 25 °C were established. The resulting values are reported in this thesis (Papers 3, 4, 5, 7, 8 and 9).

A separate temperature dependence study of the equilibrium constant for the formation of carbamate and the protonation/deprotonation of the carbamate was undertaken using $^1$H NMR spectroscopy. The outcome of the study was the determination of the equilibrium constants and thermodynamic parameters such as enthalpy, entropy and Gibbs free energy of reaction. A $\Delta H_m^o$-$\Delta S_m^o$ plot generates a linear correlation for carbamate formation and this relationship helps provide a guide to the selection of an amine(s) solvent for CO$_2$ capture, in terms of enthalpy.
A linear $\Delta H_m^o-\Delta S_m^o$ plot also occurs for carbamate protonation. All the relevant values are detailed in **Papers 1 and 6.**

The basicity of the amine is a very important characteristic in the absorption/desorption process; hence potentiometric titrations were used in the determination of the protonation constants of amines from 15 °C to 45 °C. The resulting protonation constants, enthalpies, entropies and Gibbs free energies are given in **Paper 2.** Also trends in $\Delta H_m^o$ are correlated with systematic changes in composition and structure of the selected series of amines/alkanolamines, while $\Delta H_m^o-\Delta S_m^o$ plots generated linear correlations for the mono-, di-, and trialkanolamines, the $–\text{CH}_2\text{OH}$ and $–\text{CH}_2\text{CH}_2\text{OH}$ substituted piperidines, and the alkylamines. These relationships provide a guide to the selection of an amine(s) solvent for CO$_2$ capture. Wherever possible, a comparison with the literature values for the kinetic, carbamate stability and the amine protonation are given in the papers.
Introduction
1.1 **Greenhouse effect**

The global community is currently facing a significant challenge in the form of climate change. The average global surface temperature has increased by approximately 0.74 °C over the past century; hence climate change is of growing concern. An average increase in the Earth's temperatures, resulting in changes in the climate, is known as global warming. This is caused by the greenhouse effect which has a natural basis but can be affected as a result of human activity, leading to the so-called enhanced greenhouse effect.

The natural greenhouse effect is a process by which absorption and emission of infrared radiation by greenhouse gases (GHG’s) like carbon dioxide (CO\(_2\)), methane (CH\(_4\)), nitrous oxide (N\(_2\)O), water vapour and chlorofluorocarbons (CFC’s) in the atmosphere warms a planet’s lower atmosphere and surface. This produces a relatively warm and hospitable environment near the Earth’s surface where humans and other life-forms have been able to develop and prosper. It is one of a large number of physical, chemical and biological processes that combine and interact to determine the Earth’s climate.

On the other hand, the enhanced greenhouse effect is caused by human activities, and in a little over 250 years from 1750 (the start of the Industrial Revolution) had led to an increase in the average concentrations of the (GHG’s) carbon dioxide (CO\(_2\)), methane (CH\(_4\)) and nitrous oxide (N\(_2\)O) by 36%, 148% and 18%, respectively, leading to an increase in the world’s average temperature. Between 2009 and 2010 the levels of greenhouse gases rose to record levels according to the World Meteorological Organisation. Humans are causing climate change by adding huge amounts of greenhouse polluting gases to our atmosphere.

The biggest source of greenhouse pollution is burning of fossil fuels (like coal and oil) for energy. Other sources include livestock wastes, agricultural crops, different industrial processes and combustion of biomass. As is apparent from Figure 1.1, of the gases released, CO\(_2\) accounts for the greatest contribution especially from the combustion of fossil-fuels, particularly power generation and accounts for around 56.6% of the observed global warming Figure 1.1.
Worldwide, the electricity sector relies heavily on coal. Despite concerns about climate change, reliance on coal because of its great abundance and low cost has been increasing worldwide since there has not been a viable alternative developed to fill the role that coal plays in the world’s energy systems. As a consequence, fossil fuels will continue to be the dominant power source for at least a couple of decades. Countries such as Australia, China, India, Poland and South Africa produce between 69% and 94% of their electricity through the combustion of coal. Coal-fired power plants, as stationary point sources, provide a great opportunity to effectively reduce CO$_2$ emissions.

That CO$_2$ is a valid target can be gleaned from the existing climate data, which show that temperature anomalies parallel a continuous increase of CO$_2$ concentration from 280 ppm (parts per million) in the 1850’s to 392 ppm by volume as of 2012. This is also evident from the Mauna Loa Observatory observations in Figure 1.2. If atmospheric CO$_2$ concentrations are to be prevented from increasing indefinitely at a fast rate, anthropogenic CO$_2$ emissions to the atmosphere must be limited by understanding from where the man-made CO$_2$ emissions originate in order to target a specific area.
1.2 Effects of global warming

The relationship between the enhanced greenhouse effect and global climate change is far from simple. It not only affects the atmosphere, but also the oceans, soil and biosphere.\textsuperscript{10-12} Scenarios studied by the Intergovernmental Panel on Climate Change (IPCC) predict that global warming will continue and get worse much faster than was originally predicated. The expected long range effects of recent climate change may have already been observed. Rising sea levels, glacier retreat, predicted Arctic ice cap shrinkage, and altered patterns of agriculture are cited as direct consequences of human activities. Predictions for secondary and regional effects include extreme weather events, an expansion of tropical diseases, changes in the timing of seasonal patterns in ecosystems, and drastic economic impact. Increasing global temperature will change the amount and pattern of precipitation, probably including expansion of subtropical deserts.\textsuperscript{6,13}

1.3 Climate change actions

International concern on climate change led to the UNFCCC (United Nations Framework Convention on Climate Change). The ultimate objective of this Convention was the “stabilization of greenhouse gas concentrations in the atmosphere at a level that
prevents dangerous anthropogenic interference with the climate system”. Some of the ways suggested by the UNFCCC to reduce the CO₂ emissions are:

- Reducing energy consumption, by increasing the efficiency of energy conversion and/or utilization (including enhancing less energy-intensive economic activities).
- Switching to less carbon intensive fuels (natural gas in place of coal).
- Sequestering CO₂ by enhancing biological absorption capacity in forests and soils.
- Carbon dioxide capture and storage (CCS), this is the only pathway that can allow the world to continue to enjoy the benefits of using coal while drastically reducing the emissions associated with coal combustion. This will provide the option of burning fossil fuels, capturing the CO₂, transporting and then storing it in a suitable place for a long period of time instead of releasing it immediately into the atmosphere. This process of carbon capture and storage has the potential to reduce future world emissions from energy by 20%. Coal is on a path to supply 28% of global energy by 2030, as part of a 57% increase in CO₂ emissions. CCS is a medium-term, low cost option that needs to be prepared immediately, as it is believed that even a 10-year delay in tackling climate change will have serious economic consequences.
- Switching to renewable energy sources including wind, solar power, etc. Biomass has also been actively pursued and the installed capacity is increasing rapidly. However, due to the constraints of current state-of-the-art technologies, alternative renewable energy sources cannot meet the requirements of our ever increasing demand for power. Nuclear power is the only option that has a comparable intensity of energy output relative to fossil fuels, but its extensive use is obstructed by its great hazard potential and by public concern.

1.4 Carbon capture and storage (CCS)

CCS is a direct emissions mitigation option, usually considered as an interim system to enable a 50 year transition away from fossil fuels. CCS is defined as a system of technologies that integrates CO₂ capture, transportation and geological storage as represented by Figure 1.3.
### 1.4.1 Capture

In traditional fossil-fuelled power plants the combustion of fuel is carried out using air, and the nitrogen (N\textsubscript{2}) in the air, as well as unused oxygen ends up in the flue gas. The central process prior to sequestration is the removal of CO\textsubscript{2} from the flue gas stream which consists typically of some 80% nitrogen, 15% CO\textsubscript{2} and the rest being water, unreacted oxygen and other gases such as NO\textsubscript{x} and SO\textsubscript{x}. The separation of CO\textsubscript{2} is important, as it avoids over compression due to the presence of large amounts of N\textsubscript{2} and lowers sequestration cost.\textsuperscript{19} Although CCS is well developed and has been used commercially in small scale industrial processes for the removal of CO\textsubscript{2} from exhaust gas for many years,\textsuperscript{20} adapting this technology to a power plants needs significant attention due to the scale of the task. Nevertheless various technologies within the CCS chain exist, with different degrees of maturity, and are competing to be the low-cost solution. There are three major technologies for CO\textsubscript{2} capture: pre-combustion, oxy-combustion and post-combustion capture. There is another well-established capture technology used for industrial process streams such as in the purification of natural gas, production of synthesis gas and manufacture of ammonia.\textsuperscript{14} After CO\textsubscript{2} is separated from flue gas, it has to be compressed to high pressure (100 to 150 bars) to facilitate transport to a storage site.

### 1.4.2 Transport

Following the successful capture of a concentrated CO\textsubscript{2} stream, the gas must be stored or utilized with minimal loss to the atmosphere. CO\textsubscript{2} has been transported in pipes since the 1970’s from enhanced oil recovery (EOR) in the U.S.A and Canada, where more than 3000 km of operational CO\textsubscript{2} pipes exists, transporting 30 Mt of CO\textsubscript{2} per year.\textsuperscript{1,6} Minimizing the water content in the CO\textsubscript{2} stream greatly reduces the corrosion rate of pipelines as well as the cost of pipeline materials.\textsuperscript{21} CO\textsubscript{2} can be gathered from multiple power plants, transported through a shared system to the coast, compressed and transported to offshore nodes. From those, CO\textsubscript{2} can be redistributed to individual storage sites.

### 1.4.3 Storage

The high density CO\textsubscript{2} fluid will be injected into geological formations deeper than 800 m to achieve permanent sequestration.\textsuperscript{22} CO\textsubscript{2} will be stored in sites like saline
aquifers, in oil and gas fields, by ocean, with industrial fixation into inorganic carbonates also available.\textsuperscript{23} Due to large volumes of CO$_2$ emissions from power generation extremely large volumes of geological storage are needed in the right places. Good choices of storage sites will retain CO$_2$ without appreciable seepage for tens of thousands of years. Monitoring will be required for decades into the future, combined with techniques to remediate deficient storage.\textsuperscript{24,25} The cost of CO$_2$ storage is highly site-specific and generally small compared to current CO$_2$ capture costs, which comprises 70\% or more of the total cost of CCS.\textsuperscript{26}

Figure 1.3: Schematic diagram of possible CCS systems. The figure shows the sources for which CCS might be relevant, as well as CO$_2$ transport and storage options.\textsuperscript{6}

1.5 CCS technology

The main principle of carbon capture is to obtain relatively pure CO$_2$ as mentioned above, Section 1.4.1.\textsuperscript{27} There are three major technologies under investigation for CO$_2$ capture: pre-combustion, oxy-combustion and post-combustion, each technology can be separated into different categories based on the complexity, degree of maturity and cost, which will be discussed in this section.
1.5.1 Pre-combustion capture

Currently this is a promising approach that involves integrated gas combined cycle (IGCC) supplemented with shift conversion. In this process, coal (or other non-gaseous fossil fuels) is first gasified to produce syngas, which consists of carbon monoxide (CO) and hydrogen (H\textsubscript{2}). The syngas is then contacted with steam and chemically shifted to CO\textsubscript{2} and H\textsubscript{2}, equation (1). The H\textsubscript{2} is then separated from the CO\textsubscript{2} and combusted in a gas turbine. Heat is recovered from the hot exhaust gas and used to produce steam for the turbine which then generates additional power.\textsuperscript{27}

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2
\]  

(1)

The advantages of pre-combustion capture are: 1) higher energy efficiency is gained from burning of gas at higher temperatures in the combined cycle, 2) there is simultaneous generation of electricity and H\textsubscript{2}, and: 3) CO\textsubscript{2} is inherently generated as a separate stream with low flow rate and high concentration. However, this technique is still in the pilot plant stage and can be integrated only into new power plants. The decreased short term flexibility and the construction costs are relatively high and high NO\textsubscript{x} emissions will require expensive scrubbers.\textsuperscript{19}

1.5.2 Oxy-fuel combustion capture

In traditional fossil-fuelled power plants, combustion of the fuel is carried out using air; however, pure oxygen (O\textsubscript{2}) can also be used, together with recycled flue gas, as an alternative to air for fuel combustion. This process is called oxy-fuel combustion capture. In most cases a cryogenic air separation unit would be used to supply pure oxygen to the boiler. Following combustion, the water is condensed and after phase separation a CO\textsubscript{2} rich gas-stream is obtained. In this process the flue gas only contains steam and CO\textsubscript{2}, which can easily be separated by cooling. Up to 100 percent of the CO\textsubscript{2} can be captured.\textsuperscript{27}

However, the drawbacks of this technology are the air separation unit, which is the most expensive component, this technology has not been developed previously for use in large-scale power plants and it is still in the pilot plant stage. To dramatically reduce the cost of oxy-combustion, more efficient technologies for pure oxygen
production need to be developed, while materials need to be improved for high-temperature operation and to improve energy efficiency.\textsuperscript{28}

1.5.3 Post-combustion capture (PCC)

Post-combustion capture is considered to be one of the most mature technologies for capture of CO\textsubscript{2}.\textsuperscript{29} There is a strong experience with and a good reputation for this technology, since it has been used for natural gas sweetening and within many other industrial applications (\textit{e.g.} in ammonia production and natural gas purification).\textsuperscript{30} Many small facilities are in operation today using amine-based solvents to capture significant flows of CO\textsubscript{2}. However, this technology has yet to be fully demonstrated at the scale of a commercial power plant. In this technique, the flue gas is passed to the absorber where it undergoes reversible interaction with amine to form CO\textsubscript{2}-amine species, and the CO\textsubscript{2}-free gas is released to the atmosphere. The CO\textsubscript{2}-rich solvent then leaves the absorber and is passed to the stripper where the CO\textsubscript{2}-amine species is decomposed, regenerating the amine (it is a cyclic process), while the pure CO\textsubscript{2} is dehydrated and sent for sequestration.\textsuperscript{27}

The major advantages of this technology are: 1) it can be readily retrofitted to existing power plants,\textsuperscript{28} or can be disconnected to provide maximum power output at times of peak electricity consumption, 2) it is already in use for small scale processes and, 3) components in the non-integrated equipment can be replaced, developed and upgraded without fundamental impact on the power plant. However, some of the challenges facing PCC are: 1) the size of the absorber/stripper column, 2) degradation of the amine-based solvent, 3) large volumes of solvent are needed, 4) toxic by-products, 5) the energy requirements of the process involved in decomposing the CO\textsubscript{2}-amine species, and, 6) cost.

1.5.4 Overview of the three technologies

In all the three different technologies the main goal is achieving relatively pure CO\textsubscript{2} for sequestration. All of the approaches require separation of gases. According to a chemist’s point-of-view, separating CO\textsubscript{2} from N\textsubscript{2} is much easier and hence PCC is the most important technology. In Table 1.1 a comparison of the three technologies is made.
Table 1.1: Comparison of the three separation technologies for carbon capture and storage (CCS). \(^{27}\)

<table>
<thead>
<tr>
<th>Post-Combustion Capture</th>
<th>Pre-Combustion Capture</th>
<th>Oxy-fuel Capture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Separation of CO(_2) from N(_2)</td>
<td>1) Separation of CO(_2) from H(_2)</td>
<td>1) Separation of N(_2) from O(_2)</td>
</tr>
<tr>
<td>2) Can be retrofitted to existing power plant</td>
<td>2) Cannot be retrofitted, so it is restricted to new plants</td>
<td>2) Cannot be retrofitted, so it is restricted to new plants</td>
</tr>
<tr>
<td>3) Existing technology</td>
<td>3) New technology</td>
<td>3) New technology</td>
</tr>
<tr>
<td>4) Currently in limited use</td>
<td>4) At developing stage</td>
<td>4) At developing stage</td>
</tr>
</tbody>
</table>

In conclusion: PCC is most liable to solve the immediate problems with CO\(_2\) capture. It is the focus of research in this thesis.

1.6 PCC in detail

PCC has a major advantage over other technologies, as discussed earlier.\(^{31}\) However this technique requires modification for application to power plants; in particular, substantial improvements in the efficiency of the process are necessary before large scale use. Though this technology is mature, it still has considerable shortfalls, such as in the understanding of the size of the absorber/stripper column (as this is associated with the stoichiometry/rate at which CO\(_2\) reacts with the amine), loading capacity and the energy requirement for the regeneration of solvent in the stripper, other issues which lack knowledge are mass transfer, CO\(_2\) partial pressures, amine degradation, corrosion, and the overall cost of the process.

Some of the commercial amine processes available, details of which are protected by patent and or secrecy, are as follows:

- MHI in Japan have developed a process named KM-CDR based on a solvent termed KS-1 (probably involving a hindered amine) tests are currently being conducted at the pilot plant scale.\(^{32}\)
- The HTC Purenergy process offers a mixed amine solvent system. It is attempting to lower costs by offering modular units that can be pre-fabricated.
• The Just Catch process, initiated by Aker Clean Carbon AS and is aimed at developing and verifying an amine-based technology in a cost efficient manner.\textsuperscript{33}

• The Cansolv system is using a solvent named Absorbent DC 101\textsuperscript{TM}. The solvent is based on tertiary amines, and probably includes a promoter to yield sufficient absorption rates to be effective for low pressure flue gas streams.\textsuperscript{34}

The chemical absorption process of CO\textsubscript{2} from flue gas is shown schematically in Figure 1.4. In PCC, CO\textsubscript{2} is directly captured from the flue gas at the end of a power plant cycle. This process is based on the reversible character of the temperature-dependent reaction of CO\textsubscript{2}, with aqueous amine solutions. The separation of CO\textsubscript{2} from flue gas is important to allow compression, transportation and storage because most of the existing power plants use air for combustion, so the CO\textsubscript{2} concentration in the flue gas is generally less than 15%, with the rest mostly being N\textsubscript{2} (80%).

![Figure 1.4: Schematic representation of an absorber-stripper column system in PCC.](image)

The flue gas from the power plant is first cooled before it is brought into contact with the solvent (amine) in the absorber. It is then pumped through an absorption column where CO\textsubscript{2} reacts with the amine-based absorbent (a \~ 30\% w/w amine-water solution) and undergoes a reversible reaction to form bicarbonate, carbonates and carbamate/carbamic acid species at temperatures typically between 40 °C and 60 °C. The gas stream has most of the CO\textsubscript{2} absorbed by the amine (producing a CO\textsubscript{2}-rich
solution) and the CO₂-free gas (mostly N₂) is released to the atmosphere. The CO₂-rich solvent leaves the absorber and is passed through a heat exchanger, where it is pre-heated before entering the stripper column which is at a high temperature (100 °C to 140°C). This heat is generated in a reboiler that is electrically heated or more effectively uses steam extracted from the power cycle. The amine is regenerated and the CO₂ stream (containing water vapour) exiting the stripper is dehydrated and CO₂ is compressed to low volumes before being sent for sequestration. The solution remaining after the stripping process is cooled in the heat exchanger before being returned to the absorber, and the capture cycle starts again.

Though this is a mature technology developed to remove acid gases from natural gas streams, the process was modified to incorporate inhibitors that reduce solvent degradation and equipment corrosion when applied to CO₂ capture from flue gas. Due to this, the solvent concentration was kept relatively low, resulting in large equipment sizes and solvent regeneration costs. The challenges associated with PCC arise when a capture and compression system is added. The overall thermal efficiency of the plant, that is the fraction of the energy released by combustion of the fuel that is transformed into electricity drops from 38.5% to 29.3% being a relative decrease of 24%. This is caused by the additional energy load from the CO₂ capture system which can be broken down into three components: 35-37

- Extraction of steam from the plant’s electricity-generating turbine to the stripper reboiler accounts for ~60%. The steam provides energy to heat the solvent, break the chemical bonds between the CO₂ and the amine solution at the operating temperature of the stripper, and evaporate water to produce a stripping gas that sweeps away the released CO₂.
- Electricity to drive the CO₂ compressors, which accounts for about ~35%.
- Electricity to drive the blowers to push the flue gas through the absorber, which accounts for ~5%.

The drop in thermal efficiency with capture has multiple effects on plant costs. First, 30% more coal must be burned to produce the same amount of electricity. 37 More importantly, for a new build plant with capture, the capital cost of the plant in $/kW increases by 61%. This is because capital investment increases by 22% (to pay for the
amine absorption process, compressors, etc.) while electrical output decreases by 24% thus, so that the investment cost expressed in $/kW increases substantially. In other words, energy drain translates into the consumption of more coal per kWh and an increase in plant capital beyond the purchase price of additional equipment. Because of the magnitude of this effect, a key goal of research is to reduce the energy cost which is related to the enthalpy of the amine basicity as discussed by McCann et al.\textsuperscript{38}

PCC has two approaches that are equally important and go hand in hand, they are: 1) a chemical engineering approach where they deal with the size of the absorber/stripper, vacuum pumps, exhausts, the overall design, operating conditions, energy consumptions, etc., and: 2) chemists approach which can provide knowledge of the chemical reactions of the amine with CO\textsubscript{2} in aqueous solution, the corresponding rate and equilibrium constants for the reactions, and the energies (activation parameters, enthalpies, and entropies) that are crucial for the complete modelling of the absorption and stripping processes, etc.

As a chemist, this thesis is focussed on the three important chemical aspects of PCC process which are interlinked: 1) the kinetics or reaction rate of absorption, 2) the equilibrium or solution composition (stoichiometry), and: 3) the thermodynamics or energies, for the regeneration of the amine, which is strongly dependent, but not entirely related to the protonation constant of the amine, represented in Figure 1.5.

![Figure 1.5: The three important aspects of PCC in a chemist point of view.](image-url)
1.7 Current understanding of PCC

All PCC technologies are based on the simple concept of selective absorption of CO$_2$ by the base solution at relatively low temperatures, and subsequent release of pure CO$_2$ at relatively high temperatures. Any chemist would insist that the simplest technology for the separation of the above gases will be based on the unique property of CO$_2$ to react with water to form different species. Its acidic property makes it dramatically different and this could be exploited in a relatively simple way. Post combustion capture, PCC, does take advantage of the acidic properties of CO$_2$.

The current understanding of the physicochemical operation to remove CO$_2$ from gas streams is by chemical absorption using aqueous amines, which is by far the most mature technology.$^{39-44}$ Amines are organic functional group molecules that contain a basic nitrogen atom with a lone pair, they react with CO$_2$ through the formation of a chemical bond the resulting product is called carbamate (discussed in section 1.7.2.2). Chemical absorption technology is well established in other industrial applications however, it presents several concerns when employing to PCC.$^{35}$ The concerns include: 1) intensive energy use is required to break the chemical bond between the absorbent and the absorbed CO$_2$ in the regeneration step ($\Delta H = -80$ to $-101$ kJ/mol depending on the species formed), which represents a high operational expense due to the energy cost related to the desorption step, 2) the amine can rapidly corrode alloy steel pipes, pumps, etc., therefore the concentration of the amine absorbent in the solution is limited in practice and consequently the CO$_2$ absorption capacity is reduced, 3) amines are prone to degradation either thermally or through chemical reactions (oxidatively), which causes the loss of active absorbents, produces extra waste streams and therefore leads to an additional operational cost, 4) owing to their volatility, amines to some extent are lost into the gas stream-replenishment, thereby adding to the cost of the process and severe environmental impacts.$^{45}$ Furthermore, attention to the nature of the solvent, the solvent stability, specific solvent cost and evaporative loses are important characteristics that need to be considered.$^{46,47,48}$

Though amines have considerable drawbacks, as discussed above, aqueous alkanolamine-based solvents have received the greatest attention scientifically and commercially for the removal of CO$_2$ because they react rapidly, selectively and
reversibly with CO$_2$, as well as being relatively inexpensive.$^{39-44}$ Another reason is that alkanolamines have an OH group, which reduces the solvent volatility through its hydrogen bonding with the water solvent.$^{14,49}$ Thus these types of compounds are less easily lost under stripper conditions hence amine systems have been the workhorse of the gas treating industry for many years, and will be pushed harder than ever for optimum performance and reliability in the future.$^{45}$ Therefore the nature, quality and quantity of the experimental and published data available on amine and amine systems are of great importance.

The available literature on carbon capture and storage is significant. In 2011, sci finder scholar gave approximately 950 publications on PCC processes when key words like post combustion capture, carbon capture using amines, solvent absorption technologies were used,$^{50}$ and this continues to grow. However, most studies have an engineering or technological focus and details of the chemistry remains less well understood.

In the following section I will highlight some of the literature available (as it is too difficult to cover all of it) and the experimental work that has been published over the years in regards to the three important aspects of PCC to chemists: 1) the reaction rate, 2) loading capacity/cyclic capacity, and 3) energy requirement for the regeneration of the amine.

The three aspects of PCC are important because in the absorber the ideal process would have a fast reaction rate between the amine and CO$_2$ and a high CO$_2$ loading capacity of the amine: CO$_2$ interactions, leading to a smaller absorber column. In the stripper column the energy required for the regeneration of the amine is strongly dependent on the enthalpy ($\Delta H$) of protonation of the amine. An amine having a large exothermic $\Delta H$ is regarded important, as it results in a greater difference in p$K_a$ between the absorber and stripper and hence to an increased energy efficiency for the process and hence reduced energy costs.
1.7.1 Literature review - Reaction rate and carbamate formation

There are two ways of looking at the available literature on PCC: Firstly, a large fraction of the literature focuses on empirical functions which are performed by chemical engineers or so called technology focus, and secondly, the process may be approached from a chemistry aspect which examines molecular mechanistic reactions which is discussed in Section 1.7.1.2. From the engineering sides of things, there are two mechanisms that have gained attention over the years, namely a) zwitterion formation, and: b) a ter-molecular reaction (Section 1.7.1.1).

1.7.1.1 Physical approach

a) Zwitterion formation

Caplow introduced a mechanism for the reaction between CO$_2$ and primary or secondary amines leading to the formation of a zwitterion followed by the removal of a proton by a base B (Equations (2) and (3), Figure 1.6). $R_1$ and $R_2$ represent substituents attached to the amine group; B represents a base molecule which may be hydroxyl ion, water or amine functionality.

\[
\begin{align*}
\text{CO}_2 + R_1R_2\text{NH} & \rightarrow R_1R_2\text{NH}^+\text{COO}^- \\
R_1R_2\text{NH}^+\text{COO}^- + B & \rightarrow R_1R_2\text{NCOO}^- + BH^+
\end{align*}
\] (2)

\[
\begin{align*}
\text{Step 1} & \\
R_1R_2\text{N} + \text{CO}_2 & \rightarrow R_1R_2\text{N}^+\text{CO}_2^- \\
\text{Step 2} & \\
R_1R_2\text{N}^+\text{CO}_2^- & \rightarrow R_1R_2\text{NCO}_2^-
\end{align*}
\]

Figure 1.6: Zwitterion formation mechanism

It is a two-step mechanism in which the first step is where CO$_2$ forms a bond to the hydrated amine group (with a hydrogen on the amine weakly bonded to the oxygen
of water) forming a zwitterion, and in step two the deprotonation of the amine takes place in the presence of base molecule. The intermediate species formed is the zwitterion. However, the formation of the zwitterion is unlikely due to the relative basicity of the amide nitrogen and the carboxylate group. As the amide-nitrogen group is weakly basic compared to the CO$_2^-$ group, it would not be protonated. As the protonation is instantaneous on the timescale of interest, the two slow kinetic steps of the mechanism would not be observed as two steps.

Danckwerts reintroduced this mechanism into the chemical engineering literature, and Blauwhoff, Mahajani and Joshi showed that this mechanism reconciled much of the data in the literature. Although Danckwerts and other investigators consider the zwitterion species to be attacked by a base which extracts a proton, they ignored the suggestion that the amine group may be hydrated before forming the zwitterion. More recent studies by da Silva and Svendsen, Ohno et al. based on quantum mechanical calculations suggested that any zwitterion species is likely to be very unstable. Hence there is considerable debate over its true veracity.

b) A ter-molecular mechanism

The second mechanism was proposed by Crooks and Donnellan, being a single step, ter-molecular reaction mechanism, in which both the bond formation between the amine nitrogen and CO$_2$ occurs simultaneously with a proton transfer to a nearby base molecule, without any distinct intermediate species, as given in equation (4) and Figure 1.7 where B is a base.

$$B + R_1R_2NH + CO_2 \rightarrow R_1R_2NCOO^- + BH^+$$  \hspace{1cm} (4)

Figure 1.7: A ter-molecular mechanism
To the knowledge of many authors there are no known true ter-molecular reactions and the mechanism has not been able to explain the results of subsequent researchers.\cite{61} Moreover, although third order reactions can be used to empirically describe a process, they are mechanistically not practicable.\cite{61}

### 1.7.1.2 Chemical approach – direct reactions

From a chemist’s perspective, a realistic mechanism is based on the direct reaction of the amine with dissolved CO$_2$, followed by deprotonation of the carbamic acid in protonation/deprotonation equilibrium.\cite{38,62-64} As a result of the studies detailed in this thesis and that of McCann et al.,\cite{62,63} a complete chemical reaction mechanism for the aqueous absorption of CO$_2$ with H$_2$O and amines in the absorber/stripper of the PCC plant has been established. The reaction scheme is complicated, and it involves a number of kinetically observable reactions which are defined by rate and equilibrium constants and protonation equilibria that are all coupled together, as shown in Figure 1.8.

![Figure 1.8: Complete reaction model for CO$_2$, H$_2$O and amine interactions.\cite{62}](image)

\textbf{Figure 1.8: Complete reaction model for CO$_2$, H$_2$O and amine interactions.}\cite{62}
There are two important ways by which CO₂ reacts in the absorber. They are: a) the interaction of CO₂ with water/hydroxide (H₂O/OH⁻) and: b) the interaction of CO₂ with an amine, noting that the amine is also in a protonation/deprotonation equilibrium.

a) Interaction of CO₂ with H₂O/OH⁻

The absorption of CO₂ in aqueous amine solutions proceeds via a complex series of simultaneous and reversible reaction pathways, as described in Figure 1.8. The dissolution of gaseous CO₂ must occur prior to further reaction of CO₂ with other species in solution, i.e. \( \text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq) \). There are two fundamental, reversible reaction(s), as given in Figure 1.8: the reversible interaction of CO₂ with water to form carbonic acid (H₂CO₃), and with OH⁻ to form bicarbonate (HCO₃⁻), equations (5) and (6) respectively. Carbonic acid is involved in two protonation equilibria, which involve bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) (equations (7) and (8)). A third protonation that is of the hydroxide ion (OH⁻) is also required to complete the interaction in solution, equation (9).

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \quad (5)
\]

\[
\text{CO}_2(aq) + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \quad (6)
\]

\[
\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^- \quad (7)
\]

\[
\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \quad (8)
\]

\[
\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} \quad (9)
\]

In the equations \( k_1, k_{-1}, k_2 \) and \( k_2 \) are the rate constants of the forward and back-reaction and \( K_3, K_4 \) and \( K_5 \) represent the equilibrium constants. All the above equations are pH dependent. The reaction of CO₂ with OH⁻ is fast at high pH and, as the concentration of free OH⁻ falls and the pH decreases, the reaction begins to slow. The mechanisms and its rate and equilibrium constants have been extensively investigated in a variety of different contexts and the associated constants are now published and summarized in Table 1.2.
Table 1.2: Some published rate and equilibrium constants for the reactions of CO$_2$ in water and the ionic product of water at 25 °C. All kinetic and equilibrium values have been corrected to zero ionic strength.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetics</th>
<th>Equilibrium</th>
<th>References</th>
</tr>
</thead>
</table>
| CO$_2$(aq) + H$_2$O $\leftrightarrow$ $k_r$ $k_f$ H$_2$CO$_3$ | $k_1 = 3.0 \times 10^{-2}$ s$^{-1}$  
$k_1 = 25.64$ s$^{-1}$ | $K_1 = 1.17 \times 10^{-4}$  
log $K_1 = -2.93$ | 65 |
| CO$_2$(aq) + OH$^-$ $\leftrightarrow$ $k_r$ $k_f$ HCO$_3^-$ | $k_2 = 12.1 \times 10^{-1}$ M$^-$s$^{-1}$  
$k_2 = 2.7 \times 10^{-4}$ s$^{-1}$ | $K_2 = 4.48 \times 10^{-1}$ M$^{-1}$  
log $K_2 = 7.65$ | 66 |
| CO$_3^{2-}$ + H$^+$ $\leftrightarrow$ $K_3$ $\rightarrow$ HCO$_3^-$ | $K_3 = 2.14 \times 10^{-10}$ M$^{-1}$  
log $K_3 = 10.33$ | 67,68 |
| HCO$_3^-$ + H$^+$ $\leftrightarrow$ $K_4$ $\rightarrow$ H$_2$CO$_3$ | $K_4 = 3.33 \times 10^{7}$ M$^{-1}$  
log $K_4 = 3.52$ | 67 |
| OH$^-$ + H$^+$ $\leftrightarrow$ $K_5$ $\rightarrow$ H$_2$O | $K_5 = 1.00 \times 10^{14}$  
log $K_5 = 14.00$ | 68 |

b) Interaction of CO$_2$ with amine

Besides the reactions of CO$_2$ with H$_2$O, the reaction of CO$_2$(aq), H$_2$CO$_3$ and HCO$_3^-$ with amine are important as described in equations (10-12).

(i) Reversible reaction of dissolved carbon dioxide with amine to form carbamic acid

$$\text{RNH}_2 + \text{CO}_2(\text{aq}) \overset{k_f}{\rightleftharpoons} \underset{k_r}{\text{RNHCO}_2\text{H}}$$  \hspace{1cm} (10)

(ii) Reversible reaction of bicarbonate with amine to form carbamate

$$\text{RNH}_2 + \text{HCO}_3^- \overset{k_f}{\rightleftharpoons} \underset{k_r}{\text{RNHCO}_2^- ( + \text{H}_2\text{O})}$$  \hspace{1cm} (11)

(iii) Reversible reaction of carbonic acid with amine to form carbamic acid

$$\text{RNH}_2 + \text{H}_2\text{CO}_3 \overset{k_f}{\rightleftharpoons} \underset{k_r}{\text{RNHCO}_2\text{H}}$$  \hspace{1cm} (12)

In which $k_7$, $k_{7r}$, $k_9$ and $k_{9r}$ are the rate constants of the forward and back-reactions respectively. Other reactions associated with the amine-CO$_2$ system include equations (13 and 14).
Other possible reaction paths include the reaction of the amine with the carbonate ion and the reactions of protonated amine with all CO$_2$ species. However, the former reaction is very slow because a nucleophilic attack by the amine nitrogen on the doubly charged anion is probably negligible. Finally, the protonated amine is not expected to be reactive as it is not a nucleophile.

### 1.7.2 Acid-base reaction and amine-carbamate formation

If the above reactions for the amine-CO$_2$ system formed a complete set it would be straightforward to model the PCC process. Unfortunately, however, depending on the amine type, CO$_2$ can potentially react via two different pathways: a) in a simple Brønsted acid-base reaction, or b) through carbamate formation.

#### a) Acid-base reaction

In the acid-base reaction, the amine behaves as a base, with which the acidic CO$_2$ (aq) can react to form protonated amine and a bicarbonate ion (HCO$_3^-$), as given in overall equation (15). Aqueous solutions of tertiary amines and some sterically-hindered primary and secondary amines exhibit this reaction behaviour.

$$
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{(step 1)}
$$

$$
\text{R}_i\text{R}_i\text{R}_i\text{N} + \text{H}^+ \rightleftharpoons \text{R}_i\text{R}_i\text{R}_i\text{NH}^+ \\
\text{(step 2)}
$$

$$
\text{R}_i\text{R}_i\text{R}_i\text{N} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}_i\text{R}_i\text{R}_i\text{NH}^+ + \text{HCO}_3^- \\
\text{Overall reaction (15)}
$$

According to Donaldson and Nguyen, tertiary alkanolamines cannot react with CO$_2$ directly to form a carbamate, because these amines lack a free proton. They are weak nucleophiles and hence act as a base and promote the hydration of CO$_2$, thereby resulting in the formation of bicarbonate HCO$_3^-$ and protonated amine. The complete mechanism might be summarized with the formation of a hydrogen bond between free
amine and water and involves the lone-pair electrons of nitrogen enhancing the reaction between water and CO$_2$.$^{53,70,71}$

A significant advantage of this interaction is that the stoichiometry of amine:CO$_2$ is 1:1, which means a high CO$_2$ loading capacity in the absorber is achieved. When the CO$_2$-rich solution is sent from the absorber to the stripper in order to be regenerated (as part of the cyclic process) less external heat would be needed, thereby reducing the overall cost of the process.$^{38,72}$ However, the major drawback of the use of tertiary amines and some sterically hindered amines is that the rate at which they react with CO$_2$ to form bicarbonates is very slow, which will adversely affect the size of the absorber column.

**b) Formation of carbamate**

Some primary and secondary amines react rapidly with CO$_2$ to form carbamates, as given in overall equation (16).$^{73}$ In step (1), an amine reacts with CO$_2$, to give the carbamic acid which immediately deprotonates, thus carbamate is formed and a proton is released, while in step (2) the proton is picked up by a second amine molecule leading to formation of a protonated amine. These reactions result in an amine:CO$_2$ ratio of 2:1. The unfavourable CO$_2$ to amine ratio results in a lower efficiency and lower CO$_2$ loading capacity in the absorber column. In addition, carbamate formation is associated with a large enthalpy of reaction when compared to amines that do not form carbamte. This is due to the additional energy requirement of the carbamate formation reaction (typically ~30 kJ/mol). Reversing this reaction in the stripper consequently requires the addition of large amounts of energy/heat, as the CO$_2$-rich solution would have to be heated and cooled between the absorber and stripper making the entire process relatively energy intensive.$^{38}$

\[
\text{RNH}_2 + \text{CO}_2(aq) \rightleftharpoons \text{RNHCOO}^- + \text{H}^+ \quad \text{(step 1)}
\]

\[
\text{RNH}_2 + \text{H}^+ \rightleftharpoons \text{RNH}_3^+ \quad \text{(step 2)}
\]

\[
2\text{RNH}_2 + 2\text{CO}_2(aq) \rightleftharpoons \text{RNHCOO}^- + \text{RNH}_3^+ \quad \text{Overall equation (16)}
\]
However the major advantage of this pathway is its fast reaction rate leading to faster absorption of CO$_2$ by the amine, which in turn requires a smaller absorber column.

### 1.7.3 PCC challenges/shortfalls

Although chemical absorption by amines is a mature technology it still has considerable shortfalls associated with the choice of the amine solvents for the absorption of CO$_2$, in particular in regard to the reaction rate, CO$_2$ loading capacity and the energy required for the regeneration of the amine. If the above direct reactions formed a complete set, it would be easier and straightforward to model and understand the PCC process, unfortunately a trade-off between the amines has to be made to get an efficient capture process. Considerable research and development efforts are currently being undertaken to determine the ideal solvent for CO$_2$ capture. Physical properties of the solvent like mass transfer, viscosity, boiling point, density, degradation, *etc.* have also been extensively studied.

Furthermore, alternative process (stripper-) configurations and alternative means of capturing CO$_2$, such as membrane separations, cryogenic separations, chemical looping, and solid adsorption processes are being studied.$^{74-77}$ Most of these alternative separation technologies have potentially major drawbacks to overcome and hence are still in the research and development stage, but may be able to improve the overall efficiency of the process in the future. These developing technologies are not in the scope of this study and will not be discussed further.

Other approaches adopted to improve the process involve using catalysts in the process like, borate, arsenite, metal ions, acetate and zinc complexes have all attracted extensive interests.$^{78-90}$ In addition, the use of amino acids and ionic liquids have also gained interest over the years as an alternative to alkanolamines. Amino acids have better resistance to degradation than alkanolamines; reactivity with CO$_2$ is comparable to aqueous alkanolamines, they are less volatile and have a higher surface tension compared to aqueous solutions of alkanolamines.$^{91-93}$ Ionic liquids have low vapour pressures, are non-flammable, thermally and chemically stable, are non-volatile and they can be modified according to the requirements of their intended use.$^{94-101}$ However,

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desorption of CO\textsubscript{2} in ionic liquid media and regeneration of the sorbent requires significant thermal energy, and the viscosity of some ionic liquids is relatively high and increases with CO\textsubscript{2} loading, leading to an additional energy penalty in pumping the sorbent through the system.\textsuperscript{102,103}

1.7.4 Kinetics and equilibrium of the reactions between CO\textsubscript{2(aq)} species and amine

1.7.4.1 Literature review

The experimental techniques used in the literature for the investigation of CO\textsubscript{2} absorption in aqueous amine solutions is detailed in this section. First investigations were undertaken mid-last century, resulting in empirical rate and equilibrium constants of a series of carbamates of ammonia, as well as propyl and butyl amines.\textsuperscript{104-106} These were not based on a mechanistically complete model, as they did not include all protonation equilibria. Reliable equilibrium constants for the interaction of CO\textsubscript{2} with ammonia and the protonation constant of the carbamate were published much later.\textsuperscript{107} This early research was based on quenching the reaction by raising the pH, and by subsequent quantitative precipitation of the carbonates as BaCO\textsubscript{3}. BaCO\textsubscript{3} precipitation of radiolabeled \textsuperscript{14}CO\textsubscript{2} is a similar technique.\textsuperscript{51}

Most of the literature in the past focusses on the indirect techniques, for example the quantitative determination of CO\textsubscript{2} partial pressure in the gas phase above the reaction solution in wetted-wall experiments.\textsuperscript{64,91,108} Such two-phase experiments suffer from relatively slow response times, and information on carbamate formation is very indirect and thus prone to error. This is also supported by Barth et al.,\textsuperscript{109} where it was recognised that the use of an indirect method might cause an error in determining the kinetic rate constants for the reaction between CO\textsubscript{2} and aqueous alkanolamines. This is because, in these indirect techniques, CO\textsubscript{2} is transferred through a gas-liquid interface which could result in the depletion of the amine in the interface.\textsuperscript{110} Moreover, these result in an overall rate constant for the absorption of CO\textsubscript{2} by amine solution and focuses on the forward reaction of carbamate formation but not on the individual equilibria and rates of the reactions of different species. The insufficient investigation on the forward reaction between CO\textsubscript{2} and amines at molecular level impeded our understanding and improvement of CO\textsubscript{2} capture by alkanolamine prior to work in this group.
A few NMR studies have been published, as quantitative $^{13}$C NMR spectroscopy delivers direct information on the concentration of all carbon-containing species; however, $^{13}$C NMR suffers from slow relaxation processes, and thus the acquisition of quantitative information via peak integrals is necessarily extremely slow. As a consequence, measuring times with accurate integration are too slow for the rates observed. Publications of this type include studies on solubility of CO$_2$ and quantitative speciation.$^{111-113}$ $^1$H NMR has also been used for speciation purposes in amine-CO$_2$ interactions.$^{114}$ Two very recent publications report the equilibria for several amine/CO$_2$ interactions using combined $^1$H and $^{13}$C NMR data.$^{111,115}$ All these studies concentrate on the thermodynamic equilibria and do not cover the kinetics. For the kinetic study a series of stopped-flow investigations, using conductometry and pH determination via color changes due to a coupled indicator have also been published.$^{42,93,109,110}$ Both methods are fast.

Another promising technique is IR spectroscopy, useful for studying aqueous CO$_2$ interactions with amine solutions, amine carbamate and CO$_2$ adsorption on mesoporous aminopropylsilane-functionalized Silica and Titania.$^{116-122}$ Jones et al.,$^{117}$ used this technique in 1958 to study the absorption of CO$_2$ in aqueous solution by observing an intense absorption band attributed to the anti-symmetric stretching vibration of CO$_2$ dissolved in water. Together with the development of FT-IR spectroscopy, absorption bands of dissolved CO$_2$ at low concentration can be recorded at high signal-to-noise ratio making quantitative analysis feasible. Falk and Miller investigated the possibility of simultaneous infrared determination of CO$_2$, HCO$_3^-$ and CO$_3^{2-}$ by FT-IR, using transmission and attenuated total reflectance (ATR) techniques.$^{116}$ Based on their results it is possible for quantitative determination of CO$_2$ however HCO$_3^-$ and CO$_3^{2-}$ bands overlap severely. Therefore, while it is feasible to determine analytically, it is affected by several drawbacks such as inaccurate quantification, absorption of other molecules and interference of water vapour bands in the region of low solute concentration.

The use of FT-IR to monitor the reaction of CO$_2$ in amine solutions has also been reported by Jackson et al.$^{121}$ and Robinson et al.$^{118}$ In the first study, the absorption and desorption of CO$_2$ in MEA solution and promoter methyltriethanolamine
(MDEA) at 40 °C was conducted and in the second study reactions of CO₂ with piperidines and piperidine derivatives at the same temperature was studied by reporting the changes in the absorbance of certain peaks. The authors mainly focused on the peak assignment of the species in the spectra rather than quantitatively analysing the capture performance. Though this technique is relatively fast, no quantitative study on carbamate formation has been published.

Recently infrared spectroscopy was also used in combination with microcalorimetry to study the adsorption of CO₂ onto mesoporous aminopropylsilane-functionalised Silica and Titania as alternatives to amines for CO₂ capture. This technique was also employed by Donon et al., to investigate the interaction between CO₂ and amine-grafted SBA-15 (a type of ordered mesoporous silica). These studies basically focused on the interpretation of the changes in IR spectra coupled with the variations in the chemical structures of the absorbents, but the kinetics of the reaction of CO₂ with the absorbents was not investigated in detail.

In a publication by Puxty et al., 76 different amine moieties were screened to measure the CO₂ absorption by using isothermal gravimetric analysis (IGA). Screening tests are a common initial step in the determination of the potential of a solvent for use in PCC applications. The measured CO₂ absorption capacity can then be compared to the absorption capacity from model calculations to validate the screening results. Screening also allows for the quick investigation of the influence of structural differences, such as chain length or steric hindrance of the amine, on the absorption capacity of a solvent.

In the recent studies on the reactions of CO₂ and HCO₃⁻ with aqueous MEA solution by McCann et al., and Conway et al., a direct technique such as proton nuclear magnetic resonance spectroscopy (¹H NMR) and stopped-flow visible spectrophotometry were employed to investigate the possible reactions between CO₂ species and an amine. The corresponding rate constants were individually determined. NMR has been shown to be a reliable and highly applicable approach. In particular, Suda et al., reported the results of CO₂ dissolved in a series of amines using NMR spectroscopy. Stopped-flow methods have shown excellent results for the study of fast chemical reactions in homogenous medium.
The equilibrium constants for the formation of carbamate for some amines at different temperatures are available in the literature. For the benchmark amine MEA, a number of publications report data at different temperatures and ionic strengths. Aroua et al., \textsuperscript{131} reported the carbamate equilibrium constant for MEA from NaOH titrations of a carbamate solution over the temperature range 298 to 328 K. Other methods such as vapour-liquid equilibrium (VLE) and \textsuperscript{1}H NMR titrations, were also used for the determination of the carbamate stability at different temperatures by a number of different research groups.\textsuperscript{112,132-134} The VLE accuracy was only up to 30\%. Sartori and Savage also investigated the carbamate stability constants of MEA, AMP and DEA by \textsuperscript{13}C NMR.\textsuperscript{135}

Several additional amines like MDEA, piperazine, ammonia, diglycolamine, diisopropylamine, 2-[(2-aminoethyl) amino ethanol] and some synthetically prepared more complex amines have also been investigated, both through NMR speciation studies and/or vapour liquid equilibrium measurements. A more direct and accurate way was used by both McCann et al. and Oscarson et al. for the determination of the enthalpy of absorption of MEA, DEA and ammonia by involving iso-thermal titration calorimetry (ITC).\textsuperscript{136,137} The method gives more reliable and robust information on the pathway to estimation of enthalpy than that obtained using only temperature dependencies, where the calculated enthalpies can have high errors. The same kind of measurements can also be used to determine heat capacities.

\textbf{1.7.4.2 Current project}

It is evident from the literature available, that in order to improve the efficiency of CO\textsubscript{2} absorption technology, improvements of the understanding of all chemical reactions that occur in solution in the cyclic process would be an invaluable tool. As a result, we have developed a complete reaction scheme in homogenous solutions for the aqueous absorption of CO\textsubscript{2(aq)} with H\textsubscript{2}O/OH\textsuperscript{-} and amine, as described in Figure 1.9. Our scheme was slightly different to the one described by McCann et al.\textsuperscript{62}, in regards to the exclusion of the reaction between H\textsubscript{2}CO\textsubscript{3} and amine to form carbamic acid (equation 13). This is because H\textsubscript{2}CO\textsubscript{3} does not exist in any significant concentration for its
reaction with amine to form a carbamic acid and thus play no role in the absorption/desorption cycle.

Figure 1.9: Our complete reaction model for CO$_2$, H$_2$O and amine interactions.

In Figure 1.9, the red and green components demonstrate the aqueous chemistry of CO$_2$ and the protonation equilibrium of the amine, respectively, while the blue component represents the interaction of the CO$_2$(aq)/H$_2$O system with the amine. The horizontal axis represents the pH change, while the vertical axis involves reaction of a species with water. The forward pointing direction represents reaction of the CO$_2$-based species with amine.

In this thesis the kinetics of the reactions of CO$_2$(aq) with MEA, ammonia, cyclic, and sterically-hindered amines, as well as the diamine piperazine have been detailed using stopped-flow spectrophotometry, with coloured indicators employed to monitor the pH changes during the reactions. Sophisticated multivariate global analyses are then performed using ReactLab-Kinetics (www.iplusconsulting.com/products/) and in-house software written in Matlab to yield the required kinetic data. Measurements for MEA and ammonia were performed from 15 °C to 45 °C, resulting in a temperature dependence study of the rate and equilibrium constants. The analysis of the kinetics in terms of Arrhenius, Eyring and van’t Hoff relationships has revealed the Arrhenius activation parameters, the enthalpies and entropies of activation, and the enthalpy and entropy for the reaction. For piperazine, and the cyclic and sterically-hindered amines,
measurements were performed at 25 °C, and the resulting rate and equilibrium constants are reported.

Further, the direct reaction of HCO$_3^-$ with MEA, the diamine piperazine, cyclic monoamines and sterically-hindered amines to form carbamate was also investigated using $^1$H NMR spectroscopy at 25 °C. This reaction is usually not considered for PCC applications, as the direct reaction of CO$_2$ with an amine is strongly dependent on the rate of the decomposition reaction of this pathway.

Global analysis of a series of measurements was used to elucidate the kinetic rate constants for the reactions, $k_7$, $k_{-7}$, and $k_9$, as well as the equilibrium constant, $K_7 (= k_7/k_{-7})$, and the protonation constant of amine-carbamate, $K_8$. As a consequence of the principle of microscopic reversibility, the kinetic rate constant for the reverse reaction of amine-carbamate to bicarbonate and amine, $k_{-9}$, was calculated based on the other rate constants in the loop as $k_{-9} = (k_9K_8k_{-7}k_1)/(k_7k_{-1}K_4)$.

My Papers 3, 4, 5, 7, 8 and 9 give the relevant rate and equilibrium constants. Where possible, a comparison with the literature values is made. Good agreement with the literature was observed for some rate and equilibrium constants but some values were either slightly lower or higher than the corresponding literature values at some temperatures. This is not surprising considering the different experimental techniques and mechanisms used to determine the rate constants. In particular the differences may reflect the method of treatment of ionic strength in the various studies. The equilibrium constant $K_7$, for the direct reaction of amine and CO$_2$(aq), was calculated based on the forward and backward rate constants. For MEA and ammonia, the temperature dependence of the equilibrium constant showed a linear behaviour and a van’t Hoff analysis of the temperature dependence in each case resulted in the enthalpies and entropies of the reactions.

The formation of carbamate, the equilibrium constant for the direct reaction of amine and HCO$_3^-$ ($K_9$) (also called the stability constant) and protonation/deprotonation of the carboxylic acid/carbamate ($K_8$) was investigated using $^1$H NMR spectroscopy from 15 °C to 45 °C. Primary and secondary amines formed carbamates whereas some sterically-hindered, substituted cyclic secondary and tertiary amines did not form
carbamates, and for such molecules the base strength is the only equilibrium constant
governing the reactivity towards CO$_2$. van’t Hoff analyses of the temperature
dependences of the equilibrium constants $K_9$ and $K_8$ yield the associated enthalpies,
entropies and Gibbs free energies. All relevant data are given in Paper 1 and Paper 6

1.7.5 Protonation of amine

1.7.5.1 Literature review

According to the literature, the basicity of an amine is the most important
criterion in the PCC process. It defines the capacity of an aqueous amine solution to
chemically absorb CO$_2$, which can be expressed using its p$K_a$, also called the
protonation/dissociation constant.\cite{38,125,138-143} According to Blauwhoff\cite{53} and Versteeg,\cite{144,145}
the basic strength of the amine (p$K_a$) serves as the first indicator for the reaction
rate/reactation pathway, depending on the availability of unprotonated base, to accept a
proton, which leads to either a faster or slower kinetics or a higher or smaller loading
capacity. A Brønsted plot gives linear correlations between the reaction rate and the
base strength of the absorbent. The basicities of the amines are influenced by their
molecular structures, and any additional substituents, leading to a modified p$K_a$ value
due to the associated inductive, electrostatic and electron delocalization (mesomeric)
effects, together with contributions from hydrogen bonding, conformational differences
and steric effects.

The energy requirement for the cyclic cooling/heating process is strongly
dependent on the enthalpy of protonation of the amine, and thus on the protonation
constant. A large value of enthalpy ($\Delta H$) will lead to a shift to favour the dissociation
reaction that releases CO$_2$ upon heating. The temperature dependence of the protonation
constant provides a measure of the reaction enthalpy that accompanies the change of the
base strength of the absorbent with temperature, which is evident from the studies of
McCann et al.,\cite{38} who developed a model for the prediction of CO$_2$ capacity associated
the enthalpy changes in amine-based solvents during the absorption/desorption of CO$_2$.
The data for the prototypical amine MEA is shown in Figure 1.10.
As shown in this figure, assuming a typical flue gas composition with a CO$_2$ pressure of 12 kPa, a 30 wt % MEA solution for CO$_2$ removal, and absorption and desorption temperatures of 40 °C and 100 °C, respectively (which results in a cyclic capacity of 0.23), the enthalpy for CO$_2$ desorption at 40 °C was found to be about 83 kJ/mol. Of this, some 50 kJ/mol is associated with deprotonation of the MEA. In terms of enthalpy changes, this contribution is more important than the formation of gaseous CO$_2$ from CO$_2$(aq) and H$_2$ (~21 kJ/mol), or the decomposition of the carbamate formed from MEA (~12 kJ/mol).

Although the heat capacity of the solution was not included in the study, it is apparent that, of the chemical reactions that occur in solution, the contribution of amine protonation/deprotonation to the enthalpy change is highly significant. Furthermore, although not strictly favourable in all cases a more exothermic enthalpy is regarded as important because it results in an increase in the amount of CO$_2$ released per unit of temperature increase. Typically this results in a reduced overall energy requirement, as the additional CO$_2$ released more than compensates for the additional energy input required by the larger enthalpy. Finding solvents with better properties for CO$_2$ absorption is one approach to improve the technology/overall process, and so it is very
important to understand the chemical characteristics of potential amine solvents. Hence understanding the temperature dependence of the protonation constant of an amine and its associated enthalpy might further lead to a cost saving operation.

Some of the approaches used to study the dissociation constants of amines, alkanolamines and amino acids in the literature are by electromotive force measurements (EMF) using a combined glass pH electrode, flow calorimetry and potentiometric titrations. The values available in the literature were determined at temperatures ranging from 273 to 398 K and at varying ionic strengths. Some of the values had large deviations, because in some studies researchers did not take activity coefficients of the compounds into consideration when determining the dissociation constants from the experimental data, hence the activity coefficients were set to unity for all species.\(^{38,138,147-167}\) In the 13 references listed all activity coefficients were set to unity as already stated in the text.

1.7.5.2 My work

Based on the literature the basicity of the amine is a key factor for the reaction rate and absorption capacity of the solvent, which is given by the protonation constant. Also, the energy requirement for the cyclic cooling/heating process is strongly dependent on the enthalpy of the protonation of the amine. In **Paper 2**: investigations of the temperature dependence of the protonation constants using potentiometric titrations were performed, and subsequent van’t Hoff analyses yielded the associated enthalpies, entropies and Gibbs free energies. All ionic activity coefficients were calculated using Debye Hückel equation (given in chapter 2, equation (3)) and the dissociation/association constants are corrected to zero ionic strength. Trends in the $\Delta H$ vs $\Delta S$ plot have established guidelines for the selection of an amine best suited for PCC.

1.8 Amines in carbon capture

The work done by Bottoms on the use of aqueous amines for the removal of CO\(_2\) and H\(_2\)S from natural gas streams was granted a patent in 1930.\(^{49}\) Initially, it involved the use of triethanolamine (TEA), as this was the first alkanolamine commercially available and was thus used in these early gas-treating plants. Triethanolamine was later found to be less attractive than other alkanolamines mainly because of its low
absorption capacity (resulting from a higher equivalent weight), its lower reactivity and its relatively poor stability. Other alkanolamines were subsequently introduced into the market as possible acid-gas absorbents, and those that proved to be of principal commercial interest for gas purification were diethanolamine (DEA), monoethanolamine (MEA) and methylidiethanolamine (MDEA). 49

Today MEA is considered as a benchmark amine for the PCC process as it has a high reactivity, low cost, low molecular weight (giving a high absorption capacity on a weight basis), reasonable thermal stability, and low thermal degradation rate. However, it suffers from oxidative degradation, forms thermally stable salts in the presence of NOx and SOx bearing gases, is corrosive, forms a relatively stable carbamate, and has a high enthalpy of reaction, which translates into a large solvent regeneration energy requirement. 42 Hence, It is thus far from being an ideal solvent in CO2 separation from flue gas. 168

Though amines have considerable drawback as discussed earlier, they are still the first choice for the post combustion capture process. Hence extensive research has been ongoing in the understanding of the effect of molecular structure on the amine and associated steric effects, hydrogen bonding, multiple amine functionality (such as di-amine), the use of activators, and mixtures of amines with various additives (e.g. for corrosion inhibition or absorption rate promotion). 135 Such considerations are used in the development of potential new, improved solvents and solvent systems, so that commercially available solvents are continuously being improved with regard to their performance for CO2 absorption, 47 in order to improve the functional efficiency of CO2 absorption technology. 52,108,113,124,133,169-197

The amines investigated in this thesis can be classified as: primary, secondary and tertiary amines. Approximately 25 amines were studied with the aim of elucidating the possible effects of their chemical structures, electronic and steric effects, hydrogen bonding and the substitution on the cyclic ring on the reaction rate of CO2 absorption, carbamate stability and the protonation of the amine. The chemical names, abbreviations adopted here and structures are illustrated below under group 1, group 2 and group 3.
a) **Group 1: Primary/sterically hindered amines**

The amines belonging to this group are classified generally as primary or else sterically hindered amines, but can be divided into three series based on the substitution on the MEA, Figure 1.11.

**Series 1**: MEA > AP > AMP, the addition of a –CH$_3$ group at the $\alpha$-carbon gives AP and with further addition of a second –CH$_3$ increases the steric hindrance, resulting in AMP.

**Series 2**: MEA > BIS > TRIS, substitution on the MEA at the $\alpha$-carbon with one –CH$_2$OH group gives BIS, and a second substitution by another –CH$_2$OH gives TRIS, each step increasing the OH groups on the amine as well as steric hindrance.

**Series 3**: AMP > AMPD > TRIS, substitution of the first –CH$_3$ by a -CH$_2$OH gives AMPD and of the second –CH$_3$, by another -CH$_2$OH gives TRIS.

![Figure 1.11: Structures of primary/sterically hindered amines](image-url)
b) **Group 2: Secondary/cyclic-substituted amines**

In this group acyclic, cyclic and substituted cyclic alkanolamines/amines have been studied. Varying heteroatoms *i.e.* PIPD, PIPZ, MPIPZ, MORP and TMORP were investigated to check the effect of a functional group at the position *para* to the nitrogen in the ring. Substitution of –CH<sub>2</sub>OH and –CH<sub>2</sub>CH<sub>2</sub>OH at *ortho*, *meta* and *para* positions on piperidine was also investigated. DEA, an acyclic secondary amine and PYRR, a five-membered cyclic amine were also examined in this thesis. All are illustrated below, Figure 1.12.

**Figure 1.12: Structures of secondary amines**
c) Group 3: Tertiary amines

Tertiary amines have major disadvantages of having a slow reaction rate and they do not form carbamates, but the basicity of the amines plays an important role in reducing the cost associated with the regeneration of the amine and hence they have gained interest in PCC especially in blended amines. Consequently, several amines were investigated in this thesis, namely $N,N$-DMEA > $N,MDEA > TEA. These are illustrated in Figure 1.13.

![ Structures of tertiary amines ]

\[ \text{Figure 1.13: Structures of tertiary amines} \]

1.8.1 Effect of steric hindrance on CO$_2$ absorption

Sterically-hindered amines have a bulky group/substituent on the carbon atom adjacent to the amino group (the $\alpha$ carbon atom). It has been demonstrated that changes in the electronic characteristics of an amine due to varying the substituents on the $\alpha$ carbon leads to formation of unstable carbamates. The hydrolysis of the voluminous carbamates leads to a preferential bicarbonate formation process, equation (14) resulting in a high loading capacity but suffers from slow reaction rate.$^{135,172}$ Molecular orbital investigations have demonstrated that interactions between the lone pair electrons on the nitrogen and the $\pi$ and $\pi^*$ $\alpha$-methyl group orbitals results in a significant change in the electron donor properties of the amine. These interactions reduce the charge on the nitrogen and thus result in the amine becoming a weaker base, which results in the weakening of the N-H bond.$^{173}$ Examples of a well-known sterically hindered amine is given below, Figure 1.14, 2-amino-2-methyl-1-propanol (AMP)
Recently AMP has been chosen as a potential candidate absorbent.\textsuperscript{135} AMP, is the hindered form of MEA obtained by substituting two hydrogen atoms attached to the \( \alpha \)-carbon atom to the amino group in MEA by two methyl groups. These substitutions influence significantly amine properties and absorption capacity.\textsuperscript{198} The reaction of AMP with \( \text{CO}_2 \) exhibits no apparent carbamate formation in solution, leading to a high loading capacity and easy regeneration.\textsuperscript{172} Studies of reactions of AMP with \( \text{CO}_2 \) have shown that the loading of \( \text{CO}_2 \) in AMP is higher than for monoethanolamine (MEA) at temperatures between 40 °C and 80 °C.\textsuperscript{177} This is because of the stable carbamate formation in MEA leading to a lower solubility and a low stoichiometric loading of 0.5.\textsuperscript{135,199}

In 2006, da Silva \textit{et al.},\textsuperscript{195} studied carbamate stability for AMP and MEA using \textit{ab initio} calculation and a free energy of perturbation method. From their quantum mechanical calculations, it was found that AMP-carbamate species shows some steric interaction between the methyl group substituent and the carbon atom of \( \text{CO}_2 \), as the \((\text{OH})\text{C-N-C(\text{COO})}\) angle tightens from 114.53° in MEA-carbamate to 111.38° in AMP-carbamate, suggesting that the N-atom, together with the carbamate functionality, is forced away from one of the methyl groups. Recently, Ciftja \textit{et al.},\textsuperscript{200} have used \( ^{13}\text{C} \) nmr studies to establish the formation of AMP-carbamate in highly concentrated AMP solutions (30 wt\%) at \( T = 298 \text{K} \). The stability constant of AMP is 0.46, thus the formation of carbamate is very low under all conditions typically concentrations of the order \( 10^{-2} \) and \( 10^{-5} \) hence neglected by many researchers.\textsuperscript{199,201-204}
In 2003, Park et al.,\textsuperscript{113} studied 2-amino-2-hydroxymethyl-1-3-propandiol (AHPD) a sterically hindered amine and compared it with MEA. It was observed that, at 25 °C, when the partial pressure of CO\textsubscript{2} was increased the loadings in aqueous AHPD solutions far exceeded that of MEA, but was lower at lower CO\textsubscript{2} partial pressures. The bulky structure of AHPD appears to be hindering both the formation of the carbamate at low partial pressure, and hence the CO\textsubscript{2} solubility of aqueous MEA provided by the relatively large amount of carbamate formed dominates in this region. With increasing partial pressure, there is a ‘cross-over’ of the CO\textsubscript{2} solubility based on the reaction stoichiometry of bicarbonate versus carbamate formation. Reports also claim that sterically hindered amines exhibit higher levels of degradation resistance compared to un-substituted alkanolamines.\textsuperscript{135,205-207}

1.8.2 Multiple amine functionality

Another area of interest is the use of compounds with more than one amine functionality. The presence of multiple amine functionalities potentially allows a higher amine:CO\textsubscript{2} loading capacity (\textit{i.e.} stoichiometry). Piperazine (PIPZ) is the most widely used di-amine in CO\textsubscript{2} capture applications, particularly as a rate promoter for CO\textsubscript{2} absorption in carbonate and tertiary amine solutions. Figure 1.15 gives the molecular structure of PIPZ.

![Figure 1.15: Structure of piperazine (PIPZ)](image)

Investigations have found that, at low CO\textsubscript{2} loadings the dominant reaction products present are PIPZ-carbamate, protonated PIPZ-carbamate as well as unreacted PIPZ. At high CO\textsubscript{2} loadings the dominant reaction products are diprotonated PIPZ,
protonated PIPZ-carbamate and PIPZ-dicarbamate (which is not present in significant concentrations), all the relevant structures are given in my Paper 8. CO₂ absorption with PIPZ has been reported as 2 moles of CO₂ per mole of amine, thus increasing the potential CO₂ capacity of the solvent. In a study conducted by Bishnoi and Rochelle, the absorption of CO₂ into aqueous PIPZ was studied using a wetted-wall column. The study determined an apparent second order rate constant for the CO₂/ PIPZ reaction as 53,000 m³/kmol.s at 25 °C, a whole order of magnitude higher than the apparent MEA/CO₂ rate constant. This can be attributed to the fact that PIPZ is a secondary amine.

1.8.3 Molecular structure

The behaviour of amine-based solvents for CO₂ absorption, and their basicity, are found to be affected by structural effects as was identified in the study of different amines for CO₂ absorption by Puxty et al. In this study 2-piperidineethanol (2-PIPDE) and 3-piperidinemethanol (3-PIPDM) achieved a CO₂ absorption capacity of approximately 1 mole CO₂/mole amine. This is due to the distance of the hydroxyl groups from the cyclic ring, which makes it suitable for forming a stable intramolecular hydrogen bond with the nitrogen atom in a six-membered ring. This intramolecular hydrogen bonding between the hydroxyl and amine groups may decrease the basicity (pKa) of the secondary amines and may also destabilize carbamate formation. The molecular structures are given in Figure 1.16.

The quantum mechanical ab initio methods were used by da Silva et al., to study the stability of carbamate. They suggested that alcohol groups in the amine molecular structure tend to reduce the basicity. For instance, comparing primary amines, example ethyl-amine to ethanolamine, the addition of an alcohol group leads to reduced base strength of over 1 pKa unit.
In a study by Bonenfant et al., piperidine (PIPD) (a 6-membered ring) was shown to have a lower CO₂ absorption capacity than pyrrolidine (PYRR) (a 5-membered ring); molecular structures shown in Figure 1.17. This behaviour in PIPD may be due to the 6 membered ring causing the lone pair on the nitrogen atom to be located in a sp² hybrid orbital, and that might decrease the accessibility for CO₂ binding to the amine. In PYRR, a higher CO₂ absorption capacity was observed. The ring in PYRR might favour accessibility of CO₂ to the lone pair electron on nitrogen atom.
An important development in alkanolamine technology is the addition of activators or promoters to aqueous tertiary amine solutions, such as N-methyldiethanolamine (N-MDEA), Figure 1.18. The reason for the use of such a blend is related to the relatively high rate of reaction of CO\(_2\) with the activator and the advantages of N-MDEA concerning regeneration, leading to a higher loading capacity in the absorber column while maintaining a low heat of regeneration in the stripper section of the process. One such activated system consists of piperazine activated N-MDEA. It has been used successfully for the removal of CO\(_2\) in ammonia plants.\(^{178,179,181-183,185,189,190,192,196}\) The addition of PIPZ to N-MDEA act as an effective activator,\(^{179}\) leading to an increase in the CO\(_2\) loading capacity of the system.\(^{190}\) However, the kinetics of these reactions are slower than those of primary and secondary amines.\(^{169}\) This system has a high stoichiometry (~1 mol CO\(_2\)/mol N-MDEA)\(^{178}\) compared to that of MEA (~0.5 mol CO\(_2\)/mol of MEA).\(^{133}\)

![Figure 1.18: Structure of N-methyldiethanolamine (N-DMEA)](image)

### 1.8.5 Blended amines

Aqueous solutions of N-MDEA, molecular structure given in Figure 1.18, are not a viable option for CO\(_2\) capture due to a slower reaction rate with CO\(_2\) compared to MEA.\(^{194}\) To overcome the slow reaction rate of tertiary alkanolamines, the use of blended alkanolamines has been suggested.\(^{170,171,188,197}\) These blends consist of solutions of primary or secondary alkanolamines with a tertiary alkanolamine. Blends enhance both the absorption rate of CO\(_2\) and also CO\(_2\) loading capacity, resulting in a reduction in the energy requirements for regeneration. Most of the experimental data on
absorption/desorption and solubility presented in the scientific literature relate to blends of MEA/N-MDEA, DEA/N-MDEA. 72,175,176,178,180,186,194

1.9 Summary

Reversible chemical absorption involving an amine is the best investigated of the PCC technologies. The main shortfalls of PCC applications are fairly well understood and studies in these areas are ongoing particularly understanding the effect of molecular structure on the amine and the associated steric effects, hydrogen bonding, more than one amine functionality (diamine), blended amines, etc. to improve the overall capture process.

The engineering of any PCC plant will rely heavily on the solvent type and its behaviour. Chemists can provide knowledge of the chemical reactions of the amine with CO$_2$ in aqueous solution, the corresponding rate and equilibrium constants for the reactions, and the energies (activation parameters, enthalpies and entropies) that are crucial for the complete modelling of the absorption and stripping processes for a complete cycle of post combustion capture plant.
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Experimental
2.1 Reaction mechanism

In this chapter the three important aspects of PCC, namely: the kinetics, carbamate stability and the pK of the amine are systematically investigated using various techniques. We have developed a complete reaction scheme Figure 2.1 (also Figure 1.9 in chapter 1), where all the reactions of amine with CO₂ and all carbonate species in aqueous solutions were included (note that $K_n$ represents an equilibrium constant and $k_n$ and $k_{n-1}$ are forward and backward reaction rate constants, $A =$ primary and secondary amines).

![Complete reaction model for CO₂, H₂O and amine interactions](image)

Figure 2.1: Complete reaction model for CO₂, H₂O and amine interactions

In Figure 2.1 the dashed pathway (red) is the interaction of CO₂ with H₂O, the relevant rate and equilibrium constants are well investigated in literature.⁵⁻⁶ The interaction of amine with CO₂(aq)/CO₂ species (blue pathway) is thoroughly investigated in this thesis. For the investigations of the rate and the equilibrium constants stopped-flow spectrophotometry and $^1$H NMR spectroscopy were used. The protonation of the amines was studied using potentiometric titrations. The chemical names of the amines investigated, abbreviations adopted and structures are illustrated in Section 1.8 of chapter 1 under group 1, group 2 and group 3.

2.2 Chemicals

High purity CO₂ gas (BOC gases), N₂ (Core gases), potassium hydrogen phthalate (KHP AJAX Chemicals Ltd), thymol blue (Sigma-Aldrich, A.C.S. reagent),
alizarin red S (BDH chemicals), bromothymol blue (AJAX Chemicals Ltd), phenolphthalein indicator (analytical grade) sodium carbonate Na$_2$CO$_3$ (Merck, 99.9%) and potassium hydrogen carbonate KHCO$_3$ (BDH chemicals, >99%) were all used without further purification. Sodium hydroxide NaOH (Merck) was used without further purification and standardised by KHP (phenolphthalein indicator). Hydrochloric acid (AJAX Chemicals Ltd.) was used without further purification and concentration determined by the standardised sodium hydroxide. The amine purities range from 95-99% and were obtained from (Sigma – Aldrich, Reagent plus). Ultra high purity Millipore Milli-Q water was boiled to remove CO$_2$ gas, eliminating the influence of CO$_2$ gas impurities and was used to make up all solutions. All the chemicals were stored in a glove bag and prepared fresh as required for the experiment.

2.3 Kinetic measurement

The kinetics of the interactions of amine and CO$_2$ is not well investigated on a molecular level and very little information is available in the literature. To resolve the above issue and to gain a deeper understanding of the complete mechanism, the kinetics of the reaction of aqueous amine with CO$_2$(aq) has been investigated thoroughly in this thesis. The reaction of CO$_2$(aq) with amine are fast and a number of simultaneous reactions occur at the same time, which requires sophisticated interpretation and analysis of the measured data; and no simple spectrophotometric measurements allow the direct observation of the reactions.

To investigate the direct reaction of CO$_2$(aq) with amines, stopped flow spectrophotometry was used, as this reaction is relatively fast and occurs on millisecond time scale. Also, $^1$H NMR spectroscopy has been employed to investigate the slow reversible reaction between HCO$_3^-$ and amine. The following are the forward and back reaction rates; $k_7$, $k_7^-$, $k_9$ and $k_9^-$ based on the reaction scheme Figure 2.1. None of the interacting species feature useful absorption spectra in the visible or near-UV regions, so pH changes as a result of reactions in solution were followed spectrophotometrically via coupling to appropriate indicators. The kinetics of most of the amines were measured at 25 °C except for NH$_3$ and MEA, where a complete temperature dependence study was undertaken from 15 °C to 45 °C, allowing the determination of activation and thermodynamic values of all relevant rate and equilibrium constants. The experimental
section of **Papers 3, 4, and 5** give a detail explanation of the concentration profiles, the chemicals used for the experiments and the data analyses. However, the experimental setup for the stopped flow spectrophotometer in the laboratory at the University of Newcastle will be detailed below and an example of the kinetic spectra for MORP/HCO$_3^-$ will be shown in Section 2.3.2.

### 2.3.1 Stopped flow spectrophotometer

The instrument used was an Applied Photophysics DX-17 stopped-flow spectrophotometer equipped with a J & M Tidas MCS500 3 - diode array detector. Figure 2.2 a) is the stopped-flow setup at the University of Newcastle, and 2 b) is a schematic of the two driving syringes. Two types of stopped-flow measurements were conducted in this work to cover the entire reaction scheme so that it could be globally analysed. This includes the entire forward and the backward reaction rate and equilibrium constants.

**Type 1 measurement:** Forward reactions where in one syringe a mixture of amine and an appropriate indicator and in the other syringe saturated CO$_2$(aq) was present.

**Type 2 measurement:** Back reactions where a pre-equilibrated carbamate solution in one syringe was present and in the other syringe HCl was present.

The two driving syringes were pushed together in a ratio of 1:1 and the process terminated by using a stopping syringe. Both the solutions from syringe 1 and 2 are mixed in the mixing chamber, where a light passes through the solution (light intensity 40%) and the pH changes during the reactions of CO$_2$(aq) in the amine solutions as a result of release of protons from the carbamic acid and carbonic acid formed were observed with time over the wavelength range 400-700nm via coupling to pH indicators. This is illustrated in Figure 2.3 a) and b), where the absorbance changes due to the protonation of the indicator were measured.
Figure 2.2: a) Stopped-flow set up, b) enlarged view of the driving syringes

Figure 2.3: Absorbance data for the reaction of 6 mM MORP with 6 mM CO$_2$(aq) at 25 °C in the presence of 12.5 µM indicator (thymol blue): (a) three dimensional representation of absorbance vs wavelength vs time, (b) absorbance vs wavelength at selected time intervals

Each measurement was repeated a minimum of five times to check reproducibility and to allow for standard deviations to be derived for the calculated rate constants (see Figure 2.4). Samples were thermostatted (Julabo F20) to within ±0.1°C and the exact temperature recorded via a thermocouple within the stopped flow apparatus.
2.3.2 $^1$H NMR spectroscopy

Two series of NMR kinetic measurements were performed depending on the reaction under investigation.

**Type 1:** For the investigation of carbamate formation with HCO$_3^-$ at high pH, aqueous amine solution mixed with different amounts of acid or base added was mixed with potassium hydrogen carbonate solution.

**Type 2:** For the investigation of the decomposition of the carbamate at high pH, carbamate was generated by mixing the amine with sodium carbonate and, after equilibration, the relative concentration of carbamate and amine were quantified by $^1$H NMR spectroscopy. The resulting solution was mixed with HCl or NaOH and the disappearance of the amine carbamate with time was monitored.

The resultant mixture from type 1 or 2 was transferred to a NMR tube and the initial $^1$H NMR spectrum was recorded approximately 5 minutes after mixing. The spectra were recorded thereafter at predetermined time intervals automatically by the NMR spectrometer to establish the time resolved kinetics. All $^1$H NMR kinetic measurements were performed at 25 °C. Figure 2.5 shows a series of $^1$H NMR spectra over different time interval for MORP/HCO$_3^-$ solution at 25 °C. From Figure
2.5, MORP gives rise to two triplets, while the addition of HCO$_3^-$ gives rise to two additional triplets corresponding to the carbamate. At the start of the measurement, there was very little carbamate present, a slight chemical shift of the peaks was observed but with increasing time the peaks associated with the carbamate remained unchanged and no change in the chemical shifts was observed. In the pH region investigated in this work, all of the amines and their carbamates are involved in pH-dependent equilibria. As a consequence, the chemical shifts are pH-dependent and on the slow NMR timescale the peak integrals represent the sum over the concentrations of the protonated and deprotonated forms of the amine and the carbamate/carbamic acid. For the analysis using our in-house software, only the well separated peak integrals were used to calculate the concentration of amine and carbamates.

![Figure 2.5: Series of $^1$H NMR spectra’s over different time interval for MORP/HCO$_3^-$ solution at 25 °C.](image)

2.4 Equilibrium studies

The carbamate stability is an important aspect of PCC, as it defines the stoichiometry of the reaction. Based on Figure 2.1, the carbamate stability constant $K_9$ and the protonation/deprotonation of the carbamate $K_8$ was investigated in this thesis.
using $^1$H NMR spectroscopy. It is much easier to study this pathway experimentally using this method and hence it is easier to evaluate an equilibrium constant for this reaction. This has been the dominant reaction pathway used in the literature for which carbamate stability constants have been reported.$^7$-$^1^5$ As an example, morpholine (MORP) will be used to describe the experimental procedure and the data analysis. The first step before the equilibrium study was to check the purity of the amine in water.

MORP is a secondary cyclic symmetrical amine with the addition of an oxygen atom located in the para position (to the amine nitrogen) in the ring structure. In the database by Saito et al.,$^{1^6}$ the $^1$H NMR spectrum of pure MORP (solvent used CDCl$_3$) contains two triplets and a singlet. The relevant spectra are shown in Figure 2.6. The literature reports two triplets with peaks at ~3.67 ppm for the O-CH$_2$ group and at ~2.86 ppm for the N-CH$_2$ group. Further a singlet at ~2.59 ppm is assigned for the hydrogen atom attached to the nitrogen. The $^1$H NMR spectrum of MORP in water showed a similar peak pattern but at very slightly different chemical shifts, this is due to the different solvents. Two triplets were observed at ~3.72 ppm for the O-CH$_2$ group and the peak at ~2.84 ppm for the N-CH$_2$ group. The singlet from the hydrogen that is attached to nitrogen was not observed, due to its fast exchange with water on the $^1$H NMR time scale.

![Figure 2.6: $^1$H NMR for MORP from (a) the literature database and (b) determined in this project](image-url)
To investigate the carbamate stability of each amine, a stock solution of 0.020 M amine and 0.040 M Na$_2$CO$_3$ was prepared using ultra-high purity Milli-Q water, which had been boiled to remove CO$_2$ gas. Samples were prepared in a series of 5 mm-diameter NMR tubes, each containing a sealed glass capillary containing TSP (3-(trimethylsilyl)propionic acid-$d_4$, sodium salt) as the reference in D$_2$O, which was the locking agent (Figure 2.7). The tubes were filled with 1.5 mL of stock solution with different volumes of standardised 1.0 M HCl, in increments of 10 µL, being added to each series of tubes. The NMR tubes (over $\frac{3}{4}$ full of solution) were capped and further sealed with “Parafilm” to ensure that no CO$_2$ was lost, although it should be appreciated that at higher acidities some CO$_2$ must escape from solution into the gas phase above the liquid. The solutions were mixed by through shaking.

![NMR tube with a capillary](image)

**Figure 2.7: NMR tube with a capillary**

All samples were thermostatted for 24 hours or until complete equilibrium had been established. Only solutions with final pH values greater than 6 were used in the data analysis, as the potential for losing CO$_2$ at lower pH values cannot be discounted, despite the precautions taken to seal the tubes. The $^1$H NMR spectra of the amine/Na$_2$CO$_3$/HCl solutions were measured on a Bruker Avance DPX-300 operating at
a frequency of 300.13 MHz, later replaced by a Bruker Ascend 400 MHz instrument. The error in our chemical shift measurements was ±0.01 ppm. An example of a series of spectra at 25 °C for MORP/Na₂CO₃ is given in Figure 2.8. The ¹H NMR spectra of MORP and its carbamate give rise to four triplets, two triplets corresponding to the hydrogen’s of the O-CH₂ and N-CH₂ of MORP and two for the equivalent methylene’s in the MORP-carbamate in both the deprotonated and protonated forms. Based on Figures 2.8 and 2.9, when no acid is added to the solution the pH is high (~11.5) as all the amine is in the deprotonated form, and very little carbamate is formed and the peaks overlap. As HCl is added to the solution the pH falls, and pH (~9.5) all the four peaks corresponding to MORP and MORP-carbamate are well separated. At neutral pH (~7), all the carbamate is decomposed while leaving free amine in the protonated form.

Figure 2.8: The pH-dependent behaviour of the ¹H NMR spectrum of a MORP/Na₂CO₃ solution with HCl addition.
Figure 2.9: Variation in the species present in the solution determined from the $^1$H NMR spectrum at different pH values.

The relative integrals of the $^1$H NMR peaks that were well separated were used to quantitatively investigate the formation of amine-carbamate species, as these are a direct measure of the hydrogen-containing species in solution. Thus the concentrations of product species could be directly evaluated. Separate signals for amine-carbamate and amine-carbamic acid cannot be individually resolved, but give rise to changes in chemical shift as the pH changes. Similar circumstances pertain to the amine and protonated amine species, which give rise to a single signal, (see Figure 2.10). For MORP O-CH$_2$, the chemical shift was from 3.69 ppm – 3.93 ppm and for N-CH$_2$ was from 2.80 ppm – 3.23 ppm. For the MORP-carbamate the chemical shift for O-CH$_2$ was from 3.63 ppm – 3.65 ppm and for N-CH$_2$ was from 3.36 ppm – 3.38 ppm. The concentration of protonated MORP-carbamate is always very small and thus the chemical shift range exhibited by the combined signal of MORP-carbamate and protonated MORP-carbamate is not observable.
For the alkanolamines/amines that did not form carbamates, no changes in the composition of the solutions were observed, except that the chemical shifts for the alkanolamine/amine changed as the pH was lowered. Again this is attributable to protonation of the amine. The limits of detection of the amine-carbamates were of the order of < ~0.5% of the major peaks of the amines/protonated amines in the $^1$H NMR spectra. This is based on the observation of the $^{13}$C satellites associated with the methyl resonances, *i.e.* from $^1J(^{13}$C,$^1$H) coupling ($^{13}$C natural abundance = 1.1%).

### 2.4.1 Data analysis

After the collection of the spectra, for the calculations of MORP and MORP-carbamate concentrations only the well separated peak signals were used to obtain peak integrals. All data analysis was performed in ReactLab-Equilibrium and in-house software written in Matlab. Based on Figure 2.1, the equations investigated were; (1) and (2) as shown below.

![Figure 2.10: Chemical shifts of MORP and its carbamate (at 25 °C) observed in the $^1$H NMR spectra](image-url)
\[
A + \text{HCO}_3^- \xrightleftharpoons[K_9]{K_9} \text{ACO}_2^- + \text{H}^+ \\
\text{ACO}_2^- + \text{H}^+ \xrightleftharpoons[K_i]{K_i} \text{ACO}_2\text{H}
\]

(1)

(2)

In the data analysis model, the known parameters have to be fixed to literature values while the unknowns have to be fitted. In this case the fitted parameters were the carbamate stability constant and the protonation of the carbamate, while the fixed parameters were the species size and charge, the counter ions that are present and their charge and concentrations, the solvent type and the temperature of the reaction, concentration of MORP/Na\textsubscript{2}CO\textsubscript{3} and HCl and the protonation constant of MORP at required temperatures. Other fixed parameters were \(K_1, K_2, K_3\) and \(K_4\) which are the equilibrium constants linking CO\textsubscript{2(aq)}, HCO\textsubscript{3}–, CO\textsubscript{3}\textsuperscript{2–}. The p\(K_w\) values for the different temperatures were taken from a literature reference.\textsuperscript{18} Rather than maintaining approximately constant ionic strength using excess inert salts in the titration, activity coefficient corrections were applied to all charged species based on Debye-Hückel equation (3).

\[
\log \gamma_i = \frac{-Az_i^2\sqrt{\mu}}{1+A\sqrt{\mu}}
\]

(3)

In this equation, the activity coefficient \(\gamma_i\) is a function of the ionic strength \(\mu\), the charge \(z_i\) of the \(i\)th component, and the parameter A, which is defined by the dielectric constant of the solvent and also the temperature.\textsuperscript{19,20}

The analysis of the equilibrium concentration data showed good agreement between the experimental and the calculated values. An example of the experimental data and fitted curves for the MORP/CO\textsubscript{3}\textsuperscript{2–}/HCl system at the four different temperatures is shown in Figure 2.11. The markers represent experimental values based on \textsuperscript{1}H NMR integrated intensities and the lines represent calculated values based on the fitted model for the four different temperatures examined.
Figure 2.11: Equilibrium concentration profiles for the titration of MORP/Na$_2$CO$_3$ (0.040 M/0.080 M with added 2.0 M HCl) at 288, 298, 308 and 318 K. The MORP species (protonated + deprotonated) are depicted by the empty markers and the MORP-carbamate species (protonated + deprotonated) correspond to the filled markers.

Studies for other alkanolamine/amines showed similar results, although the spectra were more complex as a consequence of the increased complexity of their molecular structures. Nevertheless, individual peaks attributable to both amine and the amine-carbamate (and their protonated forms) could be identified in all measurements, and the peak positions over the course of the titration showed similar trends to those of MORP when carbamate formation occurred.

From the data analysis $K_9$ (i.e. carbamate formation) and $K_8$ (protonation of the carbamate anion) were obtained at several temperatures from 15 °C to 45 °C. The standard molar enthalpy change $\Delta H^\circ$ and the standard molar entropy change $\Delta S^\circ$ were calculated using a van’t Hoff plot of $\ln K$ against $1/T$ (Figure 2.12), equation (4). The molar Gibbs free energy change ($\Delta G^\circ$) under standard state conditions was calculated from $\Delta H^\circ$ and $\Delta S^\circ$ using equation (5).
\[ \ln K = -\frac{\Delta H^\phi}{RT} + \frac{\Delta S^\phi}{R} \]  
(4)

\[ \Delta G^\phi = \Delta H^\phi - T\Delta S^\phi \]  
(5)

![Figure 2.12: The log $K_9$ vs 1/T plot for MORP/Na$_2$CO$_3$ vs HCl.](image)

The temperature dependence equilibrium constants for $\ln K_9$ and $\ln K_8$ and the relevant thermodynamic parameters: enthalpy, entropy and Gibbs free energy values are published in Paper 1: Investigations of primary and secondary amine carbamate stability by $^1$H NMR spectroscopy for post combustion capture of carbon dioxide.

### 2.5 Potentiometric titrations

There are various methods for determining protonation constants, the most common being potentiometric titrations. Modern titrations utilize computerized instrumentation as illustrated in Figure 2.13, in which the classical burette is substituted by a computer controlled system such as a Metrohm 665 Dosimat automatic burette. The measurement itself also has been computerised, making the entire titration method automatic rather than a time-consuming manual process.
Figure 2.13: Schematic representation of an automated potentiometric titration set-up

Figure 2.13 shows a schematic representation of a computer-controlled potentiometric pH titration. Titrations using this set-up were carried out under a nitrogen atmosphere and thermostatted at selected temperatures from 15 °C to 45 °C using an external water bath. A Metrohm 665 Dosimat automatic burette fitted with a 1 mL dispenser unit was used to add the titrant solution. The pH electrode used was a slim, 125 mm Metrohm 6.0234.100 micro-pH glass electrode with the internal solution of 3 M KCl. The electrode was connected to the computer via a National Instruments NI-DAQ 7 board that amplified and translated the electrode signal to mV signal that could then be recorded by the computer.

The titration was performed in the thermostatted titration vessel, with the pH electrode burette and nitrogen purge being inserted through the standard taper openings of the titration vessel lid. For each set of titrations, a known concentration of amine was initially acidified by addition of standardised HCl (0.015 M) in a ratio of 1:1.5 amine:HCl. The volumes required for a titration was 10 mL, which was transferred to the thermostatted titration vessel and back-titrated with standardised NaOH (0.10 M) to high pH. The vessel was placed on the stirrer plate which allowed for constant stirring of the solution for the duration of the titration. The titrations were repeated a minimum of three times at all the temperatures mentioned above to evaluate reproducibility.
The first step in the analyses process was the collection of raw data, which was obtained by data acquisition programs, developed using an Excel-Matlab link. The set-up requires the user to enter the experimental parameters into an Excel user-interface, while the instruments were controlled by the matrix-based computer program language Matlab via a digital/analogue I/O port. The appropriate Excel file for each measurement type was opened from a Matlab Graphical User Interface (GUI), as depicted in Figure 2.14, and the measurement itself was also initiated from the GUI. Once the measurement has been initiated, Matlab GUI displayed the progress of the experiment.

The electrode signals were displayed as the measurement progresses, which enables the user to observe the titration as it develops and also aids in identifying whether the electrode was operating correctly. After each addition of titrant, it was required to determine whether or not the solution has reached equilibrium after the addition. To assess this computer rapidly recorded 100 readings in a one second period. The average mV value over the second was calculated and this process continued for one minute, and then the overall average again taken. If the determined averages from the two periods were within 0.1 mV of each other, the electrode reading was considered stable and the last average value was recorded as the reading. If the stable criteria were not met, then the process was repeated for another minute and the average calculated again. The timeout occurred after 10 sets (or 10 minutes), after which the mV reading was assumed to be constant and the last average taken as the mV reading for that step of the titration.

At each temperature the electrode was calibrated for concentration (i.e. pH = -log₁₀ [H⁺]) by means of a strong acid-strong base titration. The principle is based on GLEE (glass electrode evaluation), a computer program for glass electrode calibration.²¹ This program provides an estimate of the carbonate contamination of the base, the pseudo-Nernstian standard potential and slope of the electrode and, optionally, the concentration of the base and pKw.
2.5.1 Data analysis

After the collection of raw data, during which the required information was collected, the second step involves data processing, which is important in order to extract useful information from the chemical process. The mV signal was used directly in the analysis of the titration data and transformed into pH. To convert mV to pH see Equation (a), the slope and intercept were determined by a calibration titration with acetic acid and then the corresponding values fitted to the measurement using the appropriate software.\(^{22}\)

\[
pH = \frac{mV - \text{intercept}}{\text{slope}}
\]  
(a)
Analysis was most commonly performed using specifically developed computer programs (in this case in-house software written in Matlab), in order to determine the reaction parameters that describe the experiment. Excel was used to develop the user interface, which provided the platform whereby all data manipulation and model defining could be performed, and this interface was coupled with Matlab, which could execute the calculations required for the analysis.

The amines protonate as described in equation (6), for amines that have only one protonation step:

\[ A + H^+ \rightleftharpoons K_a A^+ \]  

(6)

In the case of multiple protonation there is an extra equation incorporated in the model resulting in another parameter to be fitted, equation (7).

\[ AH^+ + H^+ \rightleftharpoons AH_2^{2+} \]  

(7)

The data analysis model was similar to the one detailed in section 2.4.1. The parameters have to be fixed to values taken from the literature, while the unknown parameters have to be fitted using our software. Ionic strength corrections were applied to all charged species based on the Debye-Hückel equation (3).

2.5.2 Outcomes

The outcomes of the data analysis were the species concentrations as a function of change in pH and the dissociation constant of the amine at temperatures from 15 °C to 45 °C. An example of the fitting data is shown in Figure 2.15. The markers represent the experimental values while the solid lines correspond to the calculated curves based on the software. Both the experimental and the calculated values are effectively on top of each other, which defines the reproducibility of the results. The three different colours represent the three repeats at one temperature using the same stock amine and acid solutions. For all the amines investigated in this thesis, plots showed similar experimental reproducibility as shown for Figure 2.15. All three titrations were fitted globally using the software.
Figure 2.15: A example plot of the pH vs volume of NaOH added from a potentimetric titration experiment for MORP/HCl, illustrating closeness of model fit to experimental data.

Based on the concentration profile from the data fitting (Figure 2.16), the initial pH of the stock solution was low (~2) when no NaOH was added, as the species present in the solution were $\text{H}^+$ and the amine in a completely protonated form. As the titration progressed with the addition of NaOH, at a pH between 8 – 9 deprotonation of the amine occurs. With further addition of NaOH, all of the the amine is deprotonated and the dominant species at pH 12 are the free amine and $\text{OH}^-$ ions.
Figure 2.16: A concentration profile vs pH for titration of protonated amine with base

The outcome of the temperature-dependence studies of the protonation/dissociation of an amine, that is a plot of the temperature dependence of ln $K_6$ vs 1/T (as shown in Figure 2.17) is linear and a van’t Hoff analysis gives the slope and intercept, which are used to calculate the molar enthalpy ($\Delta H^o$) and molar entropy ($\Delta S^o$). The relevant protonation constants (ln $K_6$) and the thermodynamic parameters for the amines studied in this thesis are reported in Paper 2: Protonation constants and thermodynamic properties of amines for post combustion capture of CO$_2$. 
Figure 2.17: Temperature dependence of $\log K_6$ vs (T/K)$^{-1} \times 1000$ for MORP/HCl vs NaOH

2.6 Summary

The methods employed, data analyses and the outcomes of each study for the different aspects of the PCC process in this thesis are summarised in Table 2.1.

<table>
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<th>Raw data</th>
<th>Data analysis</th>
<th>Outcomes</th>
</tr>
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<td>In-house software written in Matlab</td>
<td>$k_7, k_{-7}, k_9, k_{-9}$ $(K_7, K_8, K_9)$</td>
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<td></td>
<td>(Kinetics)</td>
<td></td>
<td></td>
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<td>2.</td>
<td>$^1$H-NMR spectroscopy</td>
<td>Integrals vs volume of HCl</td>
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<td>mV vs volume of NaOH</td>
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<tr>
<td></td>
<td>(Thermodynamics)</td>
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</table>

Table 2.1: Summary of the global experimental section
2.7 References


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Publications
Investigations of primary and secondary amine carbamate stability by $^1$H NMR spectroscopy for post combustion capture of carbon dioxide

Fernandes Debra, Conway William, Burns Robert, Lawrance Geoffrey, Maeder Marcel and Puxty Graeme

Accepted: Journal of Chemical Thermodynamics
54, (2012), 183-191
Investigations of primary and secondary amine carbamate stability by $^1$H NMR spectroscopy for post combustion capture of carbon dioxide

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Abstract

Carbamate formation is one of the major chemical reactions that can occur in solution in the capture of CO$_2$ by amine-based solvents, and carbamate formation makes a significant enthalpy contribution to the absorption-desorption of CO$_2$ that occurs in the absorber/stripper columns of the PCC process. Consequently, the formation of carbamates of selected series of primary and secondary amines over the temperature range (288 to 318) K has been investigated by equilibrium $^1$H NMR studies, and the stability constants ($K_0$) for the equilibrium:

$$RNH_2 + HCO_3^- \rightleftharpoons RNHCOO^- + H_2O$$

are reported. van't Hoff analyses have resulted in standard molar enthalpies, $\Delta H_m^o$, and entropies, $\Delta S_m^o$, of carbamate formation. A $\Delta H_m^o - \Delta S_m^o$ plot generates a linear correlation for carbamate formation (providing a mean standard molar free energy, $\Delta G_m^o$, for carbamate formation of about $-7$ kJ mol$^{-1}$), and this relationship helps provide a guide to the selection of an amine(s) solvent for CO$_2$ capture, in terms of enthalpy considerations. A linear $\Delta H_m^o - \Delta S_m^o$ plot also occurs for carbamate protonation.

The formation of the carbamates has been correlated with systematic changes in composition and structure, and steric effects have been identified by comparing molecular geometries obtained using density functional B3LYP/6-311+G(d,p) calculations. Trends in steric effects have been identified in the series of compounds monoethanolamine (MEA), 1-amino-2-propanol, 2-amino-1-propanol (AP) and 2-amino-2-methyl-1-propanol (AMP). In the case of 2-piperidinemethanol, 2-piperidineethanol and 3-piperidinemethanol, strong intramolecular hydrogen bonding is shown to be the likely cause for lack of carbamate formation, and in the ring systems of pyrrolidine, morpholine, piperidine and thiomorpholine trends in carbamate formation (as given by $K_0$) have been correlated with the internal ring angle at the amine nitrogen, as well as the planarity of the environment around the nitrogen atom.

1. Introduction

The great bulk of scientific evidence points to the fact that continued and growing greenhouse gas emissions, notably CO$_2$, are threatening our established climate patterns. Power generation, particularly from fossil fuels, accounts for approximately 25% of global CO$_2$ emissions, and these are set to rise dramatically over the next 25 years [1]. A wide range of options are being investigated to reduce greenhouse gas emissions [2], and post-combustion capture of CO$_2$ (PCC) followed by, for example, storage in underground formations, has the potential to reduce these emissions. This technology can be retrofitted to existing power plants, or integrated into new plants.

Carbon dioxide capture using aqueous amines is a well established technology which has been used to separate CO$_2$ from H$_2$ or CH$_4$, and is currently used in ammonia production and in natural gas processing [3]. Chemical absorption and its subsequent desorption using aqueous amines involves two independent steps. Firstly, CO$_2$ absorption occurs at relatively low temperatures in the absorber column and, secondly, because the reaction is reversible, CO$_2$ desorption is able to occur at high temperatures in the stripper column. The regenerated amine solution is then circulated back to the absorber column and the process repeated [4].

Applying this technology to chemical absorption/desorption processes in PCC faces new challenges, particularly in regard to added energy consumption and hence cost. The majority of this energy is required for regeneration of the amine; that is, releasing CO$_2$ from the amine-solvent solution. The absorption enthalpy itself is directly important for the process as it partially determines
the temperature profile in the absorber and the energy that must be input for desorption and amine regeneration. The enthalpy of CO₂ absorption/desorption consists of both physical and chemical contributions. From the viewpoint of the chemical reactions that occur in solution, an understanding of the chemistry of the reactions of CO₂ with amines is therefore crucial to the development of new amine-based solvents that have the potential to reduce energy costs, compared to current solvents.

In the PCC process, CO₂ reacts with an aqueous amine solution via two different pathways: formation of the carbamic acid and its subsequent deprotonation to carbamate, equation (1), or a simple acid-base reaction, formation of carbonic acid followed by deprotonation, equation (2).

$$2 \text{RNH}_2 + \text{CO}_2 \rightleftharpoons \text{RNHCOO}^- + \text{RNH}_3^+,$$

$$\text{RNH}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{HCO}_3^- + \text{RNH}_3^+.$$  

In equation (1) carbamates are the amides formed upon reactions between amines and CO₂. Under relevant conditions, the carbamic acid gives up a proton to a second amine molecule to form a carbamate, resulting in an overall amine:CO₂ stoichiometry of 2:1 [5]. Both primary and secondary amines can follow this pathway, and under the conditions commonly found in PCC, the product is primarily the carbamate. The second pathway that contributes to CO₂ absorption, equation (2), is CO₂ hydration to ultimately form bicarbonate, HCO₃⁻. In this pathway an amine simply acts as a proton-accepting base, and possibly a catalyst, for the hydration of CO₂ [6,7]. The overall stoichiometry for this pathway is 1:1, so in terms of capacity it is more efficient for CO₂ absorption than the pathway given in equation (1). For tertiary (and some sterically-hindered) amines this is the only pathway that contributes to absorption of CO₂. While both pathways have advantages and limitations, equation (1) is more favourable for its faster kinetics than equation (2) [5], and as such a thorough understanding of the factors that influence the formation of carbamates is essential for the development of any new amine system.

Carbamate stability constants (Kₙ₉) noted in our study the water concentration [H₂O] is not included in the equilibrium definition of Kₙ₉; see below for a complete definition of all reactions relevant to this study) of simple amines, as defined in equation (3):

$$\text{RNH}_2 + \text{HCO}_3^- \rightleftharpoons \text{RNHCOO}^- + \text{H}_2\text{O},$$

as well as amino acids, were reported as long ago as the 1950s. Studies included the carbamates of the propyl- and butyl-amines, and were obtained by chemical precipitation methods [8–10]. Other studies included the prototypical PCC alkanolamine, monoethanolamine (MEA), as well as diethanolamine (DEA) [11]. More recently, Sartori and Savage [12] studied the carbamates of MEA, 2-amine-2-methyl-1-propanol (AMP) and DEA by ¹³C NMR spectroscopy. Aroua et al. studied carbamate formation of MEA and DEA from T = 298 to 328 K, using a NaOH titration method [13,14], and Jou et al. [15] and Park et al. [16] studied MEA (as well as DEA, AMP and their mixtures) using (vapour + liquid) equilibrium (VLE) measurements from T = 273 to 423 K [13]. ¹³C NMR spectroscopy was also used by Barth et al. [17] and Popsteinova-Jakobsen et al. [18] to study MEA (as well as diglycineamine, diisopropanolamine, butylethanolamine and methylidethanolamine) over the temperature range T = 293 to 363 K, while more recently McCann et al. used ¹³C NMR spectroscopy to study MEA (as well as 2-amine-1-propanol, propylamine and isobutylamine) at T = 303 K [19]. Isothermal titration calorimetry has also been used to study the formation of the carbamates of MEA, DEA and NH₃ at T = 298 K [20]. Studies on DEA have included that by Böttinger et al., who used a combined ¹³C NMR and VLE approach to study carbamate formation from T = 293 to 333 K [21]. More recently, Ciftja et al. have used ¹³C NMR studies to establish the formation of AMP-carbamate in highly concentrated AMP solutions (30 wt%) at T = 298 K [22].

In this study we examine the formation of carbamates of series of primary and secondary acyclic and cyclic aliphatic amines using ¹H NMR studies, and report the temperature dependence of the carbamate formation constants from T = 218 to 318 K. From these studies the standard molar enthalpies, ΔH⁰, and standard molar entropies, ΔS⁰, of carbamate formation are evaluated. The series of amines were chosen to cover a range of related geometries differing by, for example, substitution of –OH or –CH₃ groups at selected locations, thereby giving variations in electronic and stereochemical effects, and also cyclic structures with variations in ring heteroatom substitution and external pendant groups in the case of piperidine. Trends in the formation of carbamates are examined and, where possible, carbamate formation is correlated with stereochemical factors, ring strain, and electronic factors obtained from density functional B3LYP/6-31+G(d,p) calculations. This study provides a comprehensive report of enthalpy and entropy changes in solution for the reactions of carbonate species with series of amines that have been selected to demonstrate systematic changes in their structures.

2. Experimental

2.1. Materials

The primary amines monoethanolamine (MEA, ≥99%), 2-aminoo-1-propanol (AP, 98%), 2-amine-2-methyl-1-propanol (AMP, 95%), AMP hydrochloride (≥99%), 2-amine-2-methyl-1,3-propanediol (AMPD, ≥99%), 2-amine-1,3-propanediol (BIS, 98%) and 2-amine-2-hydroxymethyl-1,3-propanediol (TRIS, ≥99.9%); and the secondary/cyclic amines diethanolamine (DEA, 98.5%), piperidine (PIP, 99%), morpholine (MOR, ≥99%), thiomorpholine (TMOR, 98%), piperazine (PIPZ, 99%), 1-methylpiperazine (MPIPZ, 99%), pyrrolidine (PYR, 99%), 2-piperidinemethanol (2-PIPD, 97%), 2-piperidinedienethanol (2-PIPDE, 90%), 3-piperidinemethanol (3-PIPD, 96%), 4-piperidinemethanol (4-PIPD, 97%), 4-piperidineethanol (4-PIPDE, 97%) were obtained from Sigma-Aldrich, except for AMP hydrochloride, which was obtained from Fluka BioChemika. All amines were used without further purification. The structures of the amines used in the present study are shown in the supplementary information, figure S1. Anhydrous sodium carbonate (Uni- vari, analytical reagent, (99.9 to 100.1)% was purchased from Ajax Chemicals. Hydrochloric acid (32%, Uni-vari, analytical reagent) was obtained from Ajax Finechem. The concentration of the acid was determined by titration with Na₂CO₃ using an automated titration apparatus under a nitrogen atmosphere. All solutions were stored in a glove bag under a nitrogen atmosphere.

2.2. ¹H NMR titrations

For each amine a stock solution of 0.040 M amine and 0.080 M Na₂CO₃ was prepared using ultra-high purity Milli-Q water, which had been boiled to remove CO₂ gas. Samples were prepared in a series of 5 mm-diameter NMR tubes, each containing a sealed glass capillary containing TSP (3-(trimethylsilyl)propionic acid-d₄, sodium salt) as the reference in D₂O, with the latter as the locking agent. The tubes were filled with 1.5 mL of stock solution, and different volumes of standardised 2.0 M HCl, in increments of 10 μL, were added to each series of tubes. The NMR tubes (over ¾ full of solution) were capped and further sealed with “Parafilm” to ensure that no CO₂ was lost, although it should be appreciated that at higher acidities some CO₂ must escape from solution into the gas phase above the liquid. All samples were thermostatted for 24 h or until complete equilibrium had been established. Only solutions
with final pH values greater than 6 were used in the data analysis, as the potential for losing CO$_2$ at lower pH values cannot be discounted, despite the precautions taken to seal the tubes.

The $^1$H NMR spectra of the amine/Na$_2$CO$_3$/HCl solutions were measured on a Bruker Avance DPX-300 operating at a frequency of 300.13 MHz. Spectra were recorded using the following acquisition parameters: pulse duration, $\pi/2$ pulse, spectral width = 8223.7 Hz, number of data points (TD) = 65 K, acquisition time = 3.98 s, delay time between two transitions = 1.0 s, and number of scans = 16. All spectra were processed with Bruker BioSpin Topspin version 1.3 software. An example of a series of spectra and assignments in the case of MEA is given in the supplementary information, figure S2. The relative integrals of the $^1$H NMR peaks were used to quantitatively investigate the formation of carbamate species, as these are a direct measure of the hydrogen-containing species in solution. Thus the concentrations of amine and carbamate species could be directly evaluated as the HCl was varied, taking into account dilution. Separate species signals for carbamate and carboxylic acid cannot be individually identified because of fast exchange, but give rise to changes in chemical shift as the pH changes. Similar circumstances pertain to the amine and protonated amine species, which give rise to a single species spectrum.

For the amines that did not form carbamates, no changes in the composition of the solutions were observed, except that the chemical shifts for the amine shifted as the pH was lowered. Again this is attributable to protonation of the amine. The limits of detection of the carbamates were of the order of $\leq 0.5\%$ of the major peaks of the amines/protonated amines in the $^1$H NMR spectra. This is based on the observation of the $^{13}$C satellites associated with, for example, the methyl resonances, i.e. from $^{1}$J($^{13}$C,$^{1}$H) coupling (where the $^{13}$C natural abundance is 1.1%). An example of this is shown in the supplementary information, figure S3. This figure shows the methyl resonances of groups attached to the carbon $\alpha$ to the amine group in AP and AMP at pH $\sim 9$, a pH value at which there is extensive carbamate formation (see figure 1 for MEA). The presence of the carbamate signal is evident in the AP spectrum, but there is no evidence for carbamate formation for AMP, despite the fact that AMP is known to form a carbamate [22]. The $-CH_3$ signal in AMP-carbamate is expected to appear to lower frequencies as in AP. The stability constant for AMP-carbamate formation is very low and the presence of carbamate can only be observed in very highly concentrated solutions (30 wt%). The present studies were performed at low concentrations, with an initial amine concentration of 0.04 M in all cases, thereby allowing ionic strength corrections (see below) to be easily made, which thus results in thermodynamically correct stability constants at zero ionic strength. It is possible that in those cases where no carbamate formation could be detected in our studies, higher initial concentrations of amine might reveal that low concentrations of carbamate exist, as in the case of AMP.

2.3. Data analysis

We have recently developed a general reaction scheme that includes all relevant interactions of an amine with CO$_2$ and carbonate species in aqueous solution (note that $K_6$ represents an equilibrium constant) [23]. This is shown in the scheme below, which has been adapted to include the reactions of CO$_2$ with water to give HCO$_3$ and H$^+$($K_{CO2}$), and of CO$_2$ plus amine to give carbamate and H$^+$($K_{10}$).

In the data analysis the following equations, including equation (3), were used to fit the concentration data obtained from the $^1$H NMR integrated intensities:

$$CO_2(aq) + H_2O \overset{K_1}{\leftrightarrow} H_2CO_3.$$  (4)

$$CO_2(aq) + OH^- \overset{K_2}{\leftrightarrow} HCO_3^-.$$  (5)

$$CO_3^{2-} + H^+ \overset{K_3}{\leftrightarrow} H_2CO_3.$$  (6)

$$HCO_3^- + H^+ \overset{K_4}{\leftrightarrow} H_2O.$$  (7)

$$RNH_2 + H^+ \overset{K_5}{\leftrightarrow} RNH_3^+.$$  (8)

$$RNHCOO^- + H^+ \overset{K_6}{\leftrightarrow} RNHCOOH.$$  (9)

The equilibrium data on the reactions of CO$_2$ and the $K_6$ amine protonation equilibrium data at all four temperatures were obtained from references [24,25] and fixed during analysis. The pathway ($K_6$) given by equation (3) is much easier to study experimentally, as opposed to $K_{10}$, and hence it is easier to evaluate an equilibrium constant for this reaction (note that equation (3), $K_6$, has been the dominant reaction pathway used in the literature for which carbamate stability constants have been reported, and is often designated as $K_{aob}$[8–21]). By microscopic reversibility, it is possible to calculate values for $K_{10}$, equation (11), by the expression $K_{10} = K_9 \cdot K_{CO2}$, with equilibrium data for $K_{CO2}$ obtained from reference [26].

$$RNH_2 + CO_2 \overset{K_{10}}{\leftrightarrow} RNHCOO^- + H^+.$$  (11)

For the calculations of the concentrations of amine and carbamate only well separated peak signals were used to obtain peak integrals. All data analysis was performed in ReactLab-Equilibrium.
[27] and in-house software written in Matlab. The analysis of the equilibrium concentration data showed good agreement between the experimental and the calculated values. An example of the experimental data and fitted curves for the MEA/CO$_2$/HCl system at the four different temperatures is shown in figure 1. The markers represent experimental values based on $^1$H NMR integrated intensities and the lines represent calculated values based on the fitted model for the four different temperatures. Titrations with the other amines showed similar results, although the spectra were more complex from the increased complexity of their molecular structures. Nevertheless, individual peaks attributable to both amine and the carbamate (and their protonated forms) could be identified in all measurements, and the peak positions over the course of the titration showed similar trends to those of MEA when carbamate formation occurred.

Activity coefficient corrections were applied to all charged species. While not perfect, the corrections applied are certainly superior to the alternative of ignoring them altogether. Estimates for the activity coefficients were based on the simple Debye–Hückel equation, as given in equation (12).

$$\log_{10} \gamma_i = -\frac{A_i z_i^2 \sqrt{\mu}}{T + \sqrt{\mu}}. \tag{12}$$

In this equation $\mu$ is the ionic strength of the solution, $\gamma_i$ is the activity coefficient of species i, $z_i$ the charge on the ith component, while the parameter A is defined by the dielectric constant of the solvent and the temperature [28,29]. Nonlinear least-squares fitting of the equilibrium constants was based on standard Newton–Gauss–Levenberg/Quarquardt algorithms which also deliver error estimates for the fitted parameters [30,31]. From the data analysis log$_{10}$ $K_i$ (i.e. carbamate formation), equation (3), and log$_{10}$ $K_0$ (protonation of the carbamate anion) were obtained at $T = (288, 298, 308$ and $318)$ K.

The standard molar enthalpy change $\Delta H_m^c$ and the standard molar entropy change $\Delta S_m^c$ were calculated using a van’t Hoff plot of $\ln K$ against $1/T$, equation (13). The molar free energy change ($\Delta G_m^c$) under standard state conditions was calculated from $\Delta H_m^c$ and $\Delta S_m^c$, using equation (14).

$$\ln K = -\frac{\Delta H^c}{RT} + \frac{\Delta S^c}{R}. \tag{13}$$

$$\Delta G^c = \Delta H^c - T \Delta S^c. \tag{14}$$

2.4. Density functional theory calculations

Quantum chemical calculations were performed using Spartan’04 or ’06 (Wavefunction Inc., Irvine, CA, USA). Calculations used, unless otherwise indicated, the B3LYP density functional method, with a 6-311++G(d,p) basis set. For each molecule, all possible geometries were explored using the molecular mechanics conformer search module, and the geometries with the lowest strain energies were submitted for equilibrium geometry calculations. In several cases it was found that the second lowest strain energy configuration produced a more stable geometry, as determined by the B3LYP/6-311++G(d,p) calculations. This occurred for AP and DEA.

The charge on an atom is not a quantum chemical observable, and there is no unique way of assigning electronic charge to an atom in a molecule [32–34]. In the present study we have employed electrostatic charges, rather than Mulliken or natural charges. The Mulliken charge approach has well-known short-comings and is, moreover, sensitive to basis set size [32–34]. While electrostatic and natural charges are much less sensitive to basis set size and both have advantages and disadvantages [33,34], it was found in initial studies that the electrostatic charges offered a wider range of charge values and better differentiation between the calculated charges for very similar compounds than did natural charges. For this reason electrostatic charges were preferred. The electrostatic charge on the nitrogen atom of the amine group, Q(N)$_{ES}$, and also the oxygen atoms of the anionic carbamates, were obtained from the output available in Spartan. Note that for AP and DEA averaged values for the charge metrics were used based on the two lowest optimised geometries.

3. Results and discussion

In the present study selected series of related amines have been examined, covering primary and secondary alkanolamines and cyclic secondary amines. Not all amines formed carbamates, and reasons for this are analysed below. For those species that formed carbamates, the log$_{10}$ $K_i$ values at $T = 298$ K, as well as the derived $\Delta H_m^c$ and $\Delta S_m^c$ data are given in table 1. Full log$_{10}$ $K_i$ temperature data ($T = 288$ to $318$ K), including comparison with available literature data, and $\Delta G_m^c$ values are available in the supplementary information, table S1. Also included in table 1 are values of log$_{10}$ $K_{18}$, equation (11), which is an important reaction regarding CO$_2$ absorption by amine-based solvents in PCC applications. The log$_{10}$ $K_9$ values for the species that form carbamates range from $-3.6$ to $-5.6$, as log$_{10}$ $K_9$ is dominated by log$_{10}$ KCO$_2$, which at $T = 298$ K equals $-6.351$ [26]. Carbamate protonation, reported as log$_{10}$ $K_9$, gives the corresponding carbamic acid. The log$_{10}$ $K_9$ data and the standard molar enthalpies, $\Delta H_m^c(K_9)$ and standard molar entropies, $\Delta S_m^c(K_9)$ are given in table 1. Full temperature dependent data, as well as standard molar free energies of carbamate protonation, $\Delta G_m^c(K_9)$, are given in the supplementary information, table S2.

Few values of log$_{10}$ $K_9$ for carbamate formation have been reported, and fewer values for the standard enthalpy of carbamate formation, $\Delta H_m^c$. Most studies have concentrated on MEA and closely related compounds. Our value for log$_{10}$ $K_9 = 1.76(2)$ at $T = 298$ K is consistent with previously reported data (table S1). However, there is a considerable spread in the reported value for $\Delta H_m^c$. Values vary from $-13(2)$ to $-33(2)$ kJ mol$^{-1}$ [13,15–17], and a value for $\Delta H_m^c$ based on isothermal titration calorimetry of $-29.7(1)$ kJ mol$^{-1}$, with an accompanying value for $\Delta S_m^c$ of $-69.0(7)$ J K$^{-1}$ mol$^{-1}$, has been recently reported [20]. Our values for $\Delta H_m^c$ and $\Delta S_m^c$ are $-18(1)$ kJ mol$^{-1}$ and $-25(3)$ J K$^{-1}$ mol$^{-1}$, respectively. The former is intermediate within the reported data range for $\Delta H_m^c$, but lower than the calorimetrically-determined value, while $\Delta S_m^c$ is also lower than the reported value [20]. Smaller variations in log$_{10}$ $K_9$ and $\Delta H_m^c$ appear for DEA. Our log$_{10}$ $K_9$ value is in good agreement with the reported data (table S1), but again there is considerable variation in $\Delta H_m^c$. Values range from $-12.4$ to $-34.1$ kJ mol$^{-1}$ [14,17,21], with a calorimetrically-determined value for $\Delta H_m^c$ of $-23.7(9)$ kJ mol$^{-1}$, and a $\Delta S_m^c$ of $-63(4)$ J K$^{-1}$ mol$^{-1}$ [20]. Our values of $-18(1)$ kJ mol$^{-1}$ and $-44(4)$ J K$^{-1}$ mol$^{-1}$ for $\Delta H_m^c$ and $\Delta S_m^c$, respectively, are slightly lower than those reported in the recent calorimetric study.

3.1. Correlations of log$_{10}$ $K_9$ with electronic and structural properties; $\Delta H$–$A_S$ plots

The thermodynamic data listed in table 1 for the carbamate-forming amines can be analysed using a $\Delta H_m^c - \Delta S_m^c$ plot, as shown in figure 2. Enthalpy and entropy values derived from log$_{10}$ $K_9$ data for ammonium carbamate formation using a van’t Hoff plot are also included [35] (although the original data does not include ionic strength corrections). This plot sheds light on the structural trends for carbamate formation. The $R^2$ value (linear correlation}
coefficient) is 0.955, which effectively results from the relatively similar \( \Delta S^m \) values for carbamate formation, which has a mean \( \log_{10} K_9 \) value of 1.27 with a standard deviation of 0.56. The average \( \Delta S^m \) value is about \(-7 \) \( \text{k} \cdot \text{mol}^{-1} \). The plot therefore has predictive value, if \( \Delta H^m \) or \( \Delta S^m \) can be independently estimated either empirically, such as through comparisons with a library of related compounds, or based on theoretical calculations.

There are several trends in \( \Delta H^m \) and \( \Delta S^m \) that can be identified for amines that lead to carbamate formation:

(a) As \( \Delta H^m \) becomes more exothermic (i.e. negative), \( \Delta S^m \) also becomes more negative, thereby generating more order in the system. The complementary nature of \( \Delta H^m \) and \( \Delta S^m \) is a result of the relatively constant \( \Delta G^m \) value. As carbamate formation in equation (3) involves ionic species, it is not surprising that changes in \( \Delta S^m \) can be substantial, as there can be a large amount of solvent reorganisation and ordering of the solvent molecules associated with the reaction. Indeed, solvent reorganisation should dominate \( \Delta S^m \) in reactions involving ionic species.

(b) In the series NH₃, CO₂ → MEA-carbamate → AP-carbamate, \( \Delta H^m \) becomes more exothermic, suggesting a trend with increasing size of the aliphatic organic group, along with increasing steric hindrance around the amino nitrogen atom.

(c) For 4-PiPDM and 4-PiPDE, \( \Delta H^m \) increases with increasing length of the pendant side chain. The large negative value of \( \Delta S^m \) for 4-PiPDE is likely related to the highly fluctuating –CH₂CH₂OH group and interactions with solvent molecules through hydrogen bonding, thereby generating order, while the smaller –CH₂OH group, with one less –CH₂– group, fluctuates less and generates a less negative \( \Delta S^m \) value.

(d) In the case of the cyclic PYRR and PiP systems, \( \Delta H^m \) becomes more exothermic on decreasing the ring size, and this is consistent with a greater release of ring strain in PYRR (as discussed below) by a change in conformation and accompanying solvent reorganisation.

(e) For MiPiPZ and PiPDE, more positive values of \( \Delta S^m \) presumably result from considerable conformational change produced in their ring structures, and reorientation of the –CH₃ substituent in MiPiPZ, on carbamate formation, thereby decreasing the solvent ordering within both systems.

For the series of compounds investigated, several amines did not form carbamates under the conditions employed in the present studies (or could not be detected, such as AMP), and reasons for this are discussed below.

### 3.2. Primary amines

Of the six amines studied, MEA, AP, BIS, AMPD and TRIS, only MEA and AP formed carbamates that were observable under the reaction conditions. AMP, although it forms a carbamate [22], could not be observed under the present reaction conditions, as described above. Examination of the electrostatic charge for the amine group nitrogen atom, \( Q(N)ES \), (Table S3), shows that all calculated charges are more negative than those of the secondary amines examined, and specifically DEA, which has the least negative charge on nitrogen of any amine that forms a carbamate. Thus all of the primary amines are stronger bases than DEA based on their \( Q(N)ES \) values. Their \( \log_{10} K_9 \) values for amine protonation, which vary from 8.10 to 9.67 at \( T = 298 \) K, are also little different from that of DEA (8.86 at \( T = 298 \) K) [Supplementary information, Table S3] [25]. It also indicates that the lack of carbamate formation for BIS, AMPD and TRIS is most likely to be stereochemical in origin, rather than from a lack of basicity. Based on semi-empirical MNDO calculations, Chakraborty et al. argued that the nitrogen in AMP, relative to MEA, is softer, with a smaller HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy gap and a higher (more positive) energy for the HOMO (both effectively a measure of atom hardness) [36]. On the basis of these electronic effects, they concluded that carbamate formation was less likely in AMP. However, examination of the HOMO-LUMO gap and HOMO energy data in table S3 for the six structurally-related amines, a wider range of

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**TABLE 1**

<table>
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<tr>
<th>Amine</th>
<th>( \log_{10} K_9 )</th>
<th>( \Delta H^m ) ([kJ mol(^{-1})] for ( K_9 ))</th>
<th>( \Delta S^m ) ([J K(^{-1}) mol(^{-1})] for ( K_9 ))</th>
<th>( \log_{10} K_{10} )</th>
<th>( \Delta H^m ) ([kJ mol(^{-1})] for ( K_{10} ))</th>
<th>( \Delta S^m ) ([J K(^{-1}) mol(^{-1})] for ( K_{10} ))</th>
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<td>MEA</td>
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<td>4.59(2)</td>
<td>7.06(2)</td>
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<td>5.37(4)</td>
<td>7.39(4)</td>
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<td>9(2)</td>
<td>4.97(4)</td>
<td>8.08(4)</td>
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<tr>
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<td>-139(25)</td>
<td>4.97(3)</td>
<td>7.37(3)</td>
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<td>0.79(2)</td>
<td>-18(1)</td>
<td>-44(1)</td>
<td>5.56(2)</td>
<td>8.22(3)</td>
<td>-22(2)</td>
</tr>
<tr>
<td>PiPZ</td>
<td>1.49(1)</td>
<td>-23(1)</td>
<td>-47(3)</td>
<td>4.86(2)</td>
<td>9.02(2)</td>
<td>-13(3)</td>
</tr>
<tr>
<td>MPiPZ</td>
<td>0.92(2)</td>
<td>-7(1)</td>
<td>5(1)</td>
<td>5.43(2)</td>
<td>7.05(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>PyRR</td>
<td>2.69(3)</td>
<td>-50(4)</td>
<td>-117(3)</td>
<td>3.66(3)</td>
<td>7.65(3)</td>
<td>30(3)</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.328(4)</td>
<td>-11(1)</td>
<td>-31(2)</td>
<td>6.02(2)</td>
<td>6.76(5)</td>
<td>11(3)</td>
</tr>
</tbody>
</table>

\( ^a \) Original equilibrium constant data from reference [35]; \( \mu = 0.5 \) M.
species than used by Chakraborty et al., shows no trends that correlate with carbamate formation.

In the sequence MEA → AP → AMP, which involves successive replacement of a hydrogen on the carbon x to the amine group by a –CH3 group, QN3 becomes progressively more negative. The increasing negative charge is expected as the –CH3 group is a good electron donor. Electron donation is only slightly reduced by replacing a hydrogen on an –OH group by an –OH, as found in BIS relative to AP and TRIS relative to AMP, such that the expected increase in negative charge on nitrogen is not as great in both cases. This is not surprising, given the highly electronegative nature of oxygen. Addition of a –CH2 group at the carbon x to the amine group in BIS, to give AMPD, results in an increasing negative charge on nitrogen, as expected.

While MEA forms a carbamate, log10 K9 decreases in AP, which has a –CH3 group on the carbon x to the amine nitrogen. Addition of a second –CH3 group to the x carbon gives AMP, which does not form a carbamate that is observable under our reaction conditions. The trend is observed despite QN3 becoming progressively more negative in the sequence MEA → AP → AMP, and suggests a stereochemical effect from the –CH3 group. Likewise, BIS, AMPD and TRIS all have more negative charges on nitrogen than does MEA, yet they do not form carbamates. All of these species have –CH2OH and –CH3 groups located at the x carbon, and the stereochemical effect of the former is apparently greater than that of the latter (which is demonstrated by the fact that BIS does not form a carbamate, yet AP does), so that it is not surprising that these species do not form carbamates. Note that placement of a –CH3 group on the carbon y to the nitrogen atom, to give 1-amino-2-propanol (1-A-2-P), does result in carbamate formation [37]. Thus there is little stereochemical effect from the –CH3 group further away from the amine nitrogen atom.

The reduced stability of a carbamate with one or more –CH3 groups on the x carbon is caused by the close approach of the oxygen atoms of the –COO– group to the hydrogen atoms of one or more close –CH3 groups. This introduces a significant stereochemical strain in the molecule. da Silva and Svendsen compared the equilibrium geometries of the carbamates of MEA and AMP using B3LYP/6-311++G(d,p) calculations [38]. These calculations have been repeated in the present study, with almost identical results, and supplemented with equivalent calculations on the carbamates of AP and 1-A-2-P. The relevant data appear in table 2. The N–C (OH) angle decreases from 114.55° (114.53° [38]) in MEA-carbamate to 111.40° (111.38° [38]) in AMP-carbamate as a result of the presence of the two –CH3 groups on the carbon x to the amine nitrogen atom. This indicates that the nitrogen atom, along with the carbamate functionality, is forced away from a –CH3 on the x carbon [38]. The analogous values for AP-carbamate and 1-A-2-P-carbamate are 113.06° and 114.63°, respectively, the former intermediate between those of the MEA- and AMP-carbamates, as expected, as it has only one close –CH3 group compared to two in AMP-carbamate, while the angle in 1-A-2-P-carbamate is similar to that in MEA-carbamate, showing that there is almost no effect from a –CH3 group on the β-carbon. A consequence of a smaller N–C–(OH) angle is that the intramolecular (OC)O–H(O) bond becomes shorter, but also that the (O2)C–N–C angle increases (table 2). The O–C–(H–O)–C–N and H–C–O bond angles vary slightly (differences of only 1.50, 1.21 and 0.68°, respectively, between the MEA- and AMP-carbamates). The steric effect is also demonstrated by the progressively decreasing intramolecular hydrogen bond length, with (OC)O–H(O) distances similar for the carbamates of MEA and 1-A-2-P, and decreasing from MEA-carbamate by 0.0020 nm for AP-carbamate and a further 0.0022 nm in the case of AMP-carbamate.

An interesting comparison can also be made with carbamates of the butylamines [10]. The analogous data is given in table 2. In this case the N–C–C angles decrease from 116.5° in isobutylamine-carbamate to 109.67° (note, average of three angles!) in t-butylation-carbamate, as log10 K9 progressively decreases. This is the same trend as found above for the alkanolamines-carbamates. The (O2)C–N–C angle is constant except for t-butylation-carbamate when it increases significantly, while the closest non-bonding (C=O)–H(C) distance, other than that to the amine hydrogen, is fairly constant in the four carbamate structures. Interestingly, t-butylation forms a carbamate, yet it has three –CH3 groups on the carbon that is x to the –NH2 group. The formation of a carbamate in this case appears to be linked to a longer N–C(O2) bond in all of the butylamine-carbamate structures compared to the alkylamine-carbamates, thereby reducing steric strain from the –CH3 group(s) (table 2). The same lengthening of the N–C(O2) bond is observed in ethylamine-carbamate (0.1460 nm) relative to MEA-carbamate (0.1443 nm). This highlights the differences between the alkylamines and amines in carbamate formation.

3.3. Secondary amines; cyclic amines

DEA, PIPD, 4-PIPDM, 4-PIPDE, PIPZ, MPIPZ, MORP, TMORP and PYRR all form carbamates. Note that PIPZ also forms a dicarbamate [39]. No carbamate formation was observed for 2-PIPDM, 2-PIPDE or 3-PIPDM. For all species the nitrogen charge varies from −0.44 to −0.67 e− (supplementary information, table S3) with the least negative charge found in DEA, which forms a carbamate. The fact that there are two –CH2– groups bound to nitrogen might suggest that a stereoechemical problem could reduce carbamate stability.

### TABLE 2

Log10 K9, and the geometrically important distances and angles for the carbamates of MEA, 1-amino-2-propanol (1-A-2-P), AP, AMP and the isomeric forms of the butylamines (B3LYP/6-311++G(d,p) calculations).

<table>
<thead>
<tr>
<th>Parent amine</th>
<th>log10 K9 (T = 291 K; μ = 0 M)</th>
<th>N–C–C angles (°)</th>
<th>(O2)C–N–C angle (°)</th>
<th>d[(O–H)] (nm)</th>
<th>d[(O2)C–N] (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>1.76</td>
<td>114.55</td>
<td>121.56</td>
<td>0.1648</td>
<td>0.1443</td>
</tr>
<tr>
<td>1-A-2-P</td>
<td>Carbamate formed</td>
<td>114.63</td>
<td>121.42</td>
<td>0.1635</td>
<td>0.1442</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.98</td>
<td>113.06</td>
<td>0.1628</td>
<td>0.1444</td>
</tr>
<tr>
<td>AP</td>
<td>Very unstable carbamate formed</td>
<td>114.40</td>
<td>125.51</td>
<td>0.1606</td>
<td>0.1445</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkanolamine-carbamates</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
</tr>
<tr>
<td>1-A-2-P</td>
</tr>
<tr>
<td>Carbamate formed</td>
</tr>
<tr>
<td>AP</td>
</tr>
<tr>
<td>Very unstable carbamate formed</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amine-carbamates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl</td>
</tr>
<tr>
<td>n-Butyl</td>
</tr>
<tr>
<td>sec-Butyl</td>
</tr>
<tr>
<td>tert-Butyl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parent amine</th>
<th>log10 K9 (T = 291 K)</th>
<th>N–C–C angles (°)</th>
<th>(O2)C–N–C angle (°)</th>
<th>d[(C=O)–H(C)] (nm)</th>
<th>d[(O2)C–N] (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl</td>
<td>1.99</td>
<td>161.50</td>
<td>120.14</td>
<td>0.2492</td>
<td>0.1457</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>1.79</td>
<td>116.11</td>
<td>120.07</td>
<td>0.2483</td>
<td>0.1458</td>
</tr>
<tr>
<td>sec-Butyl</td>
<td>1.31</td>
<td>111.04, 112.90 av. 111.97</td>
<td>120.15</td>
<td>0.2313</td>
<td>0.1464</td>
</tr>
<tr>
<td>tert-Butyl</td>
<td>0.85</td>
<td>107.01, 109.67, 112.34 av. 109.67</td>
<td>123.79</td>
<td>0.2332</td>
<td>0.1461</td>
</tr>
</tbody>
</table>

a Reference [37].
b N–C–(OH) angle.
c Reference [10].
However, the $\log_{10} K_9$ values of PIPD (cyclic) and DEA (acrylic) are not that much less than that of MEA, so that having two $-CH_2-$ groups bound to the nitrogen in a secondary amine does not cause a significant stereochemical problem, such that carbamate formation does not occur. DEA has the freedom to rotate both of its $-CH_2-CH_2OH$ arms around nitrogen (and hence sweep out large volumes of space and thus block access of CO$_2$ to the amine nitrogen), unlike the ring systems, and also has a lower $\log_{10} K_9$ value than does PIPD. This, therefore, suggests that there may be some minor steric influence in DEA, although their $\log_{10} K_9$ values do parallel the $Q(N)_{ES}$ values.

All of the cyclic amines have more negative nitrogen charges than does DEA, and also have higher $\log_{10} K_6$ (amine protonation) values [25], which indicates that lack of carbamate formation for 2-PIPDM, 2-PIPDE and 3-PIPDM must be stereochemical rather than electronic in nature, or occurs for another reason. Steric hindrance cannot occur in 3-PIPDM, as the $-CH_2OH$ group is too far away from the secondary amine nitrogen atom, while 2-PIPDM is structurally similar to DEA (which does form a carbamate) and 2-PIPDE also has some structural similarities to DEA. The relative energies of the potential carbamates of 2-PIPDM and 3-PIPDM, and 2-PIPDE were actually $-34.1$ and $-40.1$, and $-42.8$ kJ mol$^{-1}$, respectively, more stable than the isomeric 4-PIPDM- and 4-PIPDE-carbamates (thermal and zero point energies are likely to be almost identical in these species, and were not included in the above calculations).

The relative increase in stability for 2-PIPDM, 3-PIPDM and 2-PIPDE is caused by the presence of intramolecular hydrogen bonding, which is not possible in 4-PIPDM and 4-PIPDE. All 2- and 3-substituted amines should therefore form carbamates based on electronic (i.e. their $Q(N)_{ES}$) values) and stereochemical considerations. No clear trend was observed in the HOMO-LUMO gap, or in the energy of the HOMO itself for these species (supplementary information, table S3). Thus it is suggested that 2-PIPDM, 2-PIPDE and 3-PIPDM do not form carbamates because the parent amines all have strong intramolecular hydrogen bonds. Further, B3LYP/6-311+G(d,p) calculations give intramolecular N $\cdots$ H(O) distances for 2-PIPDM, 2-PIPDE, and 3-PIPDM of 0.2316, 0.2021 and 0.2035 nm, respectively, for their equilibrium geometries. Diagrams of the equilibrium geometries of these three substituted piperidines are shown in the supplementary information, figure S4. It is assumed that these interactions are strong enough in aqueous solution to prevent carbamate formation, despite competition from hydrogen bonding to the solvent water molecules. While the calculated equilibrium geometries have N $\cdots$ H(O) intramolecular hydrogen bonds, alternative structures with H(O) $\cdots$ H(N) intramolecular hydrogen bonds may also be drawn. However, for 2-PIPDM, 2-PIPDE and 3-PIPDM these are $+19.0$, $+24.2$ and $+19.5$ kJ mol$^{-1}$, respectively, less stable than the structures with N $\cdots$ H(O) bonds (B3LYP/6-311+G$^{*}$ calculations).

In the absence of steric effects or strong intramolecular hydrogen bonding, it would be expected that formation of a carbamate would depend on the basicity of the amine nitrogen atom, and hence be related to the electronic charge on the nitrogen atom. However, for those species that do form carbamates, there was no overall correlation of $\log_{10} K_9$ with $Q(N)_{ES}$, even when taking a selected subset of data, such as the cyclic amines. Moreover, there was no strong correlation with the $\log_{10} K_9$ of the amine, or just for the cyclic amines. Attempted correlation with the HOMO-LUMO energy gap, or the energy of the HOMO, was also unsuccessful. This is not surprising as the make-up of the HOMO and LUMO are complex in these systems, involving contributions from several different types of atoms.

Within the ring systems steric strain will have a major effect on the basicity of the nitrogen atom. In cyclic systems basicity depends on the size of the ring and the nature of the heteroatoms (e.g. cyclic amines vs. cyclic phosphines) [40]. For the present group of amines, there are rings of different sizes, different types of substituents, and some with multiple as well as different heteroatoms. It is thus not surprising that trends are hard to discern given the limited range of species examined. However, some measure of ring strain at the secondary nitrogen can be gained from the magnitude of the internal C$\cdots$C$\cdots$C ring angle (based on B3LYP/6-311+G(d,p) calculations). When the neutral amines are arranged in decreasing order of $\log_{10} K_9$ (together with their calculated C$\cdots$C$\cdots$C angles) as follows:

\[
\text{PYRR}(105.26^\circ) > \text{PIPZ}(111.79^\circ) > 4 - \text{PIPDM}(112.32^\circ) > \text{PIPDE}(112.13^\circ) > \text{PIPD}(112.62^\circ) > \text{MORP}(111.06^\circ) > \text{MPIPZ}(111.31^\circ) > \text{TMORP}(114.18^\circ)
\]

the C$\cdots$C$\cdots$C angle correlates inversely with $\log_{10} K_9$. The smallest angle is found in the 5-membered ring PYRR, which has the highest $\log_{10} K_9$, while the largest angle is found in the 6-membered ring of TMORP, which has the lowest $\log_{10} K_9$. The remaining amines can be grouped together (with an average C$\cdots$C$\cdots$C angle $= 111.87^\circ$), and have $\log_{10} K_9$ values that are similar and intermediate between those of PYRR and TMORP. The calculated C$\cdots$H$\cdots$H angles vary accordingly, 112.75$^\circ$ for PYRR, an average of 110.63$^\circ$ for the intermediate six cyclic systems, and 110.04$^\circ$ for TMORP. Thus the sum of the bond angles around nitrogen increases from 330.76$^\circ$ in PYRR to 334.26$^\circ$ in TMORP. This indicates that the nitrogen environment becomes more planar, so that the lone pair on nitrogen assumes more p character from PYRR to TMORP, making it a weaker base towards an acid and consistent with the trend in $\log_{10} K_9$. However, the lack of absolute correlation of $\log_{10} K_9$ with the C$\cdots$C$\cdots$C angle suggests that several other factors play a role. For example, the least negative charges are found on the two amines with the lowest $\log_{10} K_9$ values, MPIPZ and TMORP, while the other cyclic amines all have similar values of $Q(N)_{ES}$. Electronic charge is, therefore, one such factor.

On formation of a carbamate, the internal ring C$\cdots$C$\cdots$C angle increases relative to that in the parent amine, and the nitrogen becomes close to coplanar with the surrounding three carbon atoms. In the X-ray crystal structures of the PIPD-carbamate and MORP-carbamate anions, the internal C$\cdots$C$\cdots$C angles are 114.44$^\circ$ and 115.1$^\circ$, respectively [41,42]. If the nitrogen and three carbon atoms were rigorously coplanar, the ($\alpha_2$)$\cdots$C$\cdots$C$\cdots$C dihedral angle would be 180$^\circ$ (the numbers following the carbon atoms are their positions around the piperidine ring). The experimental values for PIPD-carbamate and MORP-carbamate are 163.4$^\circ$ and 165.2$^\circ$, respectively, showing that the nitrogen is slightly displaced from the plane of the surrounding three carbon atoms. Similar (and more extensive) data comes from B3LYP/6-311+G(d,p) calculations. In the carbamates of PYRR, PIPD, MORP and TMORP, the calculated C$\cdots$C$\cdots$C angles are 108.36$^\circ$, 112.39$^\circ$, and 114.97$^\circ$, respectively, all greater than those in the free amines. Thus one consequence on formation of carbamates is the increase in internal C$\cdots$C$\cdots$C angle, as the environment around nitrogen becomes more planar (i.e. bonding tends towards sp$^3$ hybridization, with the nitrogen lone pair having higher p character). The change in C$\cdots$N$\cdots$C angle from the neutral amine to amine-carbamate is PYRR (+3.10$^\circ$) > PIPD (+1.35$^\circ$) > MORP (+1.33$^\circ$) > TMORP (+0.79$^\circ$). The significant change for PYRR (thereby decreasing ring strain and the nitrogen approaching sp$^3$ hybridization in the carbamate) is consistent with the high value of $\log_{10} K_9$, while the low value for TMORP is consistent with the observation that the internal ring angle does not change greatly on carbamate formation (and actually moves further away from sp$^3$ hybridization towards sp$^2$ (+p) hybridization). For PYRR, the C$\cdots$C$\cdots$C angle is able to increase from 105.26$^\circ$ in the free amine to 112.39$^\circ$ in the carbamate.
3.4. Amine carbamic acids

A further result of the fitting procedures of the $^1$H NMR data was the determination of the protonation constants, $\log_{10} K_n$, for the carbamates. These are difficult to obtain accurately, as the concentration of the carbamic acid is very low under any conditions. Protonation of carbamate requires a pH at which the overall equilibrium favours the release of CO$_2$. Few data are available for comparison, and of the present library of amines, only values for MEA and AP have been reported. The $\log_{10} K_6$ for MEA has been reported as 7.49(2) at $T = 303$ K [19] and 7.93(7) at $T = 298$ K [20], while that of AP is 8.0(2) at $T = 303$ K [19]. For MEA, there is also a value for $\log_{10} K_8$ of 6.5 at $T = 298$ K based on kinetic studies [23]. The present values, 7.06 for MEA and 7.39 for AP at $T = 298$ K are in the range of the published values.

In the present work, attempts to correlate $\log_{10} K_n$ with the calculated electrostatic charges on the oxygen atoms, Q(O)$_{138}$ of the carbamate anions were unsuccessful. However, this result is not surprising given the range of structures studied, despite the site of protonation being somewhat removed from the rest of the carbamate anion. Again there are no correlations with the HOMOLUMO energy gap or the energy of the HOMO itself for the carbamate anions.

The thermodynamic data for protonation of the carbamate anions (supplementary information, table S2) also can be analysed using a $\Delta H_m^o(K_8) - \Delta S_m^o(K_8)$ plot. This is shown in figure 3. For this relationship $R^2 = 0.967$. However, such a correlation is not surprising for protonation of the carbamate anions, as a similar correlation(s) exists for protonation of the aliphatic carbamate anions from C3 to C6 (see supplementary information, figure S5) [43,44]. These correlations result from similar $\Delta G_m^o$ values for protonation within each of the series, but different (mean) values between series (carbamates: $\Delta G_m^o = -43.1$ kJ mol$^{-1}$; carboxylates: $-27.40$ kJ mol$^{-1}$ for anions of the type R$_1R_2$CH–COO$^-$ and $-28.55$ kJ mol$^{-1}$ for the R$_1R_2R_3$–COO$^-$ anions). In the present case, changes in composition and basicity of the parent amines appear to have little effect on the carbamate protonation constants. This is not surprising as the site of protonation is far removed both spatially and electronically from the rest of the molecule.

Note that PIPZ and MPIPZ have been included in the correlation given in figure 3. Both of these amines have second amine groups, and protonation could take place at the non-carbamate amine site rather than at a carbamate oxygen atom. In this regard it should be noted that the $\Delta H_m^o(K_8)$ values for carbamate protonation for PIPZ and MPIPZ are the least exothermic, and their $\Delta S_m^o(K_8)$ values the most positive, of all the amine species investigated in the present study. However, the $\Delta H_m^o(K_6)$ and $\Delta S_m^o(K_8)$ values for PIPZ and MPIPZ fit nicely into the correlation. Moreover, the calculated electrostatic charges on the carbamate oxygen atoms, Q(O)$_{138}$ are $-0.746$ and $-0.753$ e$^-$ for PIPZ and MPIPZ, respectively, which are more negative than the Q(N)$_{138}$ values for the second amine site, $-0.572$ and $-0.145$ e$^-$, respectively, suggesting that protonation is likely to occur at the carbamate oxygen atoms.

3.5. Relevance of the $\Delta H_m^o - \Delta S_m^o$ plots for carbamate formation and protonation to CO$_2$ absorption/desorption in PCC applications

Recently, McCann et al. developed a model for the prediction of CO$_2$ capacity and associated enthalpy changes in amine-based solvents during absorption/desorption of CO$_2$ [45]. For MEA, assuming a typical flue gas composition with a CO$_2$ pressure of 12 kPa, a 30 wt% MEA solution, and absorption and desorption temperatures of (40 and 100) °C, respectively, the total enthalpy for CO$_2$ desorption at $T = 313$ K was shown to be $\sim 83$ kJ mol$^{-1}$. Of this, $\sim 50$ kJ mol$^{-1}$ is associated with deprotonation of MEA (together with a minor contribution involving ionisation of H$_2$O). This contribution was found to be more important than the formation of gaseous CO$_2$ from CO$_2$(aq) and H$_2$CO$_3$ ($\sim 21$ kJ mol$^{-1}$), or from the decomposition of MEA-carbamate ($\sim 12$ kJ mol$^{-1}$). It is apparent that of the chemical reactions that occur in solution, the contribution from protonation/deprotonation of the amine to the overall enthalpy change is highly significant. When carbamate formation occurs, a significant, although smaller, contribution to the enthalpy change also occurs.

The overall equilibrium constant for the reaction of CO$_2$ with amine (in a 1:2 ratio), as given by equation (1), is:

$$K_e = \frac{[\text{RNHCOO}^+][\text{RNH}_2]}{[\text{CO}_2][\text{RNH}_2]^+]}. \quad (15)$$

This can be related to the equilibrium constants for equation (3) ($K_9$), equation (5) ($K_9$), equation (9) ($K_9$) and $K_m$, the ionisation of water, by the expression $K_e = (K_9)/(K_9) \cdot (K_9)/K_m$. The $\Delta H_m^o$ and $\Delta S_m^o$ values follow accordingly, with data on the CO$_2$–H$_2$CO$_3$ system and amine protonation coming from published data [24–26]. Thus provided data on carbamate formation ($K_9$) and amine protonation ($K_9$) are known, thermodynamic data for equation (1) can be calculated, effectively defining all amine-based enthalpy changes in solution in PCC applications.

Previously, we have provided correlations of the enthalpy of protonation of an amine with structure, leading to suggestions for the best amine(s) to employ in PCC applications, based on this criterion [25]. Amine protonation/deprotonation provides the major contribution to the enthalpy changes that occur in solution, and a more exothermic $\Delta H_m^o$ for protonation may be regarded as important as it results in a greater difference in $\log_{10} K_9$ between the absorber and stripper and hence to an increased CO$_2$ absorption-regeneration efficiency for the process. On carbamate formation, the types of correlations found in figures 2 and 3 can also provide information on enthalpy contributions, in this case for carbamate formation and carbamate protonation. While there is as yet only a limited range of data available to provide structural and thermodynamic insights, some interpretation has been provided above. In order to decide on the best amine(s) for PCC applications these structure-enthalpy relationships need to be considered, along with consideration of the amine protonation/deprotonation reactions that occur in solution. Of course, other factors are also important, including, for example, the rate of amine degradation and disposal and the toxicity of the resulting products.
4. Conclusions

The formation of selected series of carbamates has been investigated using $^1$H NMR studies at four different temperatures ranging from $T = (288$ to $318)$ K. Many of these values have been obtained for the first time. van’t Hoff analyses have resulted in standard molar enthalpies and entropies for carbamate formation, and trends for related species have been discussed. A $\Delta H_m^\circ - \Delta S_m^\circ$ plot shows a linear relationship which provides a guide to the selection of an amine for PCC purposes based on carbamate formation. A $\Delta H_m^\circ(K_b)$–$\Delta S_m^\circ(K_b)$ plot for carbamate protonation also produces a linear correlation.

Acknowledgements

Financial support by a CSIRO Flagship grant is acknowledged, as is a University of Newcastle Tom Farrell scholarship (DF). The authors would like to thank Prof. A. McCluskey for access to Spartan’04 and Dr M. Bowyer to Spartan’06.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2012.03.030.

References

Publication-2

Protonation constants and thermodynamic properties of amines for post combustion capture of CO₂

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Accepted: Journal of Chemical Thermodynamics
(March 2012)
Protonation constants and thermodynamic properties of amines for post combustion capture of CO₂

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A R T I C L E   I N F O

Article history:
Received 1 December 2011
Received in revised form 21 February 2012
Accepted 24 February 2012
Available online 5 March 2012

Keywords:
Post combustion capture of CO₂
Amine protonation constants
Standard molar enthalpy of protonation
Standard molar entropy of protonation
CO₂ absorption

A B S T R A C T

The leading process for the post combustion capture (PCC) of CO₂ from coal-fired power stations and hence reduction in greenhouse gases involves capture by aqueous amine solutions. Of the reactions that occur in solution, which include CO₂ hydration, de-protonation of carbonic acid, amine protonation and carbamate formation, the protonation of the amine in the absorber and its subsequent de-protonation in the stripper involve the greatest enthalpy changes. In this study, protonation constants (reported as log10 Kprot) of selected series of primary, secondary and tertiary alkanolamines/amines over the temperature range 288–318 K are reported. Selected series studied involve primary, secondary and tertiary mono-, di- and tri-alkanolamines, secondary amines including heterocyclic species, and both –CH₂OH and –CH₂CH₂OH substituted piperidines. van’t Hoff analyses have resulted in the standard molar enthalpies, ΔHm°, and molar entropies, ΔSm°, of protonation. Trends in ΔHm° are correlated with systematic changes in composition and structure of the selected series of amines/alkanolamines, while ΔHm°–ΔSm° plots generated linear correlations for the mono-, di-, and tri-alkanolamines, the –CH₂OH and –CH₂CH₂OH substituted piperidines, and the alkylamines. These relationships provide a guide to the selection of an amine(s) solvent for CO₂ capture, based on a greater difference in log10 Kprot between the absorber and stripper temperatures.

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de-protonation of MEA. In terms of enthalpy changes, this contribution is more important than the formation of gaseous CO$_2$ from CO$_2$(aq) and H$_2$CO$_3$ (\textasciitilde 21 kJ mol$^{-1}$), or the decomposition of MEA-carbamate (\textasciitilde 12 kJ mol$^{-1}$). While the heat capacity of the solution was not included in the above study, it is apparent that of the chemical reactions that occur in solution, the contribution of amine protonation/de-protonation to the enthalpy change is highly significant, and consequently to the energy required for solvent regeneration. In cases where carbamate formation does not occur, such as for sterically-hindered and tertiary alkanolamines/amines, the enthalpy contribution from the protonation/de-protonation of an amine is even more important. Furthermore, a more exothermic $\Delta H^0$ is regarded as important to enthalpy changes in solution, as it results in a greater difference in $\log_{10} K_{prot}$ between the absorber and stripper and hence to an increased energy efficiency for the process and hence reduced energy costs. Thus knowledge of the temperature dependence of the $\log_{10} K_{prot}$ values for protonation, as well as the accompanying $\Delta H_m^0$ and $\Delta S_m^0$ values, is important in the selection of an amine (or amines) for FCC applications. The protonation constants of many alkanolamines/amines are available in the literature under standard state conditions (see, for example, [4]); however, the temperature dependence of many constants is often not reported. For many obscure and less common species, potentially relevant to FCC by providing trends in, for example, $K_{prot}$ as well as the enthalpy of protonation as the structure is varied, this data is unknown. In the present study, potentiometric titrations have been employed for the determination of $\log_{10} K_{prot}$ values, including their temperature dependence from 288 to 318 K, for structurally related series of acyclic, cyclic and substituted cyclic alkanolamines/amines. Thus data on all of these alkanolamines/amines have been obtained under the same conditions, thereby allowing accurate comparisons of trends in the $\log_{10} K_{prot}$ values and derived data as their structures are varied. The species include primary, secondary and tertiary mono-, di- and tri-alkanolamines, which involve increasing numbers of added $\text{-OH}$ groups, along with $\text{-CH}_3$ for $\text{-H}$ substitutions at the $\alpha$-carbon for primary alkanolamines; secondary cyclic amines with varying heteroatoms (i.e. piperidine, piperazine, $N$-methylpiperazine, morpholine and thiomorpholine); and the sequences of $\text{-CH}_2\text{OH}$ and $\text{-CH}_2\text{CH}_2\text{OH}$ substituted piperidines. van’t Hoff analyses have yielded the prot values and derived data as their structures are varied. Fitting of the titration data and transformed into pH using our software [5]. At each temperature the electrode was calibrated for concentration (i.e. pH = $-\log_{10}$ [H$^+$]) by titrating hydrochloric acid of known concentration with standardised NaOH solution. The principle is based on GLEE (glass electrode evaluation), a new computer program for glass electrode calibration [6]. The $pK_w$ values for the different temperatures were taken from reference [4]. For each set of titrations on an amine, a known mass of amine was initially acidified by addition of standardised HCl (0.015 M) in a ratio of 1:1.5 amine:HCl (diamines, 1:3). This gave an acidified solution of amine of 0.010 M, which was accurately known. From this acid solution 10.00 cm$^3$ was transferred to the thermostatted titration vessel and back titrated with standardised NaOH (0.10 M) to high pH. The titrations were repeated a minimum of three times to ensure reproducibility. The titrations were performed at $T$ = (288, 298, 308 and 318) K (\textpm 0.1 K). Nitrogen was bubbled through the acidified solutions for 10 minutes prior to beginning the titrations and subsequently passed above the solutions during the actual titrations to ensure exclusion of CO$_2$. The alkanolamines/amines protonate as described in Eq. (1), while for the diamines piperazine and 1-methylpiperazine there are two protonation steps, Eqs. (1) and (2) (note, $K_{prot1}$ = $K_{prot}$ for amines that have only one protonation step):

$$A + H^+ \underset{\text{i1}}{\overset{\text{K_{prot1}}}{\rightleftharpoons}} AH^+ \quad (1)$$

$$AH^+ + H^+ \underset{\text{i2}}{\overset{\text{K_{prot2}}}{\rightleftharpoons}} AH^+^2^+ \quad (2)$$

Rather than maintaining approximately constant ionic strength using excess inert salts in the titrations, activity coefficients were applied to all charged species. This results straightforward in thermodynamically correct protonation constants at zero ionic strength. Activity coefficient corrections were calculated from the Debye–Hückel equation (3):

$$\log_{10} \gamma_i = -\frac{A \zeta^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (3)$$

In this equation, the activity coefficient $\gamma_i$ is a function of the ionic strength $\mu$, the charge $\zeta_i$ of the $i$th component, and the parameter $A$, which is defined by the dielectric constant of the solvent and the temperature [7,8]. In the procedure employed, $\log_{10} K_{prot}$ values (for the diamines $\log_{10} K_{prot1}$ and $\log_{10} K_{prot2}$) were determined at the four temperatures. Fitting of the titration data was achieved using in-house software written in Matlab. The standard state molar enthalpy and entropy changes ($\Delta H_m^0$ and $\Delta S_m^0$) of the protonation(s) of each amine were calculated using a van't Hoff plot of $\ln K_{prot}$ against $1/T$, Eq. (4).

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4)$$

The molar standard state free energy ($\Delta G_m^0$) was calculated from $\Delta H_m^0$ and $\Delta S_m^0$ by:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

2.2. Potentiometric titrations

Potentiometric titrations were performed using a 665 Metrohm dosimatis automated burette system, with a jacketed titration vessel that was connected to a Melcor liquid chiller (Model MRC300DH2-HT-DV) that was used to control temperature. A Metrohm combined micro-pH glass electrode (Model 6.0234.100) was used for the titrations, interfaced with a National Instruments NI-DAQ 7 board arraying and translating the electrode signal, which was recorded in mV. The mV signal was used directly in the analysis of the titration data and transformed into pH using our software [5].
2.3. Density functional theory calculations

Quantum chemical calculations were performed using Spartan ‘04 (Wavefunction Inc., Irvine, CA, USA). Calculations used the B3LYP method, with a 6-311G* basis set. For each species (neutral or protonated), the molecular mechanics conformer search module was used to explore all possible geometries, and those two or three conformers with the lowest strain energies were submitted for equilibrium geometry calculations. The standard criteria for convergence in Spartan ‘04 were employed.

3. Results and discussion

3.1. Protonation constants of alkanolamines/amines

The alkanolamines/amines investigated in this work are given in table 2, along with the log10 \( K_{prot} \) values at \( T = 298 \) K and their \( \Delta H_m^\circ \) and \( \Delta S_m^\circ \) values. Representations of the structures can be found in the Supplementary data, figure S1, along with full log10 \( K_{prot} \) temperature data (288, 298, 308 and 318) K in tables S1–S4. Data on several species are reported here for the first time: these

### Table 1

<table>
<thead>
<tr>
<th>Amine</th>
<th>Mass fraction purity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary amines</strong></td>
<td></td>
</tr>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>≥0.99</td>
</tr>
<tr>
<td>Serinol (BIS)</td>
<td>0.98</td>
</tr>
<tr>
<td>2-Amino-2-hydroxymethyl-1,3-propandiol (TRIS)</td>
<td>≥0.999</td>
</tr>
<tr>
<td>2-Amino-1-propanol (AP)</td>
<td>0.96</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1-propanol hydrochloride (AMP)</td>
<td>≥0.99</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1,3-propandiol (AMPD)</td>
<td>≥0.99</td>
</tr>
<tr>
<td><strong>Tertiary amines</strong></td>
<td></td>
</tr>
<tr>
<td>Triethanolamine (TEA)</td>
<td>0.98</td>
</tr>
<tr>
<td>N-methyldiethanolamine (N-MDEA)</td>
<td>&gt;0.99</td>
</tr>
<tr>
<td>N,N-dimethylethanolamine (N,N-DMEA)</td>
<td>≥0.995</td>
</tr>
<tr>
<td><strong>Secondary amines</strong></td>
<td></td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>0.985</td>
</tr>
<tr>
<td>Morpholine (MORP)</td>
<td>≥0.99</td>
</tr>
<tr>
<td>Thiomorpholine (TMORP)</td>
<td>0.98</td>
</tr>
<tr>
<td>1-Methylpiperazine (MPIPZ)</td>
<td>0.99</td>
</tr>
<tr>
<td>Piperidine (PIPZ)</td>
<td>0.99</td>
</tr>
<tr>
<td>2-Piperidinemethanol (2-PIPDM)</td>
<td>0.97</td>
</tr>
<tr>
<td>3-Piperidinemethanol (3-PIPDM)</td>
<td>0.96</td>
</tr>
<tr>
<td>4-Piperidinemethanol (4-PIPDM)</td>
<td>0.97</td>
</tr>
<tr>
<td>2-Piperidineethanol (2-PIPDE)</td>
<td>0.90</td>
</tr>
<tr>
<td>4-Piperidineethanol (4-PIPDE)</td>
<td>0.97</td>
</tr>
</tbody>
</table>

### Table 2

Log10 \( K_{prot} \), and \( \Delta H_m^\circ \) and \( \Delta S_m^\circ \) values for primary, secondary, tertiary alkanolamines/amines, and ammonia. (Standard deviations in all values are given in parentheses.)

<table>
<thead>
<tr>
<th>Amine</th>
<th>Log10 ( K_{prot} ) (298 K; ( \mu = 0 ) M)</th>
<th>( \Delta H_m^\circ )/kJ mol(^{-1})</th>
<th>( \Delta S_m^\circ )/J K(^{-1}) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary amines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Aminoethanol (monoethanolamine) (MEA)</td>
<td>9.44(1)</td>
<td>−41(2)</td>
<td>42(5)</td>
</tr>
<tr>
<td>2-Amino-1,3-propanol (serinol) (BIS)</td>
<td>8.81(2)</td>
<td>−37.8(1)</td>
<td>41(4)</td>
</tr>
<tr>
<td>2-Amino-2-hydroxymethyl-1,3-propandiol (TRIS)</td>
<td>8.10(1)</td>
<td>−45.4(1)</td>
<td>3(3)</td>
</tr>
<tr>
<td>2-Amino-1-propanol (AP)</td>
<td>9.52(1)</td>
<td>−47(1)</td>
<td>25(2)</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1-propanol (AMP)</td>
<td>9.67(1)</td>
<td>−46.6(3)</td>
<td>29(1)</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1,3-propandiol (AMPD)</td>
<td>8.84(1)</td>
<td>−47.2(9)</td>
<td>11(3)</td>
</tr>
<tr>
<td><strong>Secondary amines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2'-Imidodihanol (diethanolamine) (DEA)</td>
<td>8.86(1)</td>
<td>−37.5(7)</td>
<td>43(2)</td>
</tr>
<tr>
<td>Piperidine (PIP)</td>
<td>11.14(2)</td>
<td>−40(3)</td>
<td>80(8)</td>
</tr>
<tr>
<td>2-Piperidinemethanol (2-PIPDM)</td>
<td>10.11(1)</td>
<td>−46(2)</td>
<td>38(8)</td>
</tr>
<tr>
<td>3-Piperidinemethanol (3-PIPDM)</td>
<td>10.39(2)</td>
<td>−46.3(2)</td>
<td>63(1)</td>
</tr>
<tr>
<td>4-Piperidinemethanol (4-PIPDM)</td>
<td>10.56(3)</td>
<td>−34(2)</td>
<td>86(6)</td>
</tr>
<tr>
<td>2-Piperidineethanol (2-PIPDE)</td>
<td>10.48(2)</td>
<td>−37.2(2)</td>
<td>78(5)</td>
</tr>
<tr>
<td>4-Piperidineethanol (4-PIPDE)</td>
<td>10.62(3)</td>
<td>−35.2(2)</td>
<td>85(8)</td>
</tr>
<tr>
<td>Piperazine (PIPZ)</td>
<td>9.77(2)</td>
<td>−36(1)</td>
<td>60(1)</td>
</tr>
<tr>
<td>2</td>
<td>5.60(2)</td>
<td>−33.6(1)</td>
<td>−5(1)</td>
</tr>
<tr>
<td>1-Methylpiperazine (MPIPZ)</td>
<td>9.31(1)</td>
<td>−37(4)</td>
<td>53(13)</td>
</tr>
<tr>
<td>2</td>
<td>5.12(1)</td>
<td>−41(2)</td>
<td>41(4)</td>
</tr>
<tr>
<td>Morpholine (MORP)</td>
<td>8.49(1)</td>
<td>−38.4(4)</td>
<td>34(1)</td>
</tr>
<tr>
<td>Thiomorpholine (TMORP)</td>
<td>8.70(1)</td>
<td>−42(1)</td>
<td>27(3)</td>
</tr>
<tr>
<td><strong>Tertiary amines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2',2'-Nitrilotriethanol (triethanolamine) (TEA)</td>
<td>7.82(1)</td>
<td>−32(1)</td>
<td>43(1)</td>
</tr>
<tr>
<td>Bis(2-hydroxyethyl)methyamine (N-methyldiethanolamine) (N-MDEA)</td>
<td>8.65(1)</td>
<td>−36(1)</td>
<td>45(4)</td>
</tr>
<tr>
<td>2-(Dimethylamino)ethanol (N,N-dimethylethanolamine) (N,N-DMEA)</td>
<td>9.23(2)</td>
<td>−34(1)</td>
<td>65(2)</td>
</tr>
<tr>
<td><strong>Ammonia</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH3</td>
<td>9.237(3)</td>
<td>−53.7(7)</td>
<td>−4(2)</td>
</tr>
</tbody>
</table>
The slope of the plot is slightly greater than that found here, which is consistent with the literature data (fig. 1). Generally good agreement of log$_{10}$K$_{prot}$ with the individual protonation constants in most cases is very small (<1.5% in log$_{10}$K$_{prot}$ over all temperatures). Data for MPIPZ and N-MDEA were only a little higher (<1.5%), while 2-PIPDE showed the greatest difference to our data (differences in log$_{10}$K$_{prot}$ of 2–5%). The small differences may be the result of how the ionic strength effect is handled. For other alkanolamines, this must be counterbalanced by the decrease in order in the attached groups, leading to an almost constant value. Thus while decreases in ΔH$_{m}^{o}$ prot increases with ionic strength a greater effect should be expected with literature studies depending on how the ionic strength effect is handled. For other alkanolamines and amines, where the log$_{10}$K$_{prot}$ data is available, good agreement with the literature data (tables S1–S5) was obtained for TRIS, AMP, AMPD, DEA, PIPE, PIP, MORP and TEA. The error associated with the individual protonation constants in most cases is very small (<1.5% in log$_{10}$K$_{prot}$ over all temperatures). Data for MPIPZ and N-MDEA were only a little higher (<1.5%), while 2-PIPDE showed the greatest difference to our data (differences in log$_{10}$K$_{prot}$ of 2–5%). The small differences may be the result of how the ionic strength has been handled in the different studies. In the present study, over the temperature range examined, the trend in log$_{10}$K$_{prot}$ vs 1/T for each alkanolamine/amine was always linear, with most R$^2$ > 0.994, with a minimum in the case of MPIPZ of 0.976.

Examination of the ΔH$_{m}^{o}$ values indicates that they are all significantly exothermic. The protonation reactions are thus enthalpically driven. Moreover, as the proton has no steric requirements because of its small size, on addition to the amine nitrogen any trends in ΔH$_{m}^{o}$ should reflect electronic influences from variations in the attached groups, although changes in solvent reorganisation must play a significant role. Of all species studied, ammonia has the most exothermic ΔH$_{m}^{o}$ and the lowest absolute value of ΔS$_{m}^{o}$. This is shown by AP and AMP relative to MEA, and AMPD relative to BIS. This is attributable to the presence of more electron donating –CH$_3$ groups, which increases the basicity of the nitrogen atom. A similar increase in the exothermic ΔH$_{m}^{o}$ value occurs for 1-amine-2-propanol, where the –CH$_3$ group is now attached to the β carbon (ΔH$_{m}^{o}$ = –50.4 kJ · mol$^{-1}$, and log$_{10}$K$_{prot}$ = 9.46, 298 K, μ = 0 M [4]). The presence of more hydrophobic –CH$_3$ groups apparently decreases ΔS$_{m}^{o}$ in the substituted species relative to MEA.

Successive replacement of –H by –CH$_3$–OH around the amine nitrogen, to give the sequence of primary, secondary and tertiary amines MEA → DEA → TEA, leads to a progressively less exothermic ΔH$_{m}^{o}$, which might be associated with the presence of increasing numbers of more electron-withdrawing groups, thereby reducing the basicity of the nitrogen atom. However, similar trends in ΔH$_{m}^{o}$ are observed in the alkanolamines RNH$_2$, RNH and RN$_2$ (R = Et, Pr), which do not have any –OH groups in their structures [Et: ΔH$_{m}^{o}$ = –57.1, –53.1 and –43.1 kJ · mol$^{-1}$, respectively; Pr: ΔH$_{m}^{o}$ = –57.6, –54.8 and –43.9 kJ · mol$^{-1}$, respectively, T = 298 K, μ = 0 M [4]). In both of these alkyl-substituted sequences it is the secondary amine that has the highest log$_{10}$K$_{prot}$ (Et: log$_{10}$K$_{prot}$ = 10.67, 11.00, 10.72, respectively; Pr: log$_{10}$K$_{prot}$ = 10.57, 10.92, 10.66, respectively, T = 298 K, μ = 0 M [4]). This stems from the well-known effects of hydrogen bonding in aqueous solution versus electronic (i.e. inductive) effects that are opposed, leading to the secondary amine having the highest log$_{10}$K$_{prot}$, although when examined in detail the reasons for this have been found to be complex [14,15]. Trends in ΔS$_{m}^{o}$ for the alkanolamines have been comprehensively discussed in the literature [16–18]. In the present series of alkanolamines, inductive effects (with the electron withdrawing –OH on the –CH$_2$–OH groups) and increasing solvation effects (from the –OH groups) on sequential replacement vary in a regular manner from MEA → DEA → TEA. This leads to the observed trends in log$_{10}$K$_{prot}$ and ΔH$_{m}^{o}$. Thus even though there are increasing numbers of the hydrophobic –CH$_3$– groups being introduced, it is apparent that the presence of multiple –OH groups have an overriding effect on ΔH$_{m}^{o}$. In contrast, the effects on ΔS$_{m}^{o}$ from these two factors presumably cancel, leading to an almost constant value. Thus while decreases in entropy are expected from the increasing numbers of hydrophobic groups, this must be counterbalanced by the decrease in order in the hydrogen bonding environment of the solvent by the increasingly large solute species, despite the greater involvement of the –OH groups in hydrogen bonding. For tertiary amines, successive replacement of –CH$_3$ by –CH$_2$–OH at the amine nitrogen to give the sequence N,N-DMEA → N-MDEA → TRIS does not give rise to trends in ΔH$_{m}^{o}$ or ΔS$_{m}^{o}$.

In contrast to the clear trend found for the MEA-DEA-TEA series, successive replacement of –H or –CH$_3$ by –CH$_2$–OH at the carbon α to the nitrogen of a primary amine does not provide an obvious trend in ΔH$_{m}^{o}$ or ΔS$_{m}^{o}$. This is demonstrated by the sequences MEA → BIS → TRIS and AMP → AMPD → TRIS. Presumably solvent reorganisation that results from changes in hydrogen bonding is complex in these two series.

In the sequence of substituted piperidines 2-PIPDM → 3-PIPDM → 4-PIPDM, ΔH$_{m}^{o}$ becomes progressively less exothermic as substitution occurs at a site further removed from the nitrogen location, likely because of changes to the intramolecular hydrogen bonding following protonation of the amine nitrogen, combined with changes in solvation [19]. Concomitantly, ΔS$_{m}^{o}$ becomes more positive along this sequence. B3LYP/6-311G$^*$ calculations show that for the equilibrium geometries of 2-PIPDM, 2-PIPDE and 3-PIPDM, there are fairly strong intramolecular hydrogen bonds, with (H)N..H(O) distances of 0.2234, 0.1996 and 0.2011 nm, respectively, while for the protonated species there are now intramolecular hydrogen bonds of the type (N^+H=O), with bond lengths of 0.2095, 0.1811 and 0.1843 nm, respectively.
Neutral 4-PIPDM and 4-PIPDE or their protonated species cannot form these intramolecular hydrogen bonds. Thus significant changes in the intramolecular hydrogen bonds occur on protonation for 2-PIPDM, 2-PIPDE and 3-PIPDM. Notably, da Silva and Svendsen have shown that intramolecular hydrogen bonds have a major effect in determining the log10 $K_{prot}$ values of the alkylamines [20], which in turn must affect the $\Delta H_m^{o}$ and $\Delta S_m^{o}$ values. The same trend for $\Delta H_m^{o}$ (and $\Delta S_m^{o}$) is observed for 2-PIPDE → 4-PIPDE, although the chain length here may play a role, as the difference in $\Delta H_m^{o}$ is not as great.

3.2. $\Delta H_m^{o}$–$\Delta S_m^{o}$ plot and implications for the selection of an amine for PCC applications

The data in table 2 can be analysed using a $\Delta H_m^{o}$–$\Delta S_m^{o}$ plot. Linear relationships in $\Delta H$–$\Delta S$ plots are common in solution chemistry [21], and are found for the enthalpies and entropies of solution of series of non-polar or weakly polar atoms or molecules in non-interacting solvents (the so-called Barclay-Butler rule) [22], in the ionisation of aliphatic carboxylic acids from C3 to C6 and also amino acids [17,18], and for the enthalpies ($\Delta H^f$) and entropies ($\Delta S^f$) of activation in kinetic studies. In the present equilibrium studies, a plot of $\Delta H_m^{o}$ against $\Delta S_m^{o}$ for the alkanolamines listed in table 2 (plus 1-aminopropanol, monopropanolamine and N-methylethanolamine, Supplementary data, table S5) generates linear correlations for the primary, secondary and tertiary mono-, di- and tri-alkanolamines, and the substituted piperidines ($R^2 = 0.9952, 0.9955, 1.000$ (only two species!) and 0.9996, respectively). These are shown in figure 2. The data for 11 alkylamines ($RNH_2, ROH$ and RN, where $R$ = Me, Et and Pr, plus isopropylamine and t-butylamine; Supplementary data, table S5) have also been included ($R^2 = 0.954$). Four sequences, with the exclusion of the substituted piperidines, are approximately parallel. The trends for all five series indicate that those species that exhibit a lower positive $\Delta S_m^{o}$ have a more exothermic $\Delta H_m^{o}$, and vice versa. Thus increasing entropy, caused by more internal degrees of freedom and increasing solvent reorganisation, leads to less exothermic $\Delta H_m^{o}$ values. The correlations intersect the $\Delta H_m^{o}$ axis at −62.1 (alkylamines), −56.9 (monoalkanolamines), −50.8 (dialkanolamines), and −46.4 kJ·mol$^{-1}$ (trialkanolamines), with the substituted piperidines at −56.5 kJ·mol$^{-1}$. (These values are, of course, approximate $\Delta G_m^{o}$ values for each of the five groups, which are almost constant within each sequence.) Thus any addition of −OH to a structure causes a change of $\sim$5 kJ·mol$^{-1}$ (at constant $\Delta S_m^{o}$), leading to a more positive $\Delta H_m^{o}$, and hence to a less efficient heat difference between the absorber and stripper in PCC applications. Consequently, $\Delta H_m^{o}$ is more exothermic as follows (for a constant $\Delta S_m^{o}$ value):

alkylamines > NH$_3$ > monoalkanolamines > dialkanolamines > trialkanolamines

Moreover, for each of the three alkanolamine sequences (excluding the substituted piperidines), $\Delta H_m^{o}$ generally is more exothermic according to the sequence:

primary > secondary > tertiary species

From figure 2 it is apparent that increasing the length of the n-alkyl chain leads to progressively more exothermic $\Delta H_m^{o}$ values. Data on increasing n-alkyl chain length (C4, C5 and C6) have been included in the Supplementary data, table S5, but figure 2 has been limited to C3 chains. For the alkylamines, the effect of increasing chain length on $\Delta H_m^{o}$ has been discussed in the literature [16,17]. The trends observed in figure 2 will help guide the selection of suitable amine-based compounds for PCC applications. The maximum exothermic value for $\Delta H_m^{o}$ for the types of compounds studied is $\sim$62 kJ·mol$^{-1}$, which is close to the value for t-butylamine. Provided that a more negative $\Delta H_m^{o}$ for protonation of the amine group is regarded as important to heat changes (this results in a greater difference in log10 $K_{prot}$ between absorber and stripper), it is apparent that the best amine is based around a primary amine, H$_2$N–CR$_2$R$_3$, with a rigid structure. The R groups may involve steric hindrance, depending on whether or not carbamate formation is considered desirable (this leads to faster kinetics of CO$_2$ adsorption, but to a lower absorption uptake per mole of amine than for an amine that does not generate a carbamate). The introduction of at least one −OH (to reduce volatility and increase solubility through hydrogen bonding with the water solvent) would be advantageous. As regards rigidity of the R groups, increasing (alkyl) chain length may be important, but an
alternative would be to use one or more rigid groups, such as a substituted phenyl or heterocyclic aromatic ring, with a substituent on the ring that may form hydrogen bonds with water [for example, a sulfonate, −SO₃⁻, which would also require a counter cation such as Na⁺ (and would decrease amine volatility), or a nitro group, −NO₂]. Aliphatic bicyclo[2.2.2]octane compounds (with, for example, external amine groups) are another possibility, although these may fluctuate excessively and thus have unappealing entropy contributions.

The five sequences of alkanolamines appear to obey an equation of the form \( \Delta H_m^\circ = k \Delta S_m^\circ + \text{constant} \), where the slope \( k \) has the dimension of temperature, and is formally known as the iso-equilibrium temperature, \( T_{iso} \) (for enthalpies and entropies of activation it is the analogous iso-kinetic temperature) [21]. However, it has been shown that a \( \Delta H - \Delta S \) plot does not provide an appropriate way to establish if a \( T_{iso} \) exists for a series of compounds [23–25]. The best way to demonstrate if a series of compounds is linked by an iso-equilibrium temperature is to plot, in the present case, log₁₀ \( K_{prot} \) against \( 1/T \) for each compound [23–25]. Linear relationships will intersect at a common value of \( 1/T \) if the compounds are part of a series with the same \( T_{iso} \) value. No common value of \( T_{iso} \) was observed for any sequence (except for the substituted piperidines, see below), and it is concluded that none of these sequences of compounds form connected series, but that the compounds in each sequence are only linked by similar log₁₀ \( K_{prot} \) (and hence \( \Delta S_m^\circ \)) values. This is not surprising as there are considerable variations in structure for each sequence, involving primary and/or secondary and tertiary amines. For the trialkanolamines the log₁₀ \( K_{prot} \) vs \( 1/T \) data for TRIS and TEA intersect, but as there are only two members in this group, more examples should be investigated. In contrast, the five substituted piperidines (3-piperidine-ethanol is not commercially available) form a series with a \( T_{iso} \) of (252 ± 2) K, as shown in figure 3. This is not surprising as all have highly similar structures, with just the −CH₂OH and −CH₂CH₂OH pendant arms located at different substitution sites around the piperidine ring.

4. Conclusions

The temperature dependence of the protonation constants (\( K_{prot} \)) of selected series of primary, secondary and tertiary amines relevant to PCC applications have been determined, leading to evaluation of their molar enthalpies and entropies of protonation by van’t Hoff analyses. Many of these values have been determined here for the first time. Trends in the \( \Delta H_m^\circ \) and \( \Delta S_m^\circ \) values have been discussed, and a \( \Delta H_m^\circ - \Delta S_m^\circ \) plot has established guidelines for the selection of an amine (or amines) best suited for PCC of CO₂ involving amine-based aqueous solutions. This is based on greater differences in log₁₀ \( K_{prot} \) between the absorber and stripper for the amine species, which will lead to more energy efficient process.

Acknowledgements

Financial support by a CSIRO Flagship grant is acknowledged, as is a University of Newcastle Tom Farrell scholarship (DF). The authors would like to thank Prof. A. McCluskey for access to Spartan ’04.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2012.02.031.

References

Publication-3

Towards Rational Design of Amine Solutions for PCC Applications: The Kinetics of the Reaction of CO$_2$(aq) with Cyclic and Secondary Amines in Aqueous Solution

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Accepted: Environmental Science and Technology
(June 2012)
Toward Rational Design of Amine Solutions for PCC Applications: The Kinetics of the Reaction of CO$_2$(aq) with Cyclic and Secondary Amines in Aqueous Solution

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Supporting Information

ABSTRACT: The kinetics of the fast reversible carbamate formation reaction of CO$_2$(aq) with a series of substituted cyclic secondary amines as well as the noncyclic secondary amine diethanolamine (DEA) has been investigated using the stopped-flow spectrophotometric technique at 25.0 °C. The kinetics of the slow parallel reversible reaction between HCO$_3^-$ and amine has also been determined for a number of the amines by $^1$H NMR spectroscopy at 25.0 °C. The rate of the reversible reactions and the equilibrium constants for the formation of carbamic acid/carbamate from the reactions of CO$_2$ and HCO$_3^-$ with the amines are reported. In terms of the forward reaction of CO$_2$(aq) with amine, the order with increasing rate constants is as follows: diethanolamine (DEA) < morpholine (MORP) ~ thiomorpholine (TMORP) < N-methylpiperazine (N-MPIPZ) < 4-piperidinemethanol (4-PIPDM) ~ piperidine (PIPD) < pyrrolidine (PYR). Both 2-piperidinemethanol (2-PIPDM) and 2-piperidineethanol (2-PIPDE) do not form carbamates. For the carbamate forming amines a Brønsted correlation relating the protonation constant of the amine to the carbamic acid formation rate and equilibrium constants at 25.0 °C has been established. The overall suitability of an amine for PCC in terms of kinetics and energy is discussed.

INTRODUCTION

The recognition of atmospheric CO$_2$ levels amidst the important issues relating to global climate change has induced an urgent need for the development of technologies designed to reduce harmful CO$_2$ emissions associated with the production of electricity from coal-fired power stations. Post combustion capture (PCC) is the current frontline capture technology, separating and capturing CO$_2$ from other flue gas constituents following combustion, but prior to their emission into the atmosphere. The most developed capture processes employ an amine solvent to chemically and reversibly bind the CO$_2$. The resulting pure gas is then sent for storage, while the amine solvent is recycled back for further absorption.1

In order to advance the development of PCC toward the ideal solvent system, detailed knowledge and understanding of the fundamental chemical processes involved in the capture and release of the CO$_2$ is very advantageous. The chemistry of the complete PCC process can be loosely divided into three components which are interlinked: the ‘kinetics’ or rates of absorption, the ‘equilibrium’ or solution composition, and the ‘thermodynamics’ or energies, including enthalpies and entropies of the reaction as well as of activation. The complete set of parameters for these three components fulfills the chemical requirements for modeling and along with the physical constants and mass transfer information the optimization of the PCC process can proceed through modeling without the need for expensive testing at the pilot scale, significantly reducing time and cost. Furthermore, the discovery of new, novel solvents will be guided by the interpretation of the outcomes of such studies.

Typical developed absorption processes utilize aqueous monoethanolamine (MEA) as the capture solvent for its favorable reaction kinetics with CO$_2$ although degradation and unfavorable equilibrium and thermodynamic properties reduce the otherwise ideal properties of MEA for PCC applications. Ammonia has also been considered as a capture solvent because of its resistance to degradation and favorable thermodynamic properties. Unfortunately, however, being a low molecular weight solvent ammonia suffers from evaporation losses and plants must be operated at much lower temperatures than with the traditional process, resulting in slow absorption kinetics. Amines such as 2-amino-2-methyl-1-propanol (AMP) are sterically hindered amines with favorable equilibrium and...
thermodynamic properties but suffer from slow kinetics as a result of the hindrance.\textsuperscript{2,3} Tertiary amines are another class of amine which have been used as solvents for PCC. These amines act only as bases in solution and do not form carbamates, the consequence again being slower absorption rates.\textsuperscript{4}

Besides MEA, a CO\textsubscript{2} capture solvent which has seen significant use in PCC applications is the cyclic secondary diamine piperazine, mainly due to the superior kinetics compared to MEA. For this reason piperazine is commonly used as a ‘promoter’ in potassium carbonate solutions.\textsuperscript{5,6,7} In view of the difficult and complex nature of piperazine chemistry (two protonations and the formation of a dicarbamate) the fundamental mechanism surrounding the absorption of CO\textsubscript{2} by piperazine for the better part remains unknown.\textsuperscript{8} The investigation of other cyclic amines may reveal insight into the chemistry of the cyclic piperazine and the role in which the ring structure may play in the interaction with CO\textsubscript{2}.

The kinetics of the fast reversible reaction of CO\textsubscript{2}(aq) with the cyclic amines MORP, PIPD, N-MIPZ, PYR, TMORP, 2-PIPDE, and 4-PIPDE, as well as for the noncyclic secondary amine, DEA, has been investigated using the stopped flow spectrophotometry technique with colored pH indicators to follow the reaction kinetics. [See Table S-1 (Supporting Information) for a list of investigated amines with structure and acronym used in this report]. Also, \textsuperscript{1}H NMR spectroscopy has been employed to investigate the slow reversible reaction between HCO\textsubscript{3}\textsuperscript{−} and amine. Relationships between the amine properties (structure, protonation constant, kinetic parameters) for the interactions of the amines with CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{−} have been analyzed.

## EXPERIMENTAL SECTION

High purity CO\textsubscript{2} gas (BOC gases), N\textsubscript{2} (Coregas), sodium bicarbonate (BDH), sodium hydroxide (Merck), potassium hydrogen phthalate (KHP, Ajax), thymol blue sodium salt (Sigma-Aldrich), methyl red (M & B Laboratory Chemicals), bromothymol blue sodium salt (Ajax), alizarin red S (BDH), and hydrochloric acid (Ajax) were used without any further purification. Morpholine (MORP, Sigma-Aldrich) and piperidine (PIP, Sigma-Aldrich) were standardized by titration with the appropriate time prior to the measurements to ensure complete equilibration of the reactions.

For the investigation of carbamate formation with bicarbonate at high pH, aqueous amine solutions with different amounts of acid or base added were mixed with a potassium bicarbonate solution. The resultant mixture was transferred to an NMR tube, and the initial \textsuperscript{1}H NMR spectrum was recorded approximately 5 min after mixing. The spectra were recorded thereafter at predetermined time intervals automatically by the NMR spectrometer to establish the time-resolved kinetics.

For the investigation of the decomposition of the carbonate at high pH, carbonate was generated by mixing the amine with sodium bicarbonate, and after equilibration, the relative concentration of carbonate and amine was quantified by \textsuperscript{1}H NMR spectroscopy. The resulting solution was mixed with HCl or NaOH, and the disappearance of the carbonate with time was monitored. It was important to investigate a series of concentrations of added acid or base to cover a wide pH range; note that at low pH the reaction is fast and was measured by stopped-flow kinetics. The measured concentration profiles for the formation of the carbonate of 4-PiPD and decomposition of the carbonate of TMORP as well as the fitted curves will be given in the Results section. All initial concentrations of the reactants are given in Table S-3 in the Supporting Information. A series of typical measurements for PYR can be found in the Results section.

## STOPPED-FLOW MEASUREMENTS

The kinetics of the individual amines with CO\textsubscript{2}(aq) was performed on an Applied Photophysics DX-17 spectrophotometer equipped with a J&K Tidas MCS 500-3 diode-array detector, observing pH changes over the wavelength range 400–700 nm via coupling to indicators. Samples were thermostatted at 25.0 °C (using a Julabo F20 water bath) to within ±0.1 °C, and the exact temperatures of the reactions were recorded via a thermocouple within the stopped-flow system. Reactions were initiated by mixing aqueous solutions of amine (combined with the corresponding indicators) with water saturated with CO\textsubscript{2}/N\textsubscript{2} gas mixtures which resulted in the initial concentrations of the reactants given in Table S-2a of the Supporting Information. All [CO\textsubscript{2}] were calculated from relative gas flow rates of N\textsubscript{2} and CO\textsubscript{2} assuming ideal behavior, and the published saturation concentration.\textsuperscript{9,10} Absorption changes were due to the protonation of thymol blue (log K = 9.05 at 25.0 °C) or alizarin red S (log K = 11.0 at 25.0 °C) as a result of the release of a proton from the carbamic acid, carbonic acid, and bicarbonate that was formed. A series of typical measurements for MORP can be found in the Results section.

The decomposition of carbamic acid was initiated by mixing aqueous solutions of carbonate with HCl which included (depending on the desired pH) methyl orange (log K = 3.5 at 25.0 °C), alizarin red S (log K = 5.5 at 25.0 °C), or bromothymol blue (log K = 7.0 at 25.0 °C) indicators (or a combination of these indicators). Initially, values for the protonation constants of the indicator were sourced from the literature.\textsuperscript{11} In the final analysis, these indicator constants were also fitted and agreed well with the published values. The carbamate-containing solutions were generated by mixing amine solutions with two equivalents of bicarbonate and equilibrated for 24 h. Prior to their kinetic investigation, the composition was determined by \textsuperscript{1}H NMR spectroscopy. The initial concentrations of the reactants are given in Table S-3 in the Supporting Information. A series of typical measurements for PYR can be found in the Results section.

## NMR MEASUREMENTS

\textsuperscript{1}H NMR spectra were recorded on a Bruker Avance DPX-300 at a frequency of 300.13 MHz. All samples were measured in H\textsubscript{2}O in a 5 mm NMR tube containing an insert with TSP (3-(trimethylsilyl)-propionic acid-d\textsubscript{4} sodium salt) in D\textsubscript{2}O as a reference, with the D\textsubscript{2}O acting as the locking agent. Two series of kinetic measurements were performed depending on the reaction under investigation. All \textsuperscript{1}H NMR kinetic measurements were performed at 25.0 °C and thermostatted for an appropriate time prior to the measurements to ensure complete equilibration of the reactions.
concentrations used for the NMR studies are listed in Table S-2 of the Supporting Information.

The amines and their carbamates are the only $^1$H NMR active species in the solutions investigated, excluding the noninterfering contribution of water to the spectrum. For example, MORP features two neighboring methylene groups to the amine moiety that give rise to two triplets, while the addition of HCO$_3^-$ gives rise to two additional triplets that correspond to the carbamate. A portion of the $^1$H NMR spectrum from 3.0 ppm to 4.0 ppm of an equilibrated MORP/HCO$_3^-$ solution at 25.0 °C is shown in Figure 1.

In the pH region investigated in this work, all of the cyclic amines and their carbamates are involved in pH-dependent protonation equilibria. As a consequence, the chemical shifts are pH-dependent, and on the slow NMR time scale the peak integrals represent the sum over the concentrations of the protonated and deprotonated forms of the amine and the carbamate/carbamic acid. Typically two triplet methylene integrals were evaluated for the concentrations; however, at some pH values some peaks partially overlap. No attempt was made to deconvolute the integrals into the contributions of the two components, and in these instances only the remaining integral was used for quantification.

Data Analysis. All of the stopped-flow and $^1$H NMR data were analyzed using ReactLab Kinetics (www.jplusconsulting.com), and in-house global data analysis software which was developed in Matlab.$^{12,13}$ The complete mechanism including all interactions between CO$_2$, OH$^-$, H$_2$O, and the amine, as well as the associated protonation equilibria of CO$_3^{2-}$, HCO$_3^-$, carbamate, and the amine, is shown in Figure 2. The corresponding reactions are listed in eqs 1–9.

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]  

\[ \text{CO}_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \]  

\[ \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^- \]  

\[ \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \]  

\[ \text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} \]  

\[ \text{RNH}_2 + \text{H}^+ \rightleftharpoons \text{RNH}_3^+ \]  

\[ \text{RNH}_2 + \text{CO}_2(\text{aq}) \rightleftharpoons \text{RNHCO}_2\text{H} \]  

\[ \text{RNHCO}_2^- + \text{H}^+ \rightleftharpoons \text{RNHCO}_2\text{H} \]  

\[ \text{RNH}_2 + \text{HCO}_3^- \rightleftharpoons \text{RNHCO}_2\text{H} (+\text{H}_2\text{O}) \]  

The rate and equilibrium constants corresponding to the reaction of CO$_2$(aq) with amine, $k_9$, $k_7$, eq 7, and the reaction of HCO$_3^-$ with amine, $k_{9g}$, eq 9, have been determined in this study at 25.0 °C. Lower case $k$ values represent rate constants; upper case $K$ values are equilibrium constants. Note that the reverse reaction 9 is written as a pseudo-first-order reaction, so that the water in brackets is formally required for the stoichiometry of the equation. Approximations for the protonation constant of the carbamate, log $K_{sp}$, eq 8, have also been determined by the fitting. The carboxylic acids do not reach substantial concentrations under any conditions; as a consequence the values for the protonation constants are less well-defined. Values for the protonation constant of OH$^-$, CO$_3^{2-}$, HCO$_3^-$, and the amine, eqs 3–6, as well as the kinetics of the reaction of CO$_2$ with water and hydroxide, eqs 1 and 2, were taken from the literature.$^{9,13–18}$ An additional parameter for the protonation(s) of each of the indicator(s), eq 10, is required for the fitting of the measurement data.

\[ \text{Ind} + \text{H}^+ \rightleftharpoons \text{IndH}^+ \]  

Ionic strength effects were handled using the Debye–Hückel approximation for species activities.$^{12,19,20}$

RESULTS

A selection of representative experimental and fitted traces are presented in the Figures 3 and 4. The kinetics of reaction of MORP $([\text{MORP}]_0 = 2.0–20.0$ mM) and CO$_2$(aq) $([\text{CO}_2]_0 = 2.0$ mM) at 25.0 °C is shown in Figure 3(a). The measurement traces correspond to the absorbance changes at 590 nm due to the presence of 12.5 μM thymol blue indicator in solution. Throughout the reactions the pH changes from approximately 10 to 8. The kinetics of the decomposition of 8.0 mM PYR-carbamate in the presence of 42.0 mM HCO$_3^-$, 17.0 mM PYR, and 50.0 μM alizarin red S, and 25.0 μM methyl orange indicators with 45.0–55.0 mM HCl at 25.0 °C is shown in
In these decomposition reactions the pH changes (typically 2–4 units) exceed the range of one indicator, and thus two indicators were required.

The kinetics of the slow reaction between 0.2 M 4-PIPDM and 0.4 M HCO$_3^-$ at 25.0 °C, also in the presence of additional 0.05 M NaOH, is shown in Figure 4(a). The equilibrium concentration of carbamate is strongly pH dependent, approaching a maximum concentration at an approximate pH of 9.5 for the total concentrations investigated here. The final pH of the solution with the addition of NaOH (pH 9.47) is closer to this pH than the solution without (pH 9.3), thus explaining the correspondingly higher concentration of carbamate in the presence of NaOH. The corresponding decomposition of 0.04 M TMORP-carbamate in the presence of 0.188 M NaOH at 25.0 °C is shown in Figure 4(b).

Table 1. Rate and Equilibrium Constants in the Reactions of Amine with CO$_2$(aq) and Bicarbonate, Including the Protonation Constants of the Carbamate at 25.0 °C$^{ef}$

$$
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
& \text{DEA} & \text{TMORP} & \text{MORP} & \text{PYR} & \text{PIPD} & \text{N-MPIPZ} & \text{4-PIPDM} \\
\hline
R\text{NH}_2 + CO_2(aq) \rightleftharpoons R\text{NHCO}_2H & k_2 & 1.10(9) \times 10^2 & 3.25(1) \times 10^4 & 2.7(2) \times 10^4 & 5.8(5) \times 10^7 & 4.1(1) \times 10^3 & 2.1(3) \times 10^6 \\
\hline
R\text{NH}_2 + HCO_3^- \rightleftharpoons R\text{NHCO}_2^- & k_4 & 5(1) & 44(3) & 20(1) & 1.0(3) \times 10^9 & 39(1) & 27.0(3) & 1.1(1) \times 10^2 \\
\hline
R\text{NH}_2 + HCO_3^- \rightleftharpoons R\text{NHCO}_2^- & k_9 & 24(5) & 75(5) & 1.37(3) \times 10^2 & 6(1) \times 10^2 & 6.2(3) \times 10^2 & 1.51(5) \times 10^2 & 1.8(2) \times 10^2 \\
\hline
R\text{NH}_2 + HCO_3^- \rightleftharpoons R\text{NHCO}_2^- & k_9 & 2.30(4) \times 10^{-3} & 3.168(4) \times 10^{-5} & 2.226(3) \times 10^{-5} & - & 7.28(5) \times 10^{-3} & - & 2.17(2) \times 10^{-2} \\
\hline
R\text{NH}_2 + HCO_3^- \rightleftharpoons R\text{NHCO}_2^- & k_9 & 4.20(9) & 3.838(2) \times 10^{-4} & 1.9(3) \times 10^{-4} & - & 3.6(3) \times 10^{-4} & - & 1.58(2) \times 10^{-3} \\
\hline
R\text{NH}_2 + HCO_3^- \rightleftharpoons R\text{NHCO}_2^- & k_9 & 5.51(4) & 8.253(5) & 11.99(3) & 11^b & 20.2(1) & 1.5^b & 13.69(7) \\
\hline
\end{array}
$$

$^{a}$k$_{9.0}$ is calculated as follows: $k_{9.0} = [k_9 k_6 k_{-6}]/[k_6 k_{-6} K_3]$ based on microscopic reversibility. $^b$No NMR data were evaluated. $K_9$ was calculated by $K_9 = K_4 K_7/K_1 K_8$. $^c$Data are from Fernandes et al.$^{21}$ $^d$The numbers in brackets represent the standard deviation in the last digit.
Global analysis of the formation and decomposition stopped flow and \(^1\)H NMR measurements revealed rate constants for the reactions of CO\(_2\) and HCO\(_3^-\) with amine, \(k_7\), \(k_{-7}\), \(k_9\), \(k_{-9}\), and the equilibrium constants \(K_7\), \(K_9\), \(K_{-7}\), \(K_{-9}\), including the protonation equilibrium of the carbamate. Five repeats of the complete set of measurements were analyzed, allowing a careful statistical analysis of the fitting results. The final rate and equilibrium constants at 25.0 °C are listed in Table 1 together with their standard deviations in parentheses. No NMR analyses were undertaken for PYR and N-MPIPZ. The rate constants \(k_9\) and \(k_{-9}\) are not known, but the equilibrium constant \(K_9\) has been calculated as \(K_9 = K_9K_{-9}/K_9K_{-9}\). Values for \(K_9\) have also been determined by independent equilibrium studies;\(^{21}\) the agreement is excellent in most cases.

No \(^1\)H NMR signal for the carbamates of 2-PIPDM and 2-PIPDE were observed in the equilibrium solutions. Intermediate carbamate formation like that observed in ammonia solutions can also be excluded.\(^{20}\) A term for the direct reaction of CO\(_2\)(aq) and HCO\(_3^-\) with 2-PIPDM and 2-PIPDE, eqs 7 and 9, was not required during the analysis of the kinetic measurements, i.e. the data are consistent with a mechanism that does not include the formation of carbamate. Thus, the constants for these amines do not appear in Table 1.

### DISCUSSION

 Carbamate formation for the amines 4-PIPDM, 2-PIPDE, and TMORP has, to our knowledge, not been investigated, and all rate constants presented here are novel. For the remaining amines there are published values for the reaction of CO\(_2\) with the amine, \(k_7\). There are no published values for the back reaction, \(k_{-7}\), nor for their reaction with bicarbonate, \(k_9\), \(k_{-9}\).

**PIP (Our value \(k_7 = 2.43(8) \times 10^4\) M\(^{-1}\) s\(^{-1}\)).** Pipedidine has been relatively well investigated. Jensen et al.\(^{22}\) determined a rate constant of \(7.76 \times 10^3\) M\(^{-1}\) s\(^{-1}\) at 18 °C. Sharma\(^{23}\) calculated the forward rate constant based on the transient rates of absorption of PIPD in a jet apparatus, with a determined value for the rate constant of \(6.02 \times 10^5\) M\(^{-1}\) s\(^{-1}\) at 25 °C. Caplow\(^{24}\) followed the reaction at 10 °C, obtaining a second-order rate constant of \(3.2 \times 10^3\) M\(^{-1}\) s\(^{-1}\) and also reported that the parallel hydroxide pathway increased its rate with an increase of the concentration of PIPD due to higher pH.

**PYR (Our value \(k_7 = 5.8(5) \times 10^4\) M\(^{-1}\) s\(^{-1}\)).** Caplow\(^{24}\) investigated the reaction of CO\(_2\) and PYR in the presence of 0.05 M triethylamine at an ionic strength of 1.0 M (KCl) and obtained a second-order rate constant of \(1.27 \times 10^4\) M\(^{-1}\) s\(^{-1}\) which is substantially lower than the value determined here.

**MORP (Our value \(k_7 = 2.7(2) \times 10^4\) M\(^{-1}\) s\(^{-1}\)).** The rate constant \(k_7\) for MORP has been reported several times. Sharma\(^{23}\) reported a value of \(2.0 \times 10^4\) M\(^{-1}\) s\(^{-1}\) from measurements in a jet apparatus, while Alper\(^{25}\) determined a value of \(2.05 \times 10^4\) M\(^{-1}\) s\(^{-1}\) for the rate constant from stopped-flow kinetic measurements. Littel et al.\(^{26}\) have determined a value of \(6.1 \times 10^3\) M\(^{-1}\) s\(^{-1}\) at 30 °C from measurements in a stirred cell reactor. Recently, Al-Juaidi\(^{27}\) determined a value of \(2.23 \times 10^3\) M\(^{-1}\) s\(^{-1}\) from wetted wall measurements. All published values are substantially higher than the value determined here.

**N-MPIPZ (Our value \(k_7 = 4.1(1) \times 10^3\) M\(^{-1}\) s\(^{-1}\)).** N-MPIPZ serves as a model for the diamine promoter piperazone, differing only in structure by methylation of the second amine group rendering the group unreactive toward CO\(_2\). Recently Rayer et al.\(^{28}\) investigated the kinetics of the reaction of CO\(_2\) and N-MPIPZ over the temperature range 25–40 °C using the stopped-flow technique. From the Arrhenius expression the second-order rate constant at 25 °C (4.63 \(\times 10^3\) M\(^{-1}\) s\(^{-1}\)) agrees well with the corresponding rate constant determined in this study.

**2-PIPDE and 2-PIPDM** do not form carbamates under the conditions of this study, possibly as a result of moderate steric hindrance or strong intramolecular hydrogen bonding.\(^{21}\) Several rate constants for the reaction of CO\(_2\) with 2-PIPDE are available in the literature. Shen et al.\(^{29}\) reported a second-order rate constant for 2-PIPDE of 195 M\(^{-1}\) s\(^{-1}\) from wetted wall experiments at 40 °C. Xu et al.\(^{30}\) investigated the kinetics over the temperature range 10–40 °C using the pressure decrease technique and reported corresponding values of 243–1468 M\(^{-1}\) s\(^{-1}\), while Subham et al.\(^{31}\) reported values of 1147–2047 M\(^{-1}\) s\(^{-1}\) over the temperature range 30–60 °C. Both Xu et al.\(^{30}\) and Subham et al.\(^{31}\) analyzed their kinetic data with a protonation constant for 2-PIPDE of 10.14 at 25 °C,\(^{32}\) the value for which is 0.3 log units lower than that used here to analyze the kinetic measurements. The kinetics will be slightly affected by the lower protonation constant where the rate constant for the reaction of CO\(_2\) with the amine is overestimated due to the lower predicted concentration of hydroxide from the ionization of water by the amine. The amine and CO\(_2\) concentrations employed in the previous 2-PIPDE studies are much higher than those investigated in the current study. The absorption of CO\(_2\) by
a carbamate pathway may only become detectable at higher amine concentrations. Under the conditions of the current study the contribution of a direct reaction of CO$_2$ with the amine to the overall absorption of CO$_2$ in these solutions is low enough so that it can be considered as insignificant. They react effectively like a tertiary amine.

Further, with the exception of Rayer et al.$^{28}$ for N-MPIP, all published results do not take into account the reaction of CO$_2$ with hydroxide, $k_2$. This invariably leads to an overestimation of the reaction with the amine, $k_7$. Indeed, most published values for $k_7$ are higher than the ones reported here.

**Brønsted Relationships.** The Brønsted basicity of an amine is clearly an important property in PCC applications. It is closely related to the Lewis basicity which governs the rate of its reaction, $k_7$, as well as the equilibrium constant with the Lewis acid CO$_2$, $K_7$. In order to investigate the relationship we have plotted the rate constant $k_7$ and the equilibrium constant $K_7$ against the protonation constant $K_6$ in Figure 5(a) and (b). The figure also includes values for a collection of relevant acyclic amines, MEA, DEA, and ammonia. Both parts (a) and (b) of the figure clearly reveal a linear relationship between the log $K_7$ value for the amine protonation and the interactions with CO$_2$ for the cyclic amines, with significantly lower values for most of the acyclic amines.

The steric effects for all cyclic secondary amines are very similar, and thus the virtually perfect correlation between the protonation constant and the rate of the reaction with CO$_2$, $k_7$, is not surprising ($R^2 = 0.95$). A small steric reduction might operate for the (only) 5-membered ring of PYR, which reacts slightly faster than the 6-membered ring compounds.

With the exception of MEA all of the noncyclic amines included in Figure 5(a) react significantly slower than the cyclic amines. The structures of these amines are substantially different. Steric as well as electronic and solvation effects will contribute to the reduced reactivity.

The corresponding Brønsted plot for the equilibrium constant, log $K_7$, is shown in Figure 5(b) ($R^2 = 0.80$). The relationship between the protonation constant and the equilibrium constant for the formation of the amine-carbamic acid is very similar. Additionally, the remaining acyclic amines interact consistently weaker as is observed with their kinetics. The rationale is of course very similar.

**2-PIPDM and 2-PIPDE.** The absence of carbamate formation for these amines is surprising, and an explanation is not straightforward. Careful investigation of the $^{13}$C NMR (and/or $^1H$) spectra reveals no visible peaks that could be assigned to the formation of the carbamates. This observation is supported by Puxty et al.$^{33}$ who proposed that a hydroxyl group within 2 or 3 carbons of the amine nitrogen resulted in an increased absorption capacity (moles CO$_2$/mol amine) which was interpreted as the formation of an intramolecular hydrogen-bonded ring structure preventing the carbamate formation. Thus, there is no doubt that these amines do not form significant amounts of the carbamate from the equilibrium point of view. As we have demonstrated for the case of ammonia$^{20}$ intermediate (a few seconds) carbamate formation is possible. This is a very significant property of ammonia as it results in fast absorption kinetics without the stoichiometric disadvantage of carbamate formation.

We have investigated possible intermediate carbamate formation using the following procedure. The kinetics data were analyzed by two different models: (a) by excluding the carbamate formation reactions, using only the hydration reactions of CO$_2$ and the associated protonation equilibria, eqs 1–6, and (b) using a model that additionally includes the direct reversible reaction of CO$_2$(aq) with the amine, eqs 7 and 8. For 2-PIPDM and 2-PIPDE the simple model resulted in ‘perfect’ fits, and there was no improvement if the extended model was used in the fitting. This is in sharp contrast to the other cyclic amines which clearly required the extended model.

![Figure 6. CO$_2$ absorption: (left) CO$_2$ in a solution of 4-PIPDM with carbamate formation and (right) reaction with 2-PIPDE, with no carbamate formation.](image-url)
for acceptable fits to their kinetic data. All of these observations indicate that there is no intermediate nor lasting formation of carbamate with 2-PIPDM or 2-PIPDE.

**CO₂ Absorption – Comparing Fast Carbamate Formation and CO₂ Hydration.** It is interesting to compare the reactions of dissolved CO₂ with two different amines, one which does not form a carbamate and one which does. For this comparison we chose two amines with similar protonation constants but different CO₂ reaction pathways; 2-PIPDE does not form a carbamate species while 4-PIPDM does. The concentration profiles for hypothetical reactions of 0.01 M CO₂ and 0.01 M aqueous amine are displayed in Figure 6.

The left-hand panels are for 4-PIPDM which does form the carbamate, and the right-hand panels are for 2-PIPDE which does not. The top panels display the complete concentration profiles over 100 s, while the bottom panels display the initial stages of the reaction, 0.5 s for 2-PIPDE and 0.05 s for 4-PIPDM. The main difference between the two amines is the fast initial decrease in the CO₂ concentration due to carbamate formation which accounts for the reaction of about 50% of the CO₂ within about 10 ms. For 2-PIPDE a similar amount of CO₂ reacts in only some 200 ms. As a secondary result the pH drops much faster with carbamate formation; thus pH 9 is reached in some 50 ms for 4-PIPDM and in some 10 s for 2-PIPDE. Interestingly the longer term kinetics reveals the opposite. For 2-PIPDE, 95% of the CO₂ has reacted after about 20 s, while 4-PIPDM requires some 60 s. The slower reaction is due to the lower pH, with less reaction of CO₂ with hydroxide.

The final concentrations of all major species are very similar, which is a result of the very similar protonation constants of the two amines. On a msec time scale, the results confirm the expectation that carbamate formation results in faster reaction of CO₂; interestingly on a sec time scale, CO₂ reacts faster in the noncarbamate forming amine solution. Incorporation of the detailed mechanism into plant models will reveal the relative importance of these two observations under realistic PCC conditions.

**Absorption vs Desorption.** A fundamental consideration when selecting an amine for PCC is the performance of the amine across both the absorption and desorption regimes. For the absorbing process fast absorption kinetics is important as it directly correlates with the required physical size of the absorber; thus amines that form carbamates in fast reactions are advantageous, e.g. PYR. The energy requirement for the stripping process is the other important aspect. An important contribution is the cyclic capacity of the amine which defines the amount of solution that needs to be cycled, and here the carbamate formation is detrimental. It has been shown that the main contribution to the cyclic capacity and energy requirement is the enthalpy for the protonation of the amine. Large negative enthalpies result in large swings of the CO₂ concentration and thus large cyclic capacity, although this of course is only one of the many components of the overall energy consumption. Figure 7 shows the relationship between ΔH_protonation, and log kₚ for the selection of amines in this work. The ideal amine reacts fast and has a large negative enthalpy, so it would sit in the top left corner of the figure. Attempts to design better amines can be guided by graphs of this kind. However, it is clear that expansion of the amine library is required to improve and understand these relationships.

![Figure 7. PCC potential of amines as a plot of the amine-carbamate acid formation rate constant at 25.0 °C, log kₚ, and the reaction enthalpy of the amine protonation, ΔH_protonation at 25.0 °C.](image)

### CONCLUSION

The kinetics of the reversible reactions of CO₂(aq) and HCO₃⁻ at 25 °C with a series of substituted cyclic secondary amines, as well as the noncyclic secondary amine DEA, has been investigated at 25 °C. Global data analysis yielded the four rate constants and two equilibrium constants for the formation of amine-carbamate. The rate constant for the reaction of CO₂ and amine, kₚ has the following order: DEA < morpholine (MORP) ~ thiomorpholine (TMORP) < N-methylpipperazine (N-MPPZ) < 4-piperidinemethanol (4-PIPDE) ~ piperidine (PIPZ) < pyrrolidine (PYR). For the carbamate-forming amines, a Bredsted correlation relating the protonation constant of the amine to the rate and equilibrium constant at 25.0 °C has been identified. Kinetic measurements and NMR analysis of 2-PIPDM and 2-PIPDE revealed no evidence of carbamate formation.

### ASSOCIATED CONTENT

#### Supporting Information

Tables S-1–S-3. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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Published: Journal of Physical Chemistry A, 115, 6405-6412
(20$^{th}$ May 2011)
Kinetics of the Reversible Reaction of CO$_2$(aq) with Ammonia in Aqueous Solution

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ABSTRACT: The kinetics of the interactions of aqueous ammonia with aqueous carbon dioxide/carbonate species has been investigated using stopped-flow techniques by monitoring the pH changes via indicators. The reactions include the reversible formation of ammonium carbamate/carbamic acid. A complete reaction mechanism has been established, and the temperature dependence of all rate and equilibrium constants including the protonation constant of the amine between 15 and 45 °C are reported and analyzed in terms of Arhenius, Eyring, and van’t Hoff relationships.

INTRODUCTION

Carbon dioxide emissions from fossil fuel combustion are a major contributor to climate change.$^{1,2}$ Reduction of this output would be a clear means for the amelioration of the situation. Carbon capture with subsequent sequestration (CCS) is a well investigated technology that requires the separation of CO$_2$ from N$_2$, oxygen, water, and other minor constituents in the flue gas prior to its sequestration. There are several technologies used to separate CO$_2$ from flue gas streams. These include chemical solvent methods, physical absorption/adsorption methods, cryogenic methods, membrane systems, and biological fixation.$^{3–6}$ The chemical solvent methods are generally recognized as the most effective technologies at present for the low CO$_2$ partial pressure in gas, and the majority rely on the reversible absorption of CO$_2$ by aqueous amine solutions. Among the conventional CO$_2$ chemical removal processes, the monoethanolamine (MEA) process has been comprehensively studied and successfully used for CO$_2$ recovery,$^7$ as well as for natural gas sweetening.$^8$ However, the MEA process has a number of significant disadvantages, for example, a relatively low carbon dioxide loading capacity, a high energy requirement for the cyclic process, a high equipment corrosion rate, and the amine is subject to degradation by SO$_2$, NO$_2$, HCl, HF, and oxygen. It is, thus, far from being an ideal solvent in CO$_2$ separation from flue gas.$^9$ Aqueous ammonia (NH$_3$) has been proposed as an alternative to aqueous alkanolamine-based liquid absorbents for postcombustion capture (PCC) of CO$_2$.$^{9–12}$ The benefits of ammonia include a higher CO$_2$ absorption efficiency and loading capacity, and a low energy requirement for the release of CO$_2$ in the stripper. Moreover it is a less corrosive environment for the absorber material and, very importantly, it is chemically stable. Recently, Yeh et al. showed that ammonium bicarbonate requires the least thermal energy among the ammonium compounds for CO$_2$ regeneration in their semibatch absorption and regeneration studies of CO$_2$ by aqueous ammonia.$^9$ Thus, the investigation of the chemistry of the aqueous ammonia/CO$_2$ system is highly relevant to CO$_2$ capture and regeneration.

Carbon-13 NMR, near-infrared (NIR), and Raman spectroscopies have all revealed that dissolved CO$_2$, carbonic acid, bicarbonate, carbonate, and carbamate coexist in CO$_2$–H$_2$O mixtures, with quantitative analysis of the spectra providing the equilibrium concentrations for each species.$^{12–14}$ However, to our knowledge, there is little kinetic data regarding the reaction of ammonia with aqueous CO$_2$. The kinetics of the reaction of dissolved CO$_2$(aq) with ammonia was first reported by Pinsent et al in 1956.$^{15}$ These workers determined the rate constant by a rapid thermal method over the temperature range of 0 to 40 °C. Recently Derk and Versteeg and Puxty et al.$^{16,17}$ reported this rate constant with similar results. However, both sets of values were about 8 times that reported by Pinsent et al.$^{15}$ Moreover, totally different mechanisms were proposed in these kinetic studies.

In summary, the kinetics of the interactions of NH$_3$ with CO$_2$ is not well investigated. To resolve the above issue and to gain a deeper understanding of the complete mechanism, the kinetics of
The reaction of aqueous ammonia with CO2(aq) has been investigated. Due to the relatively fast reactions, the stopped-flow technique was employed and, as none of the interacting species feature useful absorption spectra in the visible or near-UV regions, pH changes as a result of reactions in solution were followed spectrophotometrically via coupling to appropriate indicators. The kinetics was measured at the temperatures 15, 25, 35, and 45 °C, allowing the determination of activation and thermodynamic values for all rate and equilibrium constants.

## EXPERIMENTAL SECTION

High purity CO2 gas (BOC), N2 (Coregas), potassium bicarbonate (BDH), sodium hydroxide (Merck), ammonia (Merck), potassium hydrogen phthalate (AJAX), hydrochloric acid (AJAX), thymol blue sodium salt (Sigma-Aldrich), bromothymol blue sodium salt (Sigma-Aldrich), alizarin red S (BDH), and methyl orange (SELBY) were used as obtained. Ammonia, NaOH, and HCl solutions were standardized by appropriate potentiometric titrations. Ultrahigh purity Milli-Q water was boiled to remove CO2 gas and used for the preparation of all solutions. All samples and solutions were stored in a N2-purged glovebag.

The kinetics of the reactions of aqueous carbon dioxide with ammonia and that of the decomposition of the carbamate/carbamic acid were performed on an Applied Photophysics DX-17 stopped-flow equipped with a J&M Tidas MCS 500-3 diode-array detector, observing the pH changes over the wavelength range 400–700 nm via coupling to the indicators. Samples were thermostatted at the temperatures 15, 25, 35, and 45 °C to within ±0.1 °C and the exact temperature was recorded by a thermo-couple located within the stopped-flow apparatus.

The reaction of aqueous carbon dioxide with ammonia was initiated by mixing aqueous solutions of ammonia and thymol blue with solutions of CO2 to result in initial concentrations of [ammonia]0 = 2.0–16.0 mM, [CO2]0 = 3.0–10.5 mM, and [indicator] = 12.5 μM. Absorption changes were due to the protonation of thymol blue as a result of the release of a proton from the carbamic acid that was formed. The decomposition of ammonium carbamate was initiated by mixing aqueous solutions of ammonium carbamate, generated by mixing 0.10 M ammonia with 0.20 M bicarbonate, and equilibrated for 24 h, with different concentrations of hydrochloric acid. Depending on the pH changes, alizarin red S, methyl orange, or a combination of these indicators was used to follow the kinetics of reaction. All concentrations used in the stopped-flow studies for NH3, NaHCO3, carbamate (calculated), and CO2, as well as the identities and concentrations of the indicators, have been listed in the Supporting Information, Tables S1–S3.

### Data Analysis

We have recently developed a reaction scheme that includes all interactions of monoethanolamine (MEA) with all CO2 and carbonate species in aqueous solution. The reaction scheme, as adapted for ammonia, is presented in Figure 1.

The interactions of CO2(aq) with water and hydroxide ions are indicated in dashed lines. Recently, the values for all rate and equilibrium constants have been redetermined comprehensively, and these values were used in the present work. Equation 1(a–f) summarizes this part of the reaction scheme as well as the protonation equilibrium of ammonia.

\[
\begin{align*}
\text{CO}_2(aq) + H_2O & \rightleftharpoons H_2CO_3 \quad \text{(a)} \\
\text{CO}_2(aq) + OH^- & \rightleftharpoons HCO_3^- \quad \text{(b)} \\
\text{CO}_3^{2-} + H^+ & \rightleftharpoons HCO_3^- \quad \text{(c)} \\
\text{HCO}_3^- + H^+ & \rightleftharpoons H_2CO_3 \quad \text{(d)} \\
OH^- + H^+ & \rightleftharpoons H_2O \\
\text{NH}_3 + H^+ & \rightleftharpoons \text{NH}_4^+ \quad \text{(f)}
\end{align*}
\]

The formation reactions of the carbamate/carbamic acid included in the mechanism are shown in eq 2, while eq 3 describes the protonation of carbamate to the carbamic acid.

\[
\begin{align*}
\text{CO}_2(aq) + \text{NH}_3 & \rightleftharpoons \text{NH}_2\text{COOH} \quad \text{(2)} \\
\text{NH}_2\text{CO}_2^- + H^+ & \rightleftharpoons \text{NH}_3\text{CO}_2H \quad \text{(3)}
\end{align*}
\]

The two rate constants (k+ and k−) of eq 2 have to be determined, together with the unknown protonation constant of the carbamate (Kc)...

MEA can also react with carbonic acid and with the bicarbonate ion and it is likely that ammonia can react similarly. The reaction of MEA with carbonic acid forms carbamic acid with release of one mole of water, and the reaction of MEA with bicarbonate forms the carbamate, again with the release of one water. Under the conditions of this investigation, which are relevant for absorption of CO2 into ammonia solution for PCC, reactions between ammonia, carbonic acid and the bicarbonate ion were not observed. The implication is that the reaction rates for these paths are significantly smaller than k−. In the case of MEA the reactions with carbonic and the bicarbonate ion were investigated under conditions where the concentration of CO2(aq) was negligible and the more rapid CO2 – MEA reaction did not mask the bicarbonate reaction. These reactions, which are much slower than the CO2 – MEA reaction, were observed using 1H NMR, which is not an applicable technique to ammonia/carbone solutions.

Note that there are additional parameters that needed to be fitted: the protonation constants for the indicators used are not published at all the temperatures. In these instances, the protonation constants were also fitted to the data. Further, the initial concentrations of aqueous CO2 ([CO2]0) were originally calculated from relative gas flow rates of N2 and CO2, assuming ideal behavior, and the published saturation concentration of the...
The accuracy of flow meters is limited (±5%) and inspection of the fits revealed that these initial concentrations were only approximately correct so that the initial concentrations of CO₂ were also fitted for the final analysis. The results were always within the error limits of the flow meter estimates. We have previously established and confirmed this procedure.¹⁹

Due to the fact that all reactions are always coupled and no reaction can be analyzed individually, global analysis of the complete set of measurements is the only method capable of analyzing the reaction mechanism. We have developed global analysis and successfully employed the technique in several other investigations.¹⁹,²⁰,²³ A total of nine data sets (six formation (forward) and three dissociation (back) reaction measurements) have been analyzed globally, resulting in one complete set of rate and equilibrium constants. At each temperature, 10 replicates of each complete data set resulted in 10 complete sets of rate and equilibrium constants, allowing a proper statistical analysis of the fitted parameters. The resulting rate and equilibrium constants from the 10 separate data sets were averaged and are collected in Table 1 together with their standard deviations (in parentheses). All individual values at all temperatures were used for the determination of activation parameters and reaction enthalpies and entropies, which are listed in Table 2.

### RESULTS

**Formation Reaction of the Carbamate.** The kinetics of the reaction of ammonia with equilibrated aqueous CO₂ solutions (containing CO₂(aq) and the carbonate species H₂CO₃⁻, HCO₃⁻, and CO₃²⁻) was studied at different temperatures from 15 to 45 °C. Thymol blue indicator was used to follow the pH changes concomitant with the reactions. Figure 2 represents the absorbance change (at 590 nm) with time for the reaction of 3.8 mM CO₂(aq) with various concentrations of ammonia (2–10 mM) at 25 °C in the presence of 12.5 μM thymol blue. The solid colored lines are the fitted curves, while the markers, in black, are the measured absorbances. There is an initial fast reaction of approximately 0.5 s (see the inset of Figure 2) followed by slower absorbance changes that were strongly dependent on the ammonia concentration. At high ammonia concentration (excess) there was a slight secondary increase of the absorption, and at low concentration there was a linear decrease to zero absorption.

The absorbance change (at 590 nm) with time in the reaction of 3.8 mM CO₂(aq) with 3.0 mM ammonia at four different temperatures (15.0, 25.0, 35.0, and 45.0 °C) is shown in Figure 3. The reaction again features a fast initial phase and a much slower second phase, both being strongly temperature dependent. This figure also displays the measured data as well as the fitted curves which are again essentially indistinguishable.

**Decomposition Reaction of Carbamate.** Figure 4 displays the absorbance changes at 520 nm observed after the acidification of the pre-equilibrated solution of 1.8 mM ammonium carbamate, 23.2 mM ammonia, and 48.2 mM HCO₃⁻ over the temperature range 15–45 °C. The pH changes during this reaction are larger than in the previous study and required the use of two indicators. To cover the whole process, 50 μM alizarin red S and 12.5 μM methyl orange were added to the solutions. The initial concentration of carbamate in these solutions was previously established and successfully employed the technique in several other investigations.¹⁹,²³

### Table 1. Calculated Rate and Equilibrium Constants for the Reactions of Aqueous Ammonia CO₂(aq), and the Protonation Constants of Ammonia and Carbamate at Different Temperatures

<table>
<thead>
<tr>
<th>Reaction</th>
<th>15 °C</th>
<th>25 °C</th>
<th>35 °C</th>
<th>45 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂(aq) + NH₃ ⇌ NH₂COOH</td>
<td>kₗ [M⁻¹ s⁻¹]</td>
<td>2.05(3) × 10⁵</td>
<td>4.5(1) × 10⁵</td>
<td>9.27(6) × 10⁵</td>
</tr>
<tr>
<td>NH₂COOH ⇌ NH₂CO₂H + H⁺</td>
<td>k₋ [s⁻¹]</td>
<td>574(5 °C)¹⁷</td>
<td>915(10 °C)¹⁷</td>
<td>107(5 °C)¹⁵</td>
</tr>
<tr>
<td>NH₂CO₂H + H⁺ ⇌ NH₃ + H₂CO₂H</td>
<td>kₚ [M⁻¹]</td>
<td>29(4)</td>
<td>68(22)</td>
<td>1.8(1) × 10⁵</td>
</tr>
<tr>
<td>NH₃ + H⁺ ⇌ NH₄⁺</td>
<td>log Kₐ</td>
<td>6.74(4)</td>
<td>6.8(2)</td>
<td>6.72(3)</td>
</tr>
<tr>
<td>NH₂COOH ⇌ NH₂CO₂⁻ + H⁺</td>
<td>log Kₐ</td>
<td>9.551(4)</td>
<td>9.237(3)</td>
<td>8.931(3)</td>
</tr>
</tbody>
</table>

### Table 2. Calculated Activation Parameters, Enthalpies, and Entropies for the Reaction of Ammonia with CO₂(aq)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Arrhenius</th>
<th>Eyring</th>
<th>van’t Hoff</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃ + CO₂ ⇌ NH₂COOH</td>
<td>Eₐ [kJ mol⁻¹]</td>
<td>A</td>
<td>ΔH [kJ mol⁻¹]</td>
</tr>
<tr>
<td>NH₂COOH ⇌ NH₂ + CO₂</td>
<td>52(1)</td>
<td>2.1 × 10⁹</td>
<td>49(1)</td>
</tr>
<tr>
<td>NH₂COO⁻ + H⁺ ⇌ NH₂CO₂H</td>
<td>68(2)</td>
<td>5.7 × 10¹³</td>
<td>65(2)</td>
</tr>
<tr>
<td>NH₃ + H⁺ ⇌ NH₄⁺</td>
<td>53.7(7)</td>
<td>6(4)</td>
<td>4(2)</td>
</tr>
</tbody>
</table>
calculated based on published equilibrium constants, including the protonation constants of ammonia, carbamate, carbonate, and the equilibrium constant for the formation of ammonium carbamate from the reaction of ammonia with bicarbonate.21,24–26

Data fitting resulted in numerical values for all variable rate and equilibrium constants as well as the concentration profiles for all reacting species. Figure 5 displays the pH and calculated concentration profiles for all relevant species in the reaction of 3.8 mM CO$_2$ (aq) with 4.0 mM ammonia at 25 °C (refer to Figure 2, red curve, for the measured absorbance changes for this reaction). Interesting insight can be gained from inspection of such profiles which is difficult to glean from the fitted constants only. The first phase of the reaction takes place in about 1 s at

25 °C (see inset of Figure 5). During this initial phase, some 30% of the CO$_2$ reacts with ammonia to form the carbamic acid, which deprotonates immediately to form the carbamate; some 20% of the CO$_2$ reacts with hydroxide to form the bicarbonate ion. During this time, the pH drops from an initial value of about 10.4 to 9; this is also evident from the increased ratio of the concentrations of ammonium ion and ammonia. This pH drop has several consequences. The reduced concentrations of ammonia and OH$^-$ both slow down the reaction with CO$_2$ and the subsequent conversion of CO$_2$ (aq) to carbonate and carbamate is significantly slower. As a secondary effect, while the pH slowly drops further to about 8, the stability of the carbamate is reduced and its concentration drops to essentially zero in around 60 s. Clearly, ammonia is an efficient rate promoter in the transformation of CO$_2$ (aq) to carbonate species.

Figure 6 shows the pH and calculated concentration profiles for the reactions of a pre-equilibrated solution of 46.4 mM ammonia and 96.4 mM HCO$_3^-$, which contains 3.6 mM ammonium carbamate at 25 °C, after the addition of 130.0 mM HCl. Under these conditions, the carbamate is protonated to carbamic acid, which decomposes very quickly, the observed half-life being approximately 0.01 s. At low pH, carbonic acid also dissociates back to carbon dioxide and water. The initial pH is about 4 and increases with time to about 5.5 due to the removal of mainly carbonic acid to form CO$_2$ (aq) and carbamic acid to form ammonia, which immediately protonates under these pH conditions.

Apart from the concentration profiles, the fitting procedure produces estimates for the parameters of the model, which in our case are the fitted rate constants and the protonation constants of the carbamate at the temperatures examined. These are listed in Table 1. All additional parameters, that is, the rate and equilibrium constants that describe the interaction of carbon dioxide with water (k$_1$, k$_{-1}$) and hydroxide (k$_2$, k$_{-2}$) and the protonation constants of carbonate (K$_{eq}$) and bicarbonate (K$_2$) were taken from previously published studies.19 The temperature-dependent protonation constant of ammonia (K$_a$) was also determined in this study by potentiometric titration and the values obtained were in good agreement to those determined by Bates et al.27

Analyses of the temperature dependence of the rate constants were based on Eyring and Arrhenius relationships. Eyring plots
for all fitted rate constants are displayed in Figure 7. Full markers are used for the forward rate constant \( k_7 \) and empty markers for the back reaction \( k_{-7} \). Plots are linear within the error limits of the individual parameters. Arrhenius and Eyring parameters are listed in Table 2.

Figure 5. Calculated concentration profiles and pH in the reaction of 3.8 mM CO\(_2\)(aq) with 4.0 mM ammonia at 25 °C. The inset is an enlargement of the first 10 s of the reaction.

Figure 6. Calculated concentration profiles and pH in the decomposition of 1.8 mM ammonium carbamate at 25 °C, in the presence of 23.2 mM ammonia, 48.2 mM HCO\(_3^-\), and 65.0 mM HCl.

Figure 7. Eyring plot of \( \ln(k_i/T) \) vs \( 1/T \) for the reaction of ammonia with CO\(_2\)(aq). Solid markers are used for the forward reaction, and empty markers are used for the backward reaction.

van’t Hoff plots of \( \ln K \) versus \( 1/T \) for the equilibrium constant \( K_7 \) and \( K_8 \) are displayed in Figure 8 and show good linearity. Analysis of the data provides the enthalpy and entropy values of the reversible reaction, and the parameters are listed in Table 2.

**DISCUSSION**

The kinetics of the reversible reactions of aqueous ammonia with carbon dioxide (aq) has been comprehensively studied from 15 to 45 °C by stopped-flow visible spectrophotometry using indicators to define the pH of the reacting solution. Rate constants and the protonation constant of ammonium carbamate, as detailed in the reaction scheme given in Figure 1, were determined by fitting the data using global analysis. Arrhenius and Eyring analyses of the temperature dependence of the rate constants yielded the activation parameters of the reactions, while van’t Hoff analysis of the equilibrium constants provided the enthalpy and entropy values for the reactions. Prior to the present study, the only processes that have been analyzed quantitatively are the equilibrium between ammonia and bicarbonate and the forward rate for the reaction of ammonia with CO\(_2\)(aq), \( k_7 \).

Analysis of the forward kinetic data reveals that aqueous ammonia reacts with CO\(_2\)(aq) rapidly to form carboxamic acid,
which at the relevant pH values deprotonates instantly to give carbamate. Due to the concomitant pH changes, the equilibrium is reversed and the carbamate eventually decomposes to generate protonated ammonia and bicarbonate. The same reaction pathways have been observed by Hong et al.\textsuperscript{11,14} In contrast, both Bai et al.\textsuperscript{16} and Yeh et al.\textsuperscript{9} have reported that bicarbonate, and not carbamate, was the main product in their semibatch absorption studies of CO\textsubscript{2} by aqueous ammonia. However, it is likely that in these studies formation of carbamate was very fast and that, under the pH conditions, the unstable carbamate simply decomposed to form bicarbonate. This is consistent with the proposed reaction scheme and kinetic data of the present study. Analysis of the backward kinetic data indicates that the ammonia-derived carbamic acid has poorer stability than the equivalent monoethanolamine carbamic acid,\textsuperscript{20} with a rate constant of 450.0 M\textsuperscript{-1} s\textsuperscript{-1} (25 °C) and 29.8 M\textsuperscript{-1} s\textsuperscript{-1} (30 °C), respectively, for the \( k_{-7} \) pathway.

The rate constant (\( k_{-7} \)) for the reaction of CO\textsubscript{2}(aq) with ammonia is one of the most important parameters in the evaluation of the efficiency of PCC. Our results show that it increases by 7.5 times as the temperature rises from 15.0 to 45.0 °C, with \( k_{-7} = (2.05 ± 0.03) \times 10^5 \) M\textsuperscript{-1} s\textsuperscript{-1} at 15.0 °C, and \( (1.54 ± 0.06) \times 10^5 \) M\textsuperscript{-1} s\textsuperscript{-1} at 45.0 °C. Pinsent et al. determined this constant over a temperature range of 0–40 °C by using a rapid thermal method,\textsuperscript{15} and their values are in agreement with our results. The reaction of CO\textsubscript{2}(aq) with hydroxide and the protonation of ammonia were both included in their mechanism. However, they assumed that the reaction of ammonia with CO\textsubscript{2}(aq) was irreversible. Surprisingly, both Pinsent et al. and our studies give an activation energy with nearly the same value. Recently, Derk and Versteeg determined the rate constant for CO\textsubscript{2}(aq) with ammonia in a stirred cell reactor and, assuming that the reaction follows a zwitterion pathway.

As carbamate formation decreases the cyclic capacity of the amine solution, its formation is an undesirable part of the interaction in postcombustion capture (PCC) of CO\textsubscript{2} by an aqueous amine. Determination of the equilibrium constant of carbamate formation could thus act as a guide to select amines that are optimal for CO\textsubscript{2} capture. The values of the equilibrium constant \( K_{eq} \) in eq 2 at 15, 25, 35, and 45 °C were calculated from our kinetic results, and they decrease moderately with temperature. Only a value for the equilibrium constant of the reaction of ammonia with bicarbonate has appeared in the literature. From the equation in the paper by Edwards et al., the equilibrium constant of the reaction between ammonia and bicarbonate at 25 and 35 °C may be obtained, with values of 3.03 M\textsuperscript{-1} at 25 °C and 2.44 M\textsuperscript{-1} at 35 °C.\textsuperscript{25} Christensson et al. determined a value by a BaCO\textsubscript{3} precipitation method at an ionic strength of 0.5 M, giving 2.13 M\textsuperscript{-1} at 25 °C and 1.94 M\textsuperscript{-1} at 35 °C.\textsuperscript{24} The estimated equilibrium constants for the reaction of MEA with CO\textsubscript{2}(aq) have been determined by McCann et al.,\textsuperscript{20} and they are much higher than that of ammonia with CO\textsubscript{2}(aq), with a value for log \( K_{eq} \) of 2.69(2) at 30 °C. Our results also demonstrate that the equilibrium concentration of the carbamate is much lower for ammonia than for monoethanolamine, as indicated by higher CO\textsubscript{2} loading for ammonia solutions.

Solvation energy is another important issue in PCC. Direct calorimetric measurements have provided accurate values for the enthalpy of absorption for carbon dioxide capture by alkanolamines, such as MEA, DEA, and MDEA.\textsuperscript{30} Recently, McCann et al.\textsuperscript{31} determined enthalpy values for the carbonate formation reaction of ammonia and bicarbonate using a direct calorimetric technique, reporting a value of \(-27.6 ± 0.9\) kJ/mol\textsuperscript{-1}. However, to our knowledge, there is no report for the enthalpy of absorption in the reaction of ammonia with CO\textsubscript{2}(aq). van’t Hoff analyses of the temperature-dependent equilibrium constants of eq 2 yield an enthalpy value of \(-16(2)\) kJ mol\textsuperscript{-1}. The enthalpy value for the hydration of carbon dioxide in aqueous (H\textsubscript{2}CO\textsubscript{3}) and basic (HCO\textsubscript{3}\textsuperscript{-}) solution has been reported as 10(2) and \(-50(1)\) kJ mol\textsuperscript{-1}, respectively.\textsuperscript{19} To calculate the overall enthalpy of absorption in CO\textsubscript{2} capture by ammonia, the enthalpies of the protonation of ammonia, carbonate, and hydroxide need to be included, all of which are available in the literature.\textsuperscript{20} Provided that the molar percentage of each species is known, the overall enthalpy of absorption can be derived.

The absorption of CO\textsubscript{2} in NH\textsubscript{3} solutions involves both neutral and ionic species. Thus, solvation (i.e., hydration) effects will play a major role in the interpretation of activation entropies for some pathways. Moreover, many species will be strongly involved in hydrogen bonding with the solvent water molecules. For the reaction between NH\textsubscript{3} and CO\textsubscript{2}(aq), \( k_7 \) and \( k_{-7} \) eq 2, to give the carbamic acid (and its reverse reaction), in the formation of the transition state the entropies of activation are relatively small (Table 2). In both reactions, \( k_7 \) and \( k_{-7} \) only neutral molecular species are involved, with a decrease in the number of species for the forward reaction and an increase for the back reaction. Thus, the entropies of activation would be expected to be negative and positive, respectively, as is observed. The small values also suggest only minor changes in hydration occur during the forward and backward pathways. While little is known about solvation of NH\textsubscript{3} and the carbamic acid, other than they should be strongly involved in hydrogen-bonding with the solvent, theoretical calculations (ab initio molecular dynamics) have shown that aquated CO\textsubscript{2} is only slightly solvated and is, effectively, hydrophobic.\textsuperscript{17} Thus, NH\textsubscript{3} and the carbamic acid
would appear to be solvated to similar extents such that little change in solvation occurs in the forward and backward directions.

To our knowledge, no direct theoretical calculations have been made on the NH$_3$–CO$_2$ system, other than those of Buckingham et al. and more recently Arstad et al., which showed that proton transfer occurred in the formation of the transition state in the reaction of CO$_2$ with two NH$_3$ molecules (to give NH$_3$COOH and NH$_3$), or CO$_2$ with NH$_3$ and H$_2$O (to give NH$_3$COOH and H$_2$O), such that the formation of the carbamic acid is effectively being catalyzed by NH$_3$ and H$_2$O, respectively. In the first study, the calculations were performed using SCF/6-31G* and Møller–Plesset/6-31G* levels of theory, with geometry determined at the 3-21G level, but no solvent environment was included in the calculations. The results indicate that for direct reaction between NH$_3$ and CO$_2$ (with a four-membered ring transition state), the activation energy is +212 kJ mol$^{-1}$. Inclusion of either H$_2$O or NH$_3$ (to give a six-membered ring transition state), reduces the activation energies to +123.5 and +104 kJ mol$^{-1}$, respectively, while the reactions are endothermic (+36 and +27 kJ mol$^{-1}$, respectively). In the second study, which was performed at the GMMP2B3 level of theory, with structures optimized at B3LYP/6-31G**, similar results were obtained. Thus, for the direct reaction between NH$_3$ and CO$_2$, the activation energy was +204 kJ mol$^{-1}$, with a reaction energy of +55 kJ mol$^{-1}$ (i.e., endothermic). Inclusion of one H$_2$O or one NH$_3$ in the transition state again reduced the activation energies to +126 and +123 kJ mol$^{-1}$, with endothermic reaction energies of +41 and +30 kJ mol$^{-1}$, respectively. The addition of a second H$_2$O in the first scenario and an H$_2$O in the second scenario further reduced the activation energies to +60 and +54 kJ mol$^{-1}$, respectively, with reaction energies, now exothermic, of −21 and −34 kJ mol$^{-1}$, respectively. Our experimental data for the enthalpies and entropies given in Table 2 for the reaction of NH$_3$ with CO$_2$, given the similarity with the extensive theoretical studies and our values, confirms that water is intimately involved in the reactions.

Finally, our kinetic results indicate that the formation of ammonium carbamate in the reaction of aqueous ammonia with CO$_2$(aq) has moderately fast rate constants, both for formation and removal. Interestingly, under particular conditions that depend strongly on pH, no ammonium carbamate accumulates in the overall reaction, which implies that ammonia has a great advantage over MEA and other alkanolamines in terms of the overall cyclic capacity of the amine.

### CONCLUSION

The kinetics of ammonia with CO$_2$(aq) was studied by the stopped-flow technique at different temperatures ranging from 15 to 45 °C. A mechanism has been proposed involving two rate constants and one equilibrium constant that were evaluated from fitting at the four different temperatures. The rate constants increase with temperature. Arrhenius and Eyring analyses of the kinetic data gave the activation energy and the activation enthalpy and entropy of reaction, respectively. The equilibrium constant $K_e$ in eq 2 decreases slightly with temperature, van’t Hoff analysis yielded the enthalpy and entropy values for the reactions as well as the protonation constant of the amine. Our calculated concentration profiles indicate that little ammonium carbamate accumulates in the overall reaction, implying that ammonia has a significant advantage over other alkanolamines in the cyclic capacity. Our results should help to guide the optimization of the performance of carbon dioxide capture by ammonia.

### ASSOCIATED CONTENT

- **Supporting Information.** A list of all initial concentrations for the kinetic experiments, including the equilibrium compositions for the back reactions, which contain calculated concentrations of the carbamate. This material is available free of charge via the Internet at http://pubs.acs.org.

### ACKNOWLEDGMENT

Financial support by a CSIRO Flagship grant is acknowledged, as is a University of Newcastle RIB grant that allowed the purchase of the J&M Tidas MCS 500-3 diode-array detector.

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Publication-5

Comprehensive Kinetic and Thermodynamic Study of the Reactions of CO$_2$ (aq) and HCO$_3^-$ with Monoethanolamine (MEA) in Aqueous Solution

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Published: Journal Physical Chemistry A, 115, 14340-14349
(28th October 2011)
Comprehensive Kinetic and Thermodynamic Study of the Reactions of CO$_2$(aq) and HCO$_3^-$ with Monoethanolamine (MEA) in Aqueous Solution

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ABSTRACT: The temperature dependence of the reversible reaction between CO$_2$(aq) and monoethanolamine (MEA) has been investigated using stopped-flow spectrophotometry by following the pH changes during the reactions with colored acid–base indicators. Multivariate global analysis of both the forward and backward kinetic measurements for the reaction of CO$_2$(aq) with MEA yielded the rate and equilibrium constants, including the protonation constant of MEA carbamate, for the temperature range of 15–45 °C. Analysis of the rate and equilibrium constants in terms of the Arrhenius, Eyring, and van’t Hoff relationships gave the relevant thermodynamic parameters. In addition, the rate and equilibrium constants for the slow, reversible reaction of bicarbonate with MEA are reported at 25.0 °C. At high pH, reactions of the amine with CO$_2$ and with bicarbonate are significant.

INTRODUCTION

The capture and sequestration of carbon dioxide following the combustion of fossil fuels for the generation of electricity is a highly topical and important task in the now globally recognized effort to reduce the effects that climate change has on our existence and lifestyles. The general consensus is that immediate reductions in carbon dioxide emissions from coal-fired power generation are required until more efficient technologies or, more importantly, renewable energy technologies can take over our energy supplies. Postcombustion capture (PCC) technologies are at the forefront of research efforts in this area and are the most promising approach capable of providing short-term reductions in CO$_2$ emissions.$^{1,2}$

The engineering aspects behind PCC are now under investigation, with a number of small PCC pilot plants retrofitted to commercial power stations operating under true industrial conditions. However, commercial and industrial scale-up and adaptation of the technology to an existing coal-fired power station are not trivial. In terms of the economics alone, the optimization of each new PCC plant by this process is expensive. One solution is to model a PCC plant by combining both the engineering and chemical data from smaller laboratory- and pilot-scale experiments. This method offers an efficient and cost-effective way to optimize a plant for scale-up and deployment.$^{3,4}$

Reversible chemical absorption involving an amine is the best investigated of the PCC technologies. The engineering of any putative plant will rely heavily on the solvent type and its behavior. Chemists can provide knowledge of the chemical reactions of the amine with CO$_2$ in aqueous solution, the corresponding rate and equilibrium constants for the reactions, and the energies (activation parameters, enthalpies, and entropies) that are crucial for the complete modeling of the absorption and stripping processes. Whereas high-level theoretical studies such as those of Xie et al.$^5$ Shim et al.$^6$ Da Silva et al.$^7$ and Arstad et al.$^8$ provide insight into the chemistry and possible mechanistic pathways, experimental evidence to validate and support the theories is required. However, the experimental investigation of such a complex system is not trivial for several reasons. The rates of the reactions, in particular, the direct reaction of CO$_2$(aq) with amine, are high; a number of simultaneous reactions occur at the same time, which requires sophisticated interpretation and analysis of the measured data; and no simple spectrophotometric measurements allow the direct observation of the reactions.

The direct interaction of CO$_2$ with amines has been surprisingly well studied. Of the amines investigated, MEA is the most common amine examined for the purposes of PCC. Most commonly the kinetics of the direct reaction between CO$_2$ and amine are examined and the rate constants for the reaction reported. Hikita et al.$^9$ reported the temperature dependence of the direct reaction between CO$_2$ and MEA, referred to in all of the following cases as k$_D$, at 15, 25, and 35 °C by the rapid-mixing temperature-change method, with the rate constants correlated.
by log \( k_1 = 10.99 - 2152/T \). This gave rate constant values for \( k_1 \) of 3235, 5888, and 10230 \( \text{M}^{-1} \text{s}^{-1} \) at 15, 25, and 35 °C, respectively. The Arrhenius activation energy was found to be 41 kJ mol\(^{-1}\). The kinetics of the reaction was interpreted as an irreversible reaction between CO2 and MEA; further, corrections for the effects of OH\(^-\) on the absorption were applied. Donaldson et al.\(^{10}\) investigated the reaction kinetics of CO2 with MEA at 25 °C by a \( ^{14} \text{C} \) tracer membrane technique, which gave a value for \( k_5 \) of 6000 \( \text{M}^{-1} \text{s}^{-1} \). For an extensive review of the MEA/CO2 kinetics prior to 1984, a review has been published by Blauhoff et al.\(^{11}\). Since then, other studies that have investigated the reaction between CO2 and MEA have appeared in the literature. Alper\(^{12}\) reported a rate constant of 5545 m\(^3\) kmol\(^{-1}\) s\(^{-1}\) at 25 °C with an Arrhenius activation energy of 46.7 kJ mol\(^{-1}\). Littel et al.\(^{13}\) reported the temperature dependence of \( k_7 \) at 45 °C (10400 M\(^{-1}\) s\(^{-1}\)) and 60 °C (25700 M\(^{-1}\) s\(^{-1}\)). Ali\(^{14}\) measured the kinetics over the temperature range of 25–40 °C and obtained values for \( k_7 \) ranging from 5545 to 13600 m\(^3\) kmol\(^{-1}\) s\(^{-1}\) with an Arrhenius activation energy of 46.6 kJ mol\(^{-1}\). Henri et al.\(^{15}\) reported a value for \( k_7 \) of 500 m\(^3\) kmol\(^{-1}\) s\(^{-1}\) at 25 °C using the stopped-flow technique, and more recently, Puxty et al.\(^{16}\) determined a value for \( k_7 \) of 2634 L mol\(^{-1}\) s\(^{-1}\) at 10 °C using the wetted-wall technique. Finally, McCann et al.\(^{17}\) published a complete quantitative analysis of the MEA system at 30 °C, and obtained a value for \( k_7 \) of 6110 M\(^{-1}\) s\(^{-1}\) for the direct reaction of CO2 with MEA. These published values for \( k_7 \) are represented graphically in Figure S below.

A significant spread of values for the rate constant \( k_7 \) is apparent from the literature. In this study, the kinetics of the reaction of \( \text{CO}_2(\text{aq}) \) with MEA has been revisited in detail using a stopped-flow spectrophotometric technique, with colored indicators employed to monitor the pH changes during the reactions. Measurements were performed at 15, 20, 25, 35, and 45 °C, and analysis of the kinetics in terms of the Arrhenius, Eyring, and van’t Hoff relationships has revealed the Arrhenius activation parameters, the enthalpies and entropies of activation, and enthalpy and entropy for the reaction.

Considering the reversibility of the carbamate formation reaction, it is surprising that only one value has been published for the rate constant, \( k_{-7} \), for the back-reaction at 30 °C, and thus, its temperature dependence and activation parameters are not known.

The protonation constant of the carbamate determines a large extent the pH dependence of the kinetic stability of the carbamate/carbamic acid; the carbamate is several orders of magnitude more stable than the carbamic acid. Although a few values for the protonation constant of carbamates have been published, to our knowledge, there is only one study on a temperature dependence, showing a very modest temperature dependence.\(^{18}\) To completely understand the pH and temperature dependence of the kinetics and thermodynamic stability of carbanates/carbamic acids, this property needs to be determined for a range of key amines.

Further, the direct reaction of \( \text{HCO}_3^- \) with MEA to form carbamate has also been confirmed here using \(^1H\) NMR spectroscopy at 25 °C. This reaction is usually not considered for PCC applications, as the direct reaction of CO2 with the amine is much faster. However, the kinetic stability of the carbamate is strongly dependent on the rate of decomposition reaction of this reaction path.

This study completes the full analysis of the MEA system and contributes constants for the modeling of the system, as well as providing the enthalpies for the calculation of chemical absorption and chemical desorption for a complete cycle of a PCC plant.

### EXPERIMENTAL SECTION

High-purity CO2 gas (BOC), N2 (Coregas), potassium bicarbonate (BDH), sodium hydroxide (Merck), monoethanolamine (Sigma-Aldrich), potassium hydrogen phthalate (AJAX), hydrochloric acid (AJAX), thymol blue sodium salt (Sigma-Aldrich), alizarin red S (BDH), and methyl orange (SELBY) were all used as obtained. MEA, NaOH, and HCl solutions were standardized by potentiometric titrations. Ultra-high-purity Milli-Q water was boiled to remove CO2 gas and used to prepare all aqueous solutions. All samples and solutions were stored in a N2-purged glovebag.

**Stopped-Flow Spectrophotometric Studies: Formation and Decomposition Reactions of MEA Carbamate.** The kinetics of the fast reactions of aqueous carbon dioxide with MEA and of the decomposition of MEA carbamate/carbamic acid were monitored on an Applied Photophysics DX-17 spectrophotometer equipped with a J&M Tidas MCS 500-3 diode-array detector, by observing the pH changes over the wavelength range 400–700 nm through coupling to colored indicators. Samples were thermostatted to within ±0.1 °C at temperatures of 15.0, 20.0, 25.0, 35.0, and 45.0 °C, and the exact temperature was recorded by a thermocouple located within the stopped-flow instrument.

The formation of MEA carbamate from aqueous carbon dioxide and MEA was initiated by mixing an aqueous solution of MEA and thymol blue (1:1 v/v) with an aqueous solution of CO2. The initial concentrations of MEA and \( \text{CO}_2(\text{aq}) \) ([MEA]0 and \([\text{CO}_2(\text{aq})]_0\) ranged from 1.0 to 16.0 mM and from 3.0 to 6.0 mM, respectively. All reactions were performed in the presence of 12.5 \( \mu \text{M} \) thymol blue (log \( K = 9.05 \) at 25.0 °C). Absorption changes are attributable to protonation of the thymol blue indicator as a result of the release of a proton from MEA carbamic acid that formed during the reaction and the parallel reaction of CO2 with H2O and OH\(^-\) to form bicarbonate, also with the release of one proton. A plot of the absorbance data obtained during the reaction of 6.0 mM MEA and 6.0 mM \( \text{CO}_2(\text{aq}) \) at 35.0 °C in the presence of 12.5 \( \mu \text{M} \) thymol blue is shown in Figure 1.

Similarly, the decomposition of MEA carbamate was initiated by mixing aqueous solutions of MEA carbamate (1:1 v/v) with solutions of hydrochloric acid ([HCl]0 = 40.0–65.0 mM). The carbamate for the reactions was generated by mixing 0.05 M MEA with 0.1 M bicarbonate and then allowing a minimum of 24 h for equilibration. The composition of the solution, specifically, the concentration of carbamate in the equilibrium solution, was determined directly by \(^1H\) NMR spectroscopy. Because of the large change in pH during the decomposition reactions, a combination of alizarin red S (log \( K = 5.5 \) at 25.0 °C)\(^{19}\) and methyl orange (log \( K = 3.5 \) at 25.0 °C) indicators was used to follow the kinetics of reaction.

Values for the protonation constant of MEA at different temperatures were taken from the potentiometric titration study of Fernandes et al.\(^{20}\)

All measurements were repeated five times, allowing for a comprehensive statistical analysis of the data.

**\(^1H\) NMR Studies: Formation and Decomposition of MEA Carbamate (at High pH).** The kinetics of the slow formation of MEA carbamate from bicarbonate and MEA was observed by \(^1H\) NMR spectroscopy at 25.0 °C by mixing a 0.05 M MEA solution (1:1 v/v) with a 0.1 M HCO3\(^-\) solution. To determine the pH
dependence of this reaction, NaOH ([OH\(^-\)]\(_0\) = 0.01–0.04 M) was added to the MEA solution before mixing. The initial spectrum was recorded after approximately 5 min, and each subsequent spectrum was recorded at predetermined time intervals to establish the kinetics of the reaction. The slow decomposition of MEA carbamate at high pH was observed by mixing (1:1 v/v) a pre-equilibrated solution of MEA carbamate containing 0.035 M MEA, 0.128 M HCO\(_3^-\), and 0.058 M carbamate with a NaOH ([OH\(^-\)]\(_0\) = 0.144–0.188 M) solution.

A glass insert containing 3-(trimethylsilyl)propionic acid-d\(_4\) sodium salt (TSP) as a reference in D\(_2\)O, the latter acting as the locking agent, was introduced into the NMR tube for all samples prior to insertion into the NMR instrument and spectral measurement.

DATA ANALYSIS

A mechanism including all of the CO\(_2\)/carbonate reactions/protonations, as well as the reaction(s) leading to the formation of MEA carbamate/carbamic acid, was applied in our previous studies of the MEA and ammonia systems with success.\(^{17,18}\) The same mechanistic approach was employed here for the temperature-dependent investigation of the reaction of MEA with CO\(_2\)(aq) and the direct reaction of MEA with HCO\(_3^-\) at 25 °C. As with ammonia, we implemented the rate constants for the reactions of CO\(_2\)(aq) with OH\(^-\) and H\(_2\)O, eqs 1 and 2, and the associated protonation equilibria of carbonate, bicarbonate, and H\(_2\)O, eqs 3–5, from our previous study and the literature.\(^{21–24}\)

\[
\begin{alignat}{2}
\text{CO}_2(aq) + \text{H}_2\text{O} & \rightleftharpoons & \text{H}_2\text{CO}_3 & \quad (1) \\
\text{CO}_2(aq) + \text{OH}^- & \rightleftharpoons & \text{HCO}_3^- & \quad (2) \\
\text{CO}_3^{2-} + \text{H}^+ & \rightleftharpoons & \text{HCO}_3^- & \quad (3) \\
\text{HCO}_3^- + \text{H}^+ & \rightleftharpoons & \text{H}_2\text{CO}_3 & \quad (4) \\
\text{OH}^- + \text{H}^+ & \rightleftharpoons & \text{H}_2\text{O} & \quad (5)
\end{alignat}
\]

This known part of the overall reaction scheme is indicated by red dashed lines in Figure 2. The reaction scheme also displays the interactions between the amine and the CO\(_2\)/carbonate group in blue and the protonation equilibrium of the amine in green. The associated amine/CO\(_2\)/HCO\(_3^-\) reactions, eqs 6–9, are also provided.

\[
\begin{alignat}{2}
\text{RNH}_2 & + \text{H}^+ & \rightleftharpoons & \text{RNH}_3^+ \quad (6) \\
\text{RNH}_2 & + \text{CO}_2(aq) & \rightleftharpoons & \text{RNHCO}_2\text{H} \quad (7) \\
\text{RNHCO}_2^- & + \text{H}^+ & \rightleftharpoons & \text{RNHCO}_2\text{H} \quad (8) \\
\text{RNH}_2 & + \text{HCO}_3^- & \rightleftharpoons & \text{RNHCO}_2^- (\text{+H}_2\text{O}) \quad (9)
\end{alignat}
\]

Global analysis of a series of measurements was used to elucidate the kinetic constants for the reactions, \(k_7\), \(k_{-7}\), and \(k_{9}\), as well as the equilibrium constant, \(K_7 (= k_7/k_{-7})\), and the protonation constant of MEA carbamate, \(K_8\). As a consequence of the principle of microscopic reversibility, the kinetic constant for the reverse reaction of MEA carbamate to bicarbonate and amine, \(k_{-9}\), was calculated based on the other constants in the
loop as $k_{-9} = (k_9 K_{-7} k_{-1} K_7)/(k_{-9} K_9)$. No efforts were made to maintain constant ionic strength; instead, Debye–Hückel approximations for species activities were applied in the numerical fitting.

All multivariate data analyses were performed using ReactLab-Kinetics (www.jplusconsulting.com/products/) and in-house software written in Matlab.

**RESULTS**

The effect of amine concentration on the kinetics of the reaction between MEA ([MEA]$_0$ = 2.0–16.0 mM) and CO$_2$(aq) ([CO$_2$]$_0$ = 6.0 mM) at 35.0 °C in the presence of 12.5 μM thymol blue, with absorbance traces at 590 nm, is depicted in Figure 3. The symbols represent the actual measurements, and the lines are the fitted absorption profiles. The concentration profiles for the measurement between 4.0 mM MEA and 6.0 mM CO$_2$(aq) are shown at the right of Figure 3. Note that the change in pH for the reaction is displayed on a secondary y axis.

From the absorbance traces, the reaction appears to become slower as the concentration of MEA increases. However, this is the result of following the pH during the reactions, as higher concentrations of amine result in increased buffer action, so that the reaction only appears to be slower. Parallel to the MEA carbamate reaction, CO$_2$ reacts with water and hydroxide to form small amounts of bicarbonate. During this reaction, the pH changes from approximately 10 to 8.

The effect of acid concentration on the decomposition of MEA carbamate at 15.0 °C is shown in Figure 4. The initial concentrations of MEA carbamate and the amine species were determined directly by $^1$H NMR spectroscopy. Mixing of the acid and the equilibrated carbamate solution results in immediate protonation of the carbonate species to form carbonic acid and of MEA carbamate to form MEA carbamic acid. The MEA carbamic acid decomposes, resulting in free amine, which immediately protonates; the carbonic acid re-equilibrates to form CO$_2$ and water. Both processes result in an increase of the pH and the partial deprotonation of carbonic acid. The pH change for this reaction is approximately from 3 to 6.

**Kinetic Fitting Results of the CO$_2$ Pathway.** Global analysis of the forward and backward stopped-flow measurements revealed the rate constants for the direct reaction of CO$_2$(aq) with MEA. The protonation constant of the carbamate was also fitted to the data. The corresponding rate and equilibrium constants are listed in Table 1 at each of the temperatures studied over the range from 15.0 to 45.0 °C.

An Eyring plot of the rate constants $k_7$ and $k_{-7}$ determined at each temperature, along with the corresponding literature values, is shown in Figure 5.
Table 1. Calculated Rate and Equilibrium Constants, Activation Parameters, and Enthalpy and Entropy Values for the Reversible Reaction of Aqueous MEA with CO$_2$(aq), Including the Protonation Constant of MEA Carbamate at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>E$_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\log K$</th>
<th>$k_f$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_r$ (M$^{-1}$)</th>
<th>$k_d$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>4.18</td>
<td>-47.3</td>
<td>-19.1</td>
<td>38(1)</td>
<td>1.10 x 10$^3$</td>
<td>61(2)</td>
<td>23(2)</td>
</tr>
<tr>
<td>20.0</td>
<td>4.78</td>
<td>-47.7</td>
<td>-20.2</td>
<td>41(8)</td>
<td>1.0 x 10$^3$</td>
<td>62(2)</td>
<td>6.5(2) x 10$^3$</td>
</tr>
<tr>
<td>25.0</td>
<td>5.8</td>
<td>-47.9</td>
<td>-20.5</td>
<td>41(8)</td>
<td>1.0 x 10$^3$</td>
<td>62(2)</td>
<td>6.5(2) x 10$^3$</td>
</tr>
<tr>
<td>35.0</td>
<td>7.6</td>
<td>-48.7</td>
<td>-20.7</td>
<td>42(1)</td>
<td>1.0 x 10$^3$</td>
<td>63(2)</td>
<td>6.6(2) x 10$^3$</td>
</tr>
</tbody>
</table>

Numbers in parentheses represent the error in the last digit.

Formation of MEA Carbamate from Bicarbonate and MEA and Its Decomposition at 25.0 °C, Followed by $^1$H NMR Spectroscopy. The kinetics of the much slower reaction between HCO$_3^-$ and MEA at high pH was studied at 25.0 °C by $^1$H NMR spectroscopy. Figure 6 displays the concentration of MEA carbamate over time for the direct reaction of HCO$_3^-$ and MEA, as well as the pH dependence of this reaction in the presence of 0.0–0.04 M NaOH. The complete species concentration profile for the reaction of 0.05 M MEA with 0.1 M HCO$_3^-$ in the presence of 0.04 M NaOH (bottom trace at the left of Figure 6) is shown at the right of Figure 6. The kinetics is slower at higher concentrations of OH$^-$ as a result of the deprotonation and, thus, the lower concentration of the bicarbonate.

The effect of the OH$^-$ concentration on the dissociation of a pre-equilibrated MEA carbamate solution containing 0.035 M MEA, 0.128 M HCO$_3^-$, and 0.058 M carbamate was studied by $^1$H NMR spectroscopy at 25.0 °C. The concentrations of carbonate over time in the presence of 0.144 and 0.188 M NaOH are shown in Figure 7. The concentration profile for the dissociation of MEA carbamate in the presence of 0.144 mM NaOH (top trace of Figure 7 at the left) is displayed at the right of Figure 7. It is clear from the MEA carbamate concentrations at the left of Figure 7 that the carbamate is reasonably stable at high pH, however, it becomes less stable as the concentration of NaOH increases, as is evident from the increased extent to which it dissociates at higher NaOH concentrations. The equilibrium concentration of the carbamate decreases as the concentration of the carbonate, which is not reactive, increases. In terms of the rate of dissociation, the reaction rate also decreases with an increase in pH. At high pH, the equilibrium consists mainly of MEA, carbonate, and free amine. The carbamate decomposes by two pathways: (a) direct decomposition to bicarbonate and amine ($k_{d}$) or (b) decomposition of MEA carboxyl acid to CO$_2$ and amine. The higher the pH, the slower the reaction by the second pathway, because less protonated MEA carbamate exists in solution.
Table 2. Calculated Rate and Equilibrium Constants \( k_{\text{c}} \), \( k_{-\text{c}} \), and \( K_{\text{f}} \) for the Reaction of Aqueous MEA with Bicarbonate at 25.0 \(^\circ\)C

<table>
<thead>
<tr>
<th>reaction</th>
<th>constant</th>
<th>25.0 (^\circ)C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{RNH}_2 + \text{HCO}_3^- \rightleftharpoons \text{RNHCO}_2^- )</td>
<td>( k_{\text{c}} ) ( (\text{M}^{-1}\text{s}^{-1}) )</td>
<td>6.0(1) ( \times ) 10(^{-3} )</td>
</tr>
<tr>
<td></td>
<td>( k_{-\text{c}} ) ( (\text{s}^{-1}) )</td>
<td>8.3(1) ( \times ) 10(^{-5} )</td>
</tr>
<tr>
<td></td>
<td>( K_{\text{f}} ) ( (\text{M}^{-1}) )</td>
<td>72.3(3)</td>
</tr>
</tbody>
</table>

Global analysis of the \(^1\)H NMR reaction data at 25.0 \(^\circ\)C generated rate and equilibrium constants for the direct reaction of HCO\(_3^-\) with MEA, namely, \( k_{\text{c}} \), \( k_{-\text{c}} \), and \( K_{\text{f}} \). Note that \( k_{-\text{c}} \) is defined as pseudo-first order rate constant. The corresponding rate and equilibrium constants are reported in Table 2.

## DISCUSSION

\( \text{CO}_2(\text{aq}) + \text{MEA}: k_7, k_{-7}, \text{and } K_7 \). Under PCC conditions, the initial absorption kinetics is dominated by the fast direct reaction of \( \text{CO}_2(\text{aq}) \) with amine. Because this reaction is the most relevant reaction for PCC, investigation of the kinetics and thermodynamics of this reaction should provide insight into the suitability of a solvent for this application. The reaction of \( \text{CO}_2 \) with MEA has been well investigated in the literature by a number of different methods, and the kinetics of this reaction was comprehensively reetermined here for the temperature range 15.0—45.0 \(^\circ\)C. Figure 5 shows an Eyring plot of the values for \( k_7 \) and \( k_{-7} \), eq 7, determined in this study, together with the corresponding literature values. Inspection of this figure reveals a good linear temperature dependence of the constants \( k_7 \) and \( k_{-7} \) for the reversible reaction of \( \text{CO}_2(\text{aq}) \) with MEA. (See the Introduction for a detailed list of published values and their graphical representation in Figure 5.) Good agreement with the literature is observed for \( k_7 \), although the values determined in this work are slightly lower than the corresponding literature values at most temperatures. This is not surprising considering the different experimental techniques and mechanisms used to determine the rate constants. Several of the published analyses did not include the parallel reactions of \( \text{CO}_2 \) with water and hydroxide; this naturally results in an overestimation of \( k_7 \). Furthermore, depending on the handling of physical constants for the absorption of \( \text{CO}_2 \), rate constants determined by gas—liquid techniques and partial pressure experiments could differ from those determined in this study, as mass-transfer phenomenon can influence the kinetics, which is not a complication in the present study.

The rate constants \( k_7 \) and \( k_{-7} \) determined in this study were found to increase with increasing temperature and to change by approximately 5-fold and 10-fold, respectively, over the 30 \(^\circ\)C temperature range studied. The expression for the forward rate constant was correlated by the Arrhenius equation with temperature as \( k_7 = 5.8 \times 10^{10} \exp \left[ -4872/T[K] \right] \). Extrapolation of \( k_7 \) to 60.0 \(^\circ\)C by this relationship gives a value of \( 2.57 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \), which is in excellent agreement with the corresponding value determined by Littel et al.\(^{13} \) of \( 2.57 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \). In an independent study by McCann et al.,\(^{17} \) the corresponding value for \( k_7 \) at 30.0 \(^\circ\)C (6120 M\(^{-1}\)s\(^{-1}\)) is also in excellent agreement with the values obtained in this study. Because of the limitations of the stopped-flow spectrophotometer, we were unable to determine the kinetics of the reactions at higher temperatures.

The back-reaction rate constant for the dissociation of MEA carbamate, \( k_{-7} \), has appeared previously in the literature only once.\(^{17} \) We performed direct stopped-flow measurements for the dissociation of MEA carbamate and determined the associated rate constant(s) for the back-reaction. As with the forward rate constant, the back-reaction rate constant shows a good linear temperature dependence, and the expression for the back-reaction was correlated by the Arrhenius equation with temperature as \( k_{-7} = 1.0 \times 10^{13} \exp \left[ -7583/T[K] \right] \). In view of the difficult nature of the dissociation experiments, the back-reaction has not previously been observed directly for MEA; rather, the rate for this reaction is more easily calculated from values of the forward rate constant, \( k_7 \), and the equilibrium constant, \( K_7 \). Using this approach, McCann et al.\(^{17} \) determined a value for \( k_{-7} \) of 29.6 s\(^{-1}\) at 30.0 \(^\circ\)C, which is significantly lower than the value obtained in this work. This discrepancy can be explained by the utilization of superior direct measurements here for the back-reaction, which was not investigated in the study by McCann et al. Although no other constants are available for the dissociation reaction, the reversibility of the reaction has been considered.\(^{13} \)

The equilibrium compositions of \( \text{CO}_2/\text{amine} \) solutions are commonly determined indirectly by gas—liquid and partial pressure measurements. The determination of the equilibrium constant for \( \text{CO}_2 \) and MEA, \( K_7 \), by these methods relies on the interpretation of the measurements and the handling of the gas absorption, chemical equilibrium, and solubility of \( \text{CO}_2 \) in the
amine solution, which is typically determined based on a CO$_2$/N$_2$O analogy.\textsuperscript{13,30} As with kinetic studies, although not as critical in equilibrium studies, the physical constants relating to the absorption of CO$_2$ into amine solutions will affect the calculated equilibrium situation. Because the concentrations of the chemical species are inferred indirectly from a chemical model and not determined directly, these methods are far from trivial, and accurate determination of the equilibrium species and constants is difficult, particularly at elevated temperatures. However, it is possible to determine the equilibrium constants from the corresponding forward and backward rate constants. The equilibrium constants for the direct reaction of CO$_2$ (aq) with MEA were determined in this work between 15.0 and 45.0°C and are listed in Table 1. The equilibrium constants show a good linear dependence on temperature, decreasing by approximately 2.5-fold over the temperature range studied here. van’t Hoff analysis of the temperature dependence results in the enthalpy and entropy of the reaction.

The overall absorption kinetics of CO$_2$ into aqueous amine solutions is determined by a number of competing parallel reactions, eqs 1, 2, 7, and 9. Under the fast reaction conditions of the stopped-flow investigation, the contributions of the reaction of CO$_2$ (aq) with H$_2$O and that of HCO$_3^-$ with MEA are negligible. This might not be the case in gas-liquid measurements, and small differences in the rate constants for these reactions, particularly if extrapolations are performed, will create the type of discrepancy between studies indicated in Figure 6. Furthermore, the contribution to absorption by hydroxide is often neglected because its concentration is much lower than that of the amine. However, at high pH (high amine concentration) and high temperature, the reaction of CO$_2$ with OH$^-$ will have a pronounced effect on the absorption kinetics, with the resulting rate constants representing the sum of the amine and hydroxide contributions. Small differences in ionic strength and temperature between studies will also give rise to the observed inconsistencies in the rate constants.

From the observed kinetic analysis and concentration profiles, the forward reaction proceeds by the fast absorption of CO$_2$ (aq) by the amine and OH$^-$ in combination, producing carbamic acid and bicarbonate, respectively. The amine is consumed quickly at approximately twice the rate of CO$_2$ because of the stoichiometry of the reaction and continuous protonation of the amine. The back-reaction proceeds at low pH through the instantaneous protonation of MEA carbamate to carbamic acid, yielding free CO$_2$ (aq) and HCO$_3^-$. All of the amine is protonated at this pH.

$\text{HCO}_3^- + \text{MEA} \rightarrow k_9, k_{-9}, \text{and } K_9$. The reactions and conditions observed within the industrial PCC process can differ substantially from those observed in the chemistry laboratory. In particular,
the depleted amine solution that returns from the stripper contains not pure amine but a substantial amount of bicarbonate. Introduction of CO₂ into such a solution will result in different processes than simple introduction into a pure amine solution. To complete the quantitative description of all processes, accurate knowledge of the kinetics of the reaction between bicarbonate and amine is also important.

In this study, the kinetics of the reversible reaction between HCO₃⁻ and MEA was investigated by ¹H NMR spectroscopy, and the rate constants for this reaction at 25.0 °C are reported in Table 2. A direct, reversible pathway leading to the formation of MEA carbamate, k₉ and k⁻⁹, eq 7, between bicarbonate and amine was introduced. The fitted traces for the ¹H NMR measurements of the reaction between HCO₃⁻ and MEA and the dissociation of carbamate in the presence of NaOH are shown in Figure 8. Two models were used to fit the data (refer to Figure 2 for a graphical representation of the model): (a) only reactions corresponding to k₉ and k⁻⁹ leading to the carbamate and (b) the full model, which incorporates the direct reversible reactions of HCO₃⁻ with MEA, k₉ and k⁻⁹, as well as those corresponding to k₇ and k⁻⁷. The predicted equilibrium situations are identical for the two models; however, the reduced model is incapable of reproducing the measurement data correctly, resulting in an underestimation of the reaction kinetics.

In the reduced model, the path of dissociation of carbamate is through carbamic acid and its subsequent dissociation into amine and CO₂. At high pH, the concentration of protonated carbamate is very small, and thus, the path is not sufficient to explain the observed kinetics. During the analysis of the forward NMR measurements, without the direct HCO₃⁻ pathway, the fitting program attempts to increase the value of k₇ to accelerate and compensate the kinetics, at the expense of the fits for the forward reaction stopped-flow measurements, where k₇ is well-defined. The protonation constant of the carbamate, K₀, remains essentially the same for both fitting cases. Although the rate constant for the reaction of CO₂ with MEA, k₉, is approximately 10⁶ higher than that for the direct HCO₃⁻ path, k₉, at 25.0 °C, little CO₂ (aq) is present under the conditions of this reaction at high pH. At high pH in the reduced mechanism, the reaction proceeds through the formation of CO₂ (aq) from (bi)carbonate, and the limiting reaction is the dissociation of carbonic acid to CO₂ (aq), k⁻⁷, which has a fixed, known, rate constant. Thus, when the concentrations of HCO₃⁻ and MEA are appreciable, the direct pathway contributes significantly to the formation of MEA carbamate. The kinetics of the HCO₃⁻ reactions with MEA are not as well investigated as that of the direct reaction with CO₂ (aq). McCann et al.¹⁷ reported values for k₉, 1.05 × 10⁻³ M⁻¹ s⁻¹, and k⁻⁹, 7.43 × 10⁻³ s⁻¹, at 30.0 °C. The rate constants are lower than those determined in this study, and consequently, the equilibrium constant is also affected. This could be a result of the significant differences in experimental conditions/concentrations between the respective NMR studies.

**Protonation of the Carbamate: K₀.** The kinetic stability of carbamate/carbamic acid is strongly pH-dependent. At 25 °C, the rate constant for the decomposition of the carbamic acid is 6 orders of magnitude higher than that for the decomposition of the carbamate. As a result, at moderately basic pH, the carbamate will decompose predominantly through its protonated form. For MEA, the decomposition through the carbamate is faster above pH 12. In this context, it is interesting to realize that, if the direct decomposition of carbamate to bicarbonate is excluded, its kinetic stability would increase linearly with pH without an upper limit.

MEA carbamic acid is kinetically and thermodynamically very labile and does not exist in appreciable concentrations at any pH. The values for the MEA carbamate protonation constant should thus be considered only an estimate, as they are only loosely defined by the data. The value for log K₀ of 6.5 is comparable to other published values, such as, 6.8 for the carbamate of ammonia at 25 °C.¹⁸

The temperature dependence of the protonation constant of MEA carbamate was determined, and within the rather large error limits, it appears to be effectively temperature-independent. Again, this result is consistent with the values for the carbamate of ammonia, ΔH° = 1.7(1) kJ mol⁻¹ and ΔS° = 6(4) J mol⁻¹ K⁻¹.¹⁸

**Thermodynamics.** Evaluation of a solvent for PCC requires knowledge of the energies involved in the absorption/desorption process. The thermodynamic constants for the absorption and desorption reactions provide insight into the suitability of a solvent for PCC. The total enthalpy of absorption can be measured calorimetrically; however, determining the contributions of the individual reactions requires knowledge of the temperature dependence of the rate and equilibrium constants. The kinetics of the reactions and their individual enthalpies define the temperature profiles in the absorber and stripper columns.

Typically, the reaction of bicarbonate with the amine, the K₀ pathway, is measured directly by calorimetry and the enthalpies and equilibrium constant reported. Recently, McCann et al.³⁴ reported the enthalpy for the bicarbonate reaction with MEA as −27.6 ± 0.9 kJ mol⁻¹. To our knowledge, there have been no theoretical studies of this reaction pathway.

Several values of the Arrhenius activation energy for the direct reaction of CO₂ (aq) with MEA are available from the studies by Hikita et al. (41.2 kJ mol⁻¹),¹⁹ Danckwerts et al. (41.8 kJ mol⁻¹),²⁸ Leder (39.7 kJ mol⁻¹),³¹ Alper (46.7 kJ mol⁻¹),²⁸ and Ali (46.6 kJ mol⁻¹).¹⁴ Good agreement is found between the activation energy determined in this work (41 ± (8) kJ mol⁻¹) and the previous determinations. The enthalpies for the direct reaction of CO₂ (aq) with MEA cannot be measured calorimetrically given that the reactions are fast. To our knowledge, the enthalpy for the direct reaction of CO₂ (aq) with MEA has not been determined experimentally and does not appear in the literature. In this study, the activation energies, enthalpies, and entropies for the individual reaction rate constants, k₉ and k⁻⁹, as well as the enthalpies and entropies for the equilibrium constant, K₀, and the protonation constant of the carbamate, K₀, were determined from the temperature dependences of the constants. The reaction enthalpy for the MEA–CO₂ reaction, −23(2) kJ mol⁻¹, is in good agreement but is slightly more exothermic than the corresponding value for ammonia, −16(2) kJ mol⁻¹, reported by Wang et al.¹⁸ If the rate and equilibrium constants for the reactions involved in the absorption of CO₂ by MEA and the species composition are known, then the continuous change in enthalpy as a function of reaction time and the total enthalpy can be calculated. However, this calculation is not addressed here.

**Computational Studies.** There have been several theoretical studies of the reaction between MEA and CO₂ to give MEA carbamic acid, as defined by k₀ in eq 6.⁵–⁸ Different aspects, such as a comparison of various reaction pathways, the stability of the potential zwitroner intermediate, and the inclusion of solvent effects through calculations involving a polarizable continuum model approach, have been the focus of several of these studies. The study by Arstad et al. showed that the reaction was catalyzed by inclusion of water and/or MEA, as is the NH₃–CO₂ reaction. Calculations were performed using the compound G3MP2B3.
approach (including zero-point energies), with geometries optimized at the B3LYP/6-31G** level. (Calculations at the B3LYP/6-31G** level of theory gave similar results, but are not discussed here.) Direct reaction between MEA and CO2 to give MEA carbamic acid was found to have an activation energy of +170 kJ mol\(^{-1}\), with an overall endothermic reaction energy of +29 kJ mol\(^{-1}\). Inclusion of one and two water molecules in the reactions reduced the activation energies to +108 and +57 kJ mol\(^{-1}\), respectively, although the reactions were still endothermic, with energies of +15 and +3 kJ mol\(^{-1}\), respectively. However, inclusion of just one extra MEA molecule in the reaction between MEA and CO2 reduced the activation energy to +78 kJ mol\(^{-1}\) and gave an exothermic reaction energy of −15 kJ mol\(^{-1}\). Addition of a water molecule at this stage reduced the activation energy to +39 kJ mol\(^{-1}\) and the reaction energy to −55 kJ mol\(^{-1}\). Our results for this reaction (Table 2) are certainly consistent with the involvement of water and MEA as part of the transition state. Interestingly, formation of (ionic) MEA carbamate in the reaction of MEA and CO2 with MEA acting as a proton acceptor, yielded an activation energy of +40 kJ mol\(^{-1}\) with just one added MEA and +32 kJ mol\(^{-1}\) with an added MEA and a H2O, although the reactions energies for both were endothermic, at +27 and +34 kJ mol\(^{-1}\), respectively.8

In another study, Xie et al.9 found activation free energies for the reaction between MEA and CO2 of +50.2 and +47.3 kJ mol\(^{-1}\), for calculations at the CCSD(T)/6-311+G(d,p) and CCSD(T)/6-311+G(2df,2p) levels of theory, respectively, with the solvent included through a CPCMD (conductor-like polarizable continuum) formalism, using Pauling atomic radii to define the cavity. (Note that the activation energies depended strongly on the choice of atomic radii, with the Pauling radii providing the highest activation energies.) The path also included an extra MEA molecule to stabilize the proposed zwitterion intermediate, although Xie et al. showed that the equilibrium concentration for such a species was on the order of 10\(^{-11}\) M. The activation energy results agree well with our experimental value for the reaction defined by \(k_0\), for which the free energy of activation is +52.0 kJ mol\(^{-1}\). A similar study by Shim et al.10 provided an activation free energy of +23 kJ mol\(^{-1}\), again using an extra MEA molecule in the path, with calculations made at the B3LYP/6-31+G(d,p) level of theory (including zero-point energies) and the solvent included through a self-consistent reaction field with the cavity defined by interlocking spheres and atomic spheres defined by Bondi radii. The value was less than that obtained by Xie et al., although it should be pointed out that, in that study, the activation free energy varied from +23.0 to +50.2 kJ mol\(^{-1}\) [CCSD(T)/6-311+G(d,p) level] and from +20.5 to +47.3 kJ mol\(^{-1}\) [CCSD(T)/6-311++G(2df,2p) level] over the range of alternative radii that were used to define the solvent cavity.

## CONCLUSIONS

The temperature dependence of the kinetics of the reversible reaction between CO2(aq) and MEA was studied by stopped-flow spectrophotometry. The rate constants for the formation and dissociation reactions of MEA carbamic acid were determined over the temperature range from 15.0 to 45.0 °C and were found to increase with temperature. Arrhenius and Eyring analyses of the rate constants for the reversible reactions of MEA with carbon dioxide and with bicarbonate resulted in activation energies (Arrhenius) and enthalpies and entropies of activation (Eyring), and van’t Hoff analysis of the equilibrium constants yielded enthalpies and entropies of reaction for the above equilibria, as well as for the protonation constant of the carbamate. The reversible parallel reaction of MEA with bicarbonate was confirmed and quantified. The decomposition of carbamate at high pH is defined by the rate constant for this path.

This work provides critical data for the complete molecular, rather than empirical, modeling and scale-up of the MEA PCC process.

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## ACKNOWLEDGMENT

Financial support from a CSIRO flagship grant and a Tom Farrell scholarship is acknowledged.

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Publication-6

A systematic investigation of carbamate stability constants by \textsuperscript{1}H NMR

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Published: International Journal of Greenhouse Gas Control, 5, 396-400 (2011)
A systematic investigation of carbamate stability constants by $^1$H NMR

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A R T I C L E   I N F O
Article history:
Received 15 October 2009
Received in revised form 20 January 2010
Accepted 23 January 2010

Keywords:
CO$_2$ capture
Carbamate equilibrium constants
Amine solvents

A B S T R A C T
A systematic, experimental investigation into carbamate stability constants using $^1$H NMR spectroscopy reveals that both steric hindrance and the acid dissociation constant of the parent amine have a significant effect on the stability of the resulting carbamates. Increasing steric hindrance was found to decrease carbamate stability, while increasing pK of the parent amine was found to increase carbamate stability. The carbamate stability constants of monoethanolamine, propylamine, isobutylamine, 2-amino-1-propanol, aminomethylpropanol and methyldiethanolamine were determined as were the carbamate protonation constants of the first four of these amines.

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1. Introduction

There is a general consensus that our greenhouse gas emissions need to be drastically reduced in the coming years if we are to avert the potentially disastrous effects of anthropogenically induced climate change (Metz et al., 2005; Stern, 2006). Given the massive scale of this problem (recent estimates put global man-made CO$_2$ emissions at 24 gigatons, Mikkelsen et al., 2010), the best solution will clearly involve a wide range of different technologies. It is becoming increasingly apparent that CO$_2$ capture and sequestration could make a significant contribution to reducing the output of CO$_2$ from fossil fuelled power plants — currently one of the largest producers of CO$_2$ (Davison, 2007; Wise and Dooley, 2009). Aqueous amine solutions are regarded as amongst the most advanced technologies available for post-combustion CO$_2$ capture (PCC) and a number of different amines and amine systems have been investigated for this purpose. Many of the best performing amines, however, have significant drawbacks associated with their use, including high heats of regeneration (resulting in significantly increased energy requirements), slow kinetics (meaning that large absorption towers are required), high toxicity, and low stability. Not surprisingly therefore, there is substantial interest in the development of potential new, improved solvents and solvent systems.

A crucial step in developing new solvents is a good understanding of the chemistry associated with CO$_2$ and aqueous amines. CO$_2$ can potentially react with an aqueous amine solution via two different pathways: in a simple acid–base reaction, or via carbamate formation. In the acid–base reaction, the amine behaves as a base, with which the acidic CO$_2$ can react. The chemical equations representing the associated reactions are shown in Eqs. (1)–(4):

$$H_2O + \text{CO}_2 \rightarrow K_1 \text{HCO}_3^- + \text{H}^+ \quad (1)$$

$$\text{HCO}_3^- \rightarrow K_2 \text{CO}_2^- + \text{H}^+ \quad (2)$$

$$\text{AH}^+ \rightarrow K_A \text{AH} + \text{H}^+ \quad (3)$$

$$\text{H}_2\text{O} \rightarrow K_W \text{OH}^- + \text{H}^+ \quad (4)$$

These reactions have been extensively investigated in a variety of different contexts and the associated constants are well known. These constants are presented in Table A1 in the supporting information.

Alternatively, CO$_2$ can react with several amines to form a carbamic acid as represented in Eq. (5). This carbamic acid can then also be deprotonated to give the carbamate, as in Eq. (6). Under the conditions most commonly used for PCC, the product will exist primarily as carbamate:

$$\text{RNH}_2 + \text{CO}_2 \rightarrow K_{\text{carb}} \text{RNHCO}_2\text{H} \quad (5)$$

$$\text{RNHCO}_2\text{H} \rightarrow K_{\text{carbH}} \text{RNHCO}_2^- + \text{H}^+ \quad (6)$$

Alternative mechanisms for carbamate formation have been suggested and used previously (Caplow, 1968; Crooks and Donnellan, 1989; Arstad et al., 2007; Li et al., 2007; Ismael...
et al., 2009), however, the above equations most accurately represent the chemistry occurring within the system (McCann et al., 2009). It should be noted that the acid–base equilibria and carbamate formation occur simultaneously and interactively. That is, the properties of the carbamate will influence absorption occurring via the acid–base pathway, through changes in pH, concentrations, etc., and vice versa (McCann et al., 2008).

Carbamate formation has been linked to fast kinetics, but reduced CO2 capacity and increased regeneration energy. As such, a thorough understanding of the factors that influence the formation of carbamate is essential for the development of any new amine system.

This topic has been investigated by a number of different research groups: Sartori and Savage (1983) investigated the carbamate stability constants of monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA) by 13C NMR (nuclear magnetic resonance). They found that for DEA and AMP, the more sterically hindered amine (AMP) had a lower carbamate stability (log K_{carb} = 1.10 and \( \approx -1 \), respectively). The structure of DEA is significantly different to the other two, so it is difficult to draw conclusions as to what contributes to the different structure of DEA is significantly different to the other two, so it is difficult to contribute to different carbamate stability (log K_{carb} = 0.30).

Several additional amines (including MDEA (Böttinger et al., 2008), piperazine (Ermatchkov et al., 2003; Böttinger et al., 2008), ammonia (Mani et al., 2006), diglycolamine, disopropylamine (Barth et al., 1984), 2-[2-(2-aminoethyl)amino]ethanol) (Jakobsen et al., 2008) and some synthetically prepared, more complex amines (Mikkelsen et al., 2009)) have also been investigated, both through NMR speciation studies and/or vapour liquid equilibrium (VLE) measurements. The list of amines for which carbamate equilibrium constants have been measured is, however, relatively short and diverse, making it extremely difficult to definitively identify factors that influence the stability of the carbamate.

Carbamate stability constants have also been investigated through molecular modelling studies (Chakraborty et al., 1988; da Silva and Svendsen, 2006). Earlier studies attributed decreased carbamate formation to the electronic effects of methyl substitution at the \( \alpha \)-carbon, rather than to a steric effect. A later study concluded that ‘trends in carbamate stability apparently cannot be explained, in terms of any single molecular characteristic’ (da Silva and Svendsen, 2006), clearly stating the need for a systematic investigation into those molecular characteristics that do influence carbamate stability.

This work describes the first systematic experimental investigation into two factors that influence the stability of carbamates in aqueous solution. Six amines were investigated, including three for which carbamate stability constants have not previously been measured. This allowed the composition of a series with few structural differences, and thus the correlation of trends in stability constant with molecular structure. The hypothesis that steric hindrance reduces stability was shown to be valid. In addition, a second factor affecting stability was found, and is nominally attributed to the pH of the parent amine. With the addition of three new carbamates, the pool of knowledge of carbamate stability constants has also been significantly increased.

### 1.1. Methodology

Pure amines, 2-amino-1-propanol (AP) hydrochloride and KHCO3/K2CO3 were obtained from Sigma–Aldrich, HCl from Ajax Finechem. N-methylidethanolamine (MDEA) was distilled under vacuum and stored under nitrogen, 2-amino-2-methyl-1-propanol (AMP), propylamine (PA), and isobutylamine (IBA) were crystallised from HCl and \( n \)-propanol to give the amines as hydrochloride salts. All amine solutions were freshly made prior to each experiment. HCl concentrations and amine protonation constants were determined by titration with standardised NaOH on an automated titration apparatus under a nitrogen atmosphere. \(^1H\) NMR spectra were recorded on a Bruker Avance DPX-300 at a frequency of 300.13 MHz at 30.0 °C. All samples were measured in D2O in a 5 mm tube containing an insert with either TSP (3-[(trimethylsilyl)propionic acid–d4, sodium salt) or 1,4-dioxane in D2O as a reference.

The monoethanolamine (MEA) titration data were taken from our previously reported results (McCann et al., 2009). For the remaining amines, solutions of amine hydrochloride (AP, PA and IBA) and KHCO3 were titrated with varying concentrations of HCl. Initial concentrations of amine, (bi-)carbonate and HCl are given in Bates and Pinching, 1951; Cox et al., 1968; Hamborg et al., 2007; Harned and Davis, 1943; Harned and Scholes, 1941; Maeda et al., 1987; Soli and Byrne, 2002; Table A2 of the supporting information. In the case of MDEA and AMP, no carbamate formation was observed in concentrated solutions of amine and (bi-)carbonate (1.7 M MDEA, 2 M KHCO3 and 2.3 M AMP-HCl, 2.7 M K2CO3), so full titrations were not conducted. Instead, maximum carbamate stability constants were estimated assuming that a maximum of 5% of the amine could be present as the carbamate without being detectable by NMR. In reality, reference peaks with integrations of approximately 2% of the amine peaks were measured, so this estimate is rather conservative.

\(^1H\) NMR and data analyses were conducted as described previously (McCann et al., 2009). All measurements were analysed together in a single global analysis for each amine. Activity coefficient corrections were applied to all charged species based on the extended Debye–Hückel equation (Eq. (7)):

\[
\log \gamma_i = \frac{-A_z^2 \sqrt{\mu}}{1 + B r_i \sqrt{\mu}}
\]  

In this equation, the activity coefficient \( \gamma_i \) is a function of the ionic strength, \( \mu \), the charge \( z \), of the \( i \)th component and of the parameters \( A \) and \( B \) that are defined by the dielectric constant of the solvent and the temperature. In water at 30 °C, \( A = 0.51 \), \( B = 0.33 \). The radii \( r_i \) are not known for several of the ionic species; the values were estimated based on published values for similar compounds (Stern and Amis, 1959; Barner and Scheuerman, 1978).

### 2. Results

Acid dissociation constants for the majority of the amines investigated are well known. However, values at 30 °C are not available for PA or IBA. These values were determined potentiometrically as part of this work. The value for IBA (10.33 ± 0.02) is similar to the published value at 25 °C (10.48) (Christensen et al., 1969). To our knowledge, no value for the acid dissociation constant of PA has previously been published.

**Fig. 1** shows the \(^1H\) NMR spectra associated with the titration of an MEA/KHCO3 solution with HCl at 30 °C. In the initial spectra, where the pH is relatively high, the peaks at approximately 2.6 and 3.4 ppm correspond to the two methylene groups of the deprotonated MEA (the NCH2 and OH2 groups respectively). As HCl is added to the solution, the pH drops and the amine group is increasingly protonated. This is accompanied by a downfield shift in both peaks to approximately 3 and 3.6 ppm.

The carbamate peaks in the earlier measurements occur at approximately 3 and 3.4 ppm (NCH2 and OH2 groups, respectively); as the pH decreases, the N-methylene peak moves slightly upfield, although this shift is difficult to see on the scale in Fig. 1. It is possible that the O-methylene peak also moves with pH, although overlap with the amine peak makes this impossible to see. The addition of HCl also results in dissociation of the carbamate, to give...
a greater proportion of the amine as the free (albeit protonated) amine. The chemical shift of the carbamate peak as HCl was added is shown in Fig. 2. The results shown in this figure include measurements where the calculated aqueous CO₂ concentration was above 30 mM, and so cannot be used in the determination of constants. In addition, the pH values below 7 are approximate only, as some gaseous CO₂ would have escaped from the solution. Nevertheless, a clear change in chemical shift is visible, and the inflection point (corresponding to the pK of the protonation) of the curve is at approximately 7.5. This is in excellent agreement with the pKₐ value determined in this work (7.49).

The change in chemical shift for the carbamate is much smaller than that observed for the amine. This observation is unsurprising, given that for the amine, the N-methylene group is very close to the site of protonation (the N of the N-methylene group). In contrast, in the case of the carbamate, the N-methylene group is much further removed from the site of protonation (the carboxylate group). The increased separation between the NMR-measured group and the site of protonation decreases the amplitude of change in chemical shift. These observations lend support to the suggestion that it is the COO⁻/CO₂⁻ group of the carbamate that is protonated (as shown in Eq. (6)), rather than the nitrogen group, as has been previously suggested (Caplow, 1968) with the zwitterion mechanism.

Fig. 3 shows the concentration profiles associated with the measurement shown in Fig. 1. The decreasing (red) concentrations are the amine species (protonated and deprotonated) and the increasing (blue) concentrations correspond to the carbamate species. The markers represent experimental values, the lines calculated values. The data markers represent only the resolved peaks: O and D represent the concentrations for resolved peaks for the NCH₂ group (first and repeat measurements), the markers × and + represent the OCH₂ group. As seen in Fig. 1, the major species at high pH is the carbamate, this species converts to the amine as HCl is added and the pH drops.

Titrations with the remaining amines showed similar results, although the spectra were more complex, due to the increased complexity of molecular structure. Nevertheless, individual peaks attributable to both the amine and the carbamate could be identified in all measurements, and peak positions over the course of the titration showed similar trends to those discussed above.

The determined log K_carb constants as well as the associated pK_carbH values are given in Table 1. Here for clarity and ease of comparison, the log K_carb constants are defined as in Eq. (8).

### Table 1

<table>
<thead>
<tr>
<th>Amine</th>
<th>Log K_carb</th>
<th>pK_carbH</th>
<th>Lit log K_carb</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>1.54 (2)</td>
<td>7.49 (5)</td>
<td>1.10 at 40°C</td>
<td>Sartori and Savage (1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.43 at 40°C</td>
<td>Park et al. (2002)</td>
</tr>
<tr>
<td>PA</td>
<td>1.67 (3)</td>
<td>7.2 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBA</td>
<td>1.69 (4)</td>
<td>7.3 (6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP</td>
<td>0.72 (3)</td>
<td>8.0 (2)</td>
<td></td>
<td></td>
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<tr>
<td>AMP</td>
<td>&lt;-0.7</td>
<td>&lt;N/A</td>
<td>&lt;-1 at 40°C</td>
<td>Sartori and Savage (1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.56 at 40°C</td>
<td>Park et al. (2002)</td>
</tr>
<tr>
<td>MDEA</td>
<td>&lt;-1.3</td>
<td>&lt;N/A</td>
<td>Carbamate does not form</td>
<td>Popsteinova Jakobsen et al. (2005), Böttunger et al. (2008)</td>
</tr>
</tbody>
</table>

Please cite this article in press as: McCann N, et al. A systematic investigation of carbamate stability constants by ¹H NMR. Int. J. Greenhouse Gas Control (2010), doi:10.1016/j.ijggc.2010.01.008
the $pK_{\text{carb}}$ are defined as acid dissociation constants.

$$RNH_2 + HCO_3^+ \rightarrow RNHCO_2^-$$ (8)

As no carbamate formation was detected for MDEA and AMP, no carbamate protonation constant for these amines could be determined. Where available, log $K_{\text{carb}}$ values reported in the literature are also presented in Table 1 and are in good agreement with the determined constants. There are many carbamate stability constants reported in the literature for MEA and AMP. Similarly, there are many reports that MDEA does not form a carbamate. The purpose of this work is not a review of this literature so only a select few of the literature reports are mentioned here. No carbamate protonation constants (other than MEA, reported previously by us) have been reported for the remaining amines, but the protonation constant for ammonium carbamate is similar (6.76 at 25°C (Christensson et al., 1978)).

3. Discussion

The purpose of this investigation was a systematic investigation into two factors that influence carbamate stability and the amines investigated were selected to represent this. As the benchmark amine for CO$_2$ capture, MEA was of significant interest; the remaining amines have similar structures. The chemical structures of the amines used are given in Fig. 4. The amines investigated can be divided into 2 main groups (PA/IBA and MEA/AP/AMP), as shown by the circles within the figure. Within each group, the major difference between the amines is the level of steric hindrance around the amine; steric hindrance is lowest in the amines at the top of the figure and highest in the amines at the bottom. MDEA belongs to neither group, but is included as an example of very high steric hindrance.

Alternatively, the amines could be divided into groups moving from left to right across the figure. In each horizontal group, the level of steric hindrance is relatively constant, but the number of hydroxyl groups on the molecule is increased. Concurrently, the $pK$ of the amine increases as the number of hydroxyl groups increases. We make no effort here to differentiate between these two factors, or ascribe trends to only one or the other — such investigations are beyond the scope of this work. From here on, however, the factor will be called a $pK$ effect, for simplicity and clarity.

The log $K_{\text{carb}}$ constants given in the table are all well defined. Their values, as a function of $pK$ and steric hindrance are presented graphically in Fig. 5. In this figure, the level of steric hindrance is an approximate, relative estimation, based on the structure of the compound, rather than a measured or calculated value. For example, the carbon $\beta$ to the amine group is relatively far removed from the site of carbamate formation, and addition of a methyl group at this site would increase steric hindrance around the amine only very slightly. In contrast, the addition of two methyl groups at the carbon $\alpha$ to the amine group would be expected to increase steric hindrance significantly. As previously hypothesised, the carbamate stability decreases with increasing steric hindrance.

Fig. 5 also shows that the amines with lower $pK$ values typically had lower carbamate equilibrium constants. It is possible that this trend is associated with electronic effects, potentially arising from the additional hydroxyl-group, which also give rise to a decreased $pK$ of the parent amine. However, further work is required to more precisely identify the cause of the decreased carbamate stability constant and is outside the scope of this work.

In contrast to the carbamate formation constants, the protonation constants, as seen in Table 1, are not as well defined. In order to prevent gaseous CO$_2$ from being released from the solution, only measurements with aqueous CO$_2$ concentrations below 30 mM were used. Consequently, the pH of the solutions typically remained reasonably high (above ~7), with the result that the carbamate $pK$ values around 7 were not well defined. Nevertheless, the change in chemical shift of the N-methylene peak of the carbamate over the course of the titration supports the suggestion of a protonation. Previous reports of a protonated ammonium carbamate with a similar $pK$ value (Christensson et al., 1978) also support the assignment of carbamate protonation values.

Within the reported errors, the carbamate acid dissociation constants are very similar for all four amines. That is, changes in both steric hindrance and $pK$ of the parent amine have little effect on the carbamate acid dissociation constant. This is not surprising as the site of protonation (the COO$^-$ group) is far removed, both spatially and electronically from where these effects occur.

4. Conclusions

A thorough understanding of the factors affecting carbamate stability is essential for the efficient and effective development of new amine-based solvent systems for CO$_2$ capture. This work represents the first systematic experimental investigation into this topic. We found conclusive experimental evidence to support the hypothesis that increasing steric hindrance of the parent amine decreases the stability of the carbamate. We also found that increasing $pK$ of the parent amine leads to increased stability of the carbamate. We have determined carbamate stability constants and
the associated protonation constants of three new amines. Such studies are of fundamental importance in the directed design of new solvents and solvent systems for CO₂ capture in the future.

Acknowledgements

This research has been supported by the Australian Government through the CSIRO Energy Transformed Flagship and the Asia Pacific Partnership on Clean Development and Climate initiative (APP).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijggc.2010.01.008.

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Publication-7

Molecular interactions between amine and carbonate species in aqueous solutions
Kinetics and Thermodynamics

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Published: Energy Procedia, 1, 995-1002
(2009)
Molecular Interactions between Amine and Carbonate Species in Aqueous Solution - Kinetics and Thermodynamics

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Abstract

Post combustion capture, PCC, of CO₂ from the flue gas stream of coal fired power stations is an attractive proposition for the reduction of CO₂ output into the atmosphere. PCC based on reversible absorption by aqueous amine solution is probably the most advanced technology. Thus the investigation of the chemistry of CO₂ absorption by such solutions is of crucial importance. A critical reaction is the formation of carbamates. There is a vast literature on this process but it is mainly based on empirical reaction mechanisms. In this contribution we present a molecularly correct mechanism for carbamate formation with primary amines. The results are derived from detailed, ¹H-NMR based, kinetic and equilibrium investigation of the interaction of monoethanolamine, MEA, with carbonate species. All rate and equilibrium constants are reported.

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Keywords: Post Combustion Capture; carbamates; CO₂ absorption; kinetics, thermodynamics

1. Introduction

There is little doubt that the increase of the CO₂ concentration in the atmosphere constitutes a serious threat to the established climate patterns of the planet. Fossil fuel based power production contributes substantially to the overall CO₂ output and thus reduction of this contribution could be an obvious candidate for overall CO₂ reduction. There are two paths to this reduction: less energy consumption and removal of the CO₂ from the output stream, and both need to be implemented parallel. Energy consumption is highly enmeshed with our lifestyle, thus it is not trivial to develop and implement useful strategies for the reduction of energy consumption by humanity. CO₂ cannot be efficiently used as a starting material for any other product. While this has been suggested it is thermodynamic nonsense. CO₂ is at the bottom of the energy scale for carbon and lifting it onto any higher level for a different chemical requires energy and the production of this energy will release more CO₂ than ever will be removed. This of course only applies to technological processes, nature does a brilliant job as sunlight is used as an...
energy source to transform CO₂ into carbohydrates. This leaves capture and subsequent sequestration as a technological alternative for ‘removal’ of CO₂.

The central process prior to sequestration is the removal of CO₂ from the flue gas stream which consists typically of some 80% nitrogen, 15% CO₂ and the rest being water, oxygen and other gases such as NOx and SOx. There are several technologies under investigation for that purpose. There are physical processes such as membrane and adsorption technologies for the separation of CO₂ from N₂. Physical separation is based on differences in molecular weight/shape or specific surface or other properties of the molecules to be separated. A promising different physical approach consists in the separation of O₂ from N₂ in air and combustion of the fuel in pure oxygen, producing pure CO₂. Any chemist would insist that the simplest technology for the separation of the above gases will be based on the unique property of CO₂ to react with water to form H₂CO₃ or carbonic acid. Its acidic property makes it dramatically different from the other gases, and this could be exploited in a relatively simple way.

Post combustion capture, PCC, does take advantage of the acid property of CO₂. Several bases are used or investigated as reactants for CO₂ in aqueous solution; they include the carbonate ion, CO₃²⁻, and ammonia, NH₃, both of which have the important property of being chemically very stable; many organic amines form another class of reactants with monoethanolamine, MEA, being the best investigated example.

All PCC technologies are based on the simple concept of selective absorption of CO₂ by the base solution at relatively low temperature and release of pure CO₂ at relatively high temperature. Ultimately the most relevant aspect for the process is the price per unit of captured CO₂, and this price is dominated by the energy requirement of the cyclic process.

In order to improve the efficiency of CO₂ absorption technology, improvement of the understanding of all chemical reactions that occur in the cyclic process is an invaluable tool. There is a very extensive literature on the interactions of CO₂ with aqueous MEA. However, the literature heavily relies on empirical functions that are used to quantitatively explain the experimental results. The alternative is the interpretation of the data in terms of a molecular reaction mechanism that describes the true interactions between the molecules that coexist in the solution.

In order to discuss the relative merits of empirical and molecular reaction mechanisms, a few fundamentals of chemical kinetics have to be recapped:

(a) In the liquid phase there are only first and second order reactions. Proper ter-molecular reactions are not known; if they are ‘observed’ they are always combination of at least two reaction steps that appear under the present circumstances as one ter-molecular reaction.

(b) Protonation exchange reactions in aqueous solution are always diffusion controlled, i.e. the equilibrium is always established instantaneously, and the reactions are immeasurably fast (at least for any classical kinetic investigation).

(c) The principle of microscopic reversibility states that any reaction path is reversible and at equilibrium there is no net reaction in any direction for any of the reaction steps in the mechanism.

We repeat, the above statements do not preclude the application of empirical mechanisms that contradict the laws. Such mechanisms can be extremely useful tools for the investigation of chemical processes, however, they are empirical functions that do not represent what the full collection of interacting molecules actually do. Nevertheless, in this contribution we make the claim that the complete molecular understanding of a process is superior to any empirical mechanism as it allows the much more straightforward extrapolation to conditions outside the range of conditions at which measurements were taken and analyzed.

2. Development of a Molecular Mechanism for the Interactions of CO₂ in Aqueous Solutions of Amines

In order to develop a molecularly correct reaction mechanism, a complete set of all species that coexist in solution at any time during the process needs to be established. Next, potential reaction paths between any members of this list of species need to be collected and investigated for their relevance.

Let us consider the reactions between a primary amine like MEA and dissolved CO₂ in aqueous solution. First there are the interactions of dissolved CO₂, CO₃(aq), with water and hydroxide ions to reversibly form carbonic acid and bicarbonate:

\[ \text{H}_2\text{O} + \text{CO}_2\text{(aq)} \rightleftharpoons \text{H}_2\text{CO}_3 \]  
\[ \text{OH}^- + \text{CO}_2\text{(aq)} \rightleftharpoons \text{HCO}_3^- \]  

(1)
These reactions are well established and all four rate constants are known, and of course the two equilibrium constants as well.\textsuperscript{1,2}

There are several species that are connected via protonation equilibria, which remember are instantaneous. Protonation constants for many amines are published.\textsuperscript{3}

\[
\begin{align*}
R-NH_2 + H^+ &\rightleftharpoons R-NH_3^+ \\
CO_3^{2-} + H^+ &\rightleftharpoons HCO_3^- \\
HCO_3^- + H^+ &\rightleftharpoons H_2CO_3
\end{align*}
\]

Please note that we use the ‘$\rightleftharpoons$’ arrow for instantaneous protonation equilibria and ‘$\leftrightarrow$’ arrows for kinetically observable reversible reactions.

At relevant pH the total reaction equation that describes the stoichiometry of the interaction is:

\[
H_2O + CO_2(aq) \rightleftharpoons H_2CO_3
\]

It is important to note that it is a 1:1 interaction between CO$_2$ and the amine.

If the above reactions were a complete set, it would be straightforward to model and quantitatively understand all aspects of the reactions. Unfortunately there is an additional way of interaction between amines and CO$_2$/carbonates. Carbamate formation is formally a simple reaction:

\[
RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + H^+
\]

In the context of PCC, carbamate formation is very important for several reasons:

(a) it affects the reactivity of dissolved CO$_2$ in the aqueous amine solution
(b) it might influence the mass transfer of gaseous CO$_2$ into the liquid phase
(c) at the pH values relevant to PCC the molar ratio of absorbed CO$_2$ to amine is only 1:2, the released proton is picked up by a second amine molecule

The unfavorable CO$_2$ to amine ratio for carbamate formation is crucial for the energy consumption for the cyclic process.\textsuperscript{4} For an increasing fraction of carbamate formation the volume of absorber solution increases and this ultimately results in increasing energy requirements as larger amounts of solution have to be heated and cooled between absorber and stripper.

Obviously the formation of carbamate is important and needs to be investigated carefully. What is the molecularly correct mechanism for its formation?

It is clear that one molecule of the amine family (R-NH$_2$ and R-NH$_3^+$) must react with one molecule of the CO$_2$/carbonate family (CO$_2$(aq), H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$). The reaction is essentially a Lewis acid-base reaction where the amine is the Lewis base and the CO$_2$ species (CO$_2$(aq) and the carbonates) is the Lewis acid. The protonated amine is not a Lewis base and thus will not be reactive, the sole reacting species is the free amine and it can, at least theoretically, react with all of the CO$_2$ species which all are Lewis acids. The 2- charged carbonate ion is clearly a very weak Lewis acid and its reactivity can be neglected. The 1- bicarbonate ion is a stronger Lewis acid but much weaker than the neutral carbonic acid and dissolved carbon dioxide. The following reactions are possible

\[
\begin{align*}
RNH_2 + H_2CO_3 &\rightleftharpoons RNHCOOH + H_2O \\
RNH_2 + HCO_3^- &\rightleftharpoons RNHCOO^- + H_2O \\
RNH_2 + CO_2(aq) &\rightleftharpoons RNHCOOH
\end{align*}
\]
Also, the protonation equilibrium of the carbamic acid needs to be included\(^5\,^6\):

\[
\text{RNHCOO}^- + \text{H}^+ \rightleftharpoons \text{RNHCOOH}
\]  \hspace{1cm} (6)

An overall reaction scheme which contains all relevant processes is best represented graphically\(^7\) (recall we use \(\rightleftharpoons\) for protonation equilibria and \(\rightarrow\) for kinetically observable reactions).

Figure 1: Graphical representation of complete reaction scheme for all interactions between CO\(_2\), carbonate species, and amine.

The task is to determine all rate constants as well as the protonation constant of the carbamate.

3. Experimental Techniques

An initial question is which technique(s) could be used to investigate such a reaction system. There are several published methodologies:

(a) The aqueous amine solution is in equilibrium with the gas phase and the CO\(_2\) partial pressure in the gas phase is measured\(^8\,-^10\). This technique is clearly not suitable for reasonably fast kinetic investigations as the response time is too slow. In addition the information on carbamate formation is only indirect and thus prone to experimental inaccuracies.

(b) The equilibrium can be frozen by raising the pH to a high value as carbamate is relatively stable under such conditions. The free carbonate is precipitated as BaCO\(_3\) and determined quantitatively.\(^11\) Again, this method is too slow for kinetic investigations and also the information on carbonate formation is only indirect.

(c) The most successful investigations are based on NMR measurements. Both \(^{13}\)C-NMR and \(^1\)H-NMR are possible. At first sight \(^{13}\)C-NMR seems to be more attractive as all interacting species (with the exception of H\(_2\)O and OH\(^-\)) give rise to NMR signals.\(^12\,^13\) However, due to slow relaxation (long T\(_1\)) of the nuclear spin very long recycle delays are required for reliable quantitative integration of the NMR peaks. Again the method is clearly too slow for kinetics. This leaves \(^1\)H-NMR as the option of choice:
measurements are possible on the time scale of one minute, quantitative integration is standard and thus concentration information readily available.\(^{14}\)

(d) For fast reactions, the only option is stopped-flow with UV-Vis absorption measurement or conductometry.\(^{15}\) As none of the relevant species has any useful absorption band in the accessible wavelength region, the reaction is followed by measuring color changes of added pH indicators which indirectly record pH changes.\(^{16-18}\) As protonation equilibria are instantaneous reactions at a millisecond time scale can be analyzed. While fast, again the measurements only deliver indirect information.

4. Experiments

\(^1\)H-NMR data were acquired for two types of experiments: \(^{7}\)
(a) Equilibrium studies where different concentrations of MEA, carbonate and acid were mixed, establishment of the equilibrium was ensured and NMR spectra were taken.
(b) Kinetic studies were performed by rapidly mixing different amounts of MEA, carbonate and HCl and the establishment of the equilibrium was followed by taking NMR spectra at 1-2 minute intervals.

For both types of experiments NMR peaks were integrated and the information translated into concentrations for MEA and carbamate. The only NMR active protons are the CH\(_2\) groups of MEA and the carbamate. Both molecules are involved in protonation equilibria which change within the pH range covered by the experiments, thus only the sum over the concentrations of protonated and deprotonated forms of the molecules are determined experimentally.

![Figure 2](image_url)

**Figure 2:** Typical \(^1\)H-NMR spectrum. The multiplet at 2.8ppm arises from the N-CH\(_2\) group of MEA, at 3.1ppm from the N-CH\(_2\) of the carbamate, at 3.5ppm from the O-CH\(_2\) group of the carbamate and at 3.6ppm from the O-CH\(_2\) group of the amine.
Figure 3: (left) A typical titration, addition of HCl to a solution of MEA and carbonate; (right) a typical kinetic experiment, formation of carbamate from MEA and carbonate. The total amine and carbamate concentrations are indicated in red and blue respectively.

The analysis of the data sets consisted of non-linear data fitting of the rate or equilibrium constants that define the processes of Figure 1. In all calculations the pH was computed during the processes and all protonation equilibria were continuously adjusted. The activities of all ionic species were estimated based on an expanded Debye-Hückel equation. Note that the direct reaction of MEA with dissolved CO2 could not be observed in our data sets as the concentration of CO2(aq) was too low under our conditions. The forward reaction rate has been determined by several groups with values in the vicinity of 5000 M\(^{-1}\)sec\(^{-1}\), see e.g.\cite{19}. No information is given about the reverse reaction.

Table 1 contains all relevant published rate and equilibrium constants, the table includes the reactions of CO2(aq) in aqueous solution as well as the protonation constants of carbonate, bicarbonate, hydroxide and MEA. These values were used in our data fitting.

<table>
<thead>
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<th>Reaction</th>
<th>Kinetics</th>
<th>equilibrium</th>
<th>References</th>
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<tr>
<td>CO2(aq) + H2O ⇌ H2CO3</td>
<td>k(<em>{1}) = 3.7 × 10(^{7}) s(^{-1}) (k(</em>{-1}) = 18) s(^{-1})</td>
<td>K(<em>{1}) = 2.06 × 10(^{-3}) (\log K(</em>{1}) = -2.69)</td>
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<td>CO2(aq) + OH(^-) ⇌ HCO3(^-)</td>
<td>k(<em>{2}) = 8.5 × 10(^{3}) M(^{-1})s(^{-1}) (k(</em>{-2}) = 2.4 × 10(^{-4}) s(^{-1})</td>
<td>K(<em>{2}) = 3.57 × 10(^{9}) M(^{-1}) (\log K(</em>{2}) = 7.55)</td>
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<td>CO3(^2-) + H(^+) ⇌ HCO3(^-)</td>
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<tr>
<td>HCO3(^-) + H(^+) ⇌ H2CO3</td>
<td>K(<em>{2}) = 5.75 × 10(^{9}) M(^{-1}) (\log K(</em>{2}) = 7.6)</td>
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<td>Wissbrun et al.\cite{21}</td>
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<tr>
<td>MEA + H(^+) ⇌ MEAH(^+)</td>
<td>K(<em>{3}) = 2.24 × 10(^{9}) M(^{-1}) (\log K(</em>{3}) = 9.35)</td>
<td></td>
<td>Bates et al.\cite{22}</td>
</tr>
<tr>
<td>OH(^-) + H(^+) ⇌ H(_2)O</td>
<td>K(<em>{4}) = 1.00 × 10(^{14}) (\log K(</em>{4}) = 14.00)</td>
<td></td>
<td>Stumm and Morgan\cite{23}</td>
</tr>
</tbody>
</table>

\(^{5}\)The rate constant for the reaction of CO2 with H2O is defined as the pseudo-first order rate constant
\(^{6}\)The protonation is defined as given in the equation; it is common to define this value differently, using the sum over the concentrations of H\(_2\)CO3 and dissolved CO2 as 'carbonic acid'.

Table 2 contains our results. Note the excellent agreement of the equilibrium constants for the formation of carbamic acid from MEA and carbonic acid and for the formation of carbamate from MEA and bicarbonate which are determined independently from the titrations and kinetically.
Table 2: Rate and equilibrium constants for the reactions of MEA with carbonic acid and bicarbonate; protonation constant for the carbamate.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetics</th>
<th>Equilibrium constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{CO}_3 + \text{RNH}_2 \xleftrightarrow{k_k}{k_2} \text{RNHCOOH} + \text{H}_2\text{O}$</td>
<td>$k_7 = 1.02(5) \times 10^3 \text{M}^{-1}\text{s}^{-1}$ $k_7 = 7.8(5) \times 10^{-3} \text{s}^{-1}$</td>
<td>$\log K_7 = 5.12(4)$ $\log K_7 = 5.33(3)$</td>
</tr>
<tr>
<td>$\text{HCO}_3^- + \text{RNH}_2 \xleftrightarrow{k_k}{k_8} \text{RNHCOO}^- + \text{H}_2\text{O}$</td>
<td>$k_8 = 3.8(6) \times 10^{-2} \text{M}^{-1}\text{s}^{-1}$ $k_8 = 2.0(4) \times 10^{-5} \text{s}^{-1}$</td>
<td>$\log K_8 = 1.28(7)$ $\log K_8 = 1.51(3)$</td>
</tr>
<tr>
<td>$\text{RNHCOO}^- + \text{H}^+ \xleftrightarrow{k_k}{k_9} \text{RNHCOOH}$</td>
<td></td>
<td>$\log K_9 = 7.59(4)$</td>
</tr>
</tbody>
</table>

5. Conclusions

The establishment of a molecularly correct mechanism for the formation of carbamates from CO$_2$/carbonates and primary amines is of fundamental importance, it is basic physical organic chemistry. It is also highly relevant for amine-based post combustion capture.

PCC is necessarily a cyclic process where the amine solution is absorbing CO$_2$ under one set of conditions, releasing it under a different set and then recycled to absorb again. Temperature is the most likely candidate for driving the cycle, but it could at least theoretically also be a cyclic pressure regime. Whatever the process is, the accurate knowledge of all chemical processes involved is invaluable.

Presently the rate and equilibrium constants for MEA have only been determined in this way at one temperature (and pressure). The determination of the activation parameters for all rate constants and reaction entropies and enthalpies for all equilibria is required for the complete modelling of an absorber plant. Of particular importance are the reaction enthalpies as they define the ultimately important energy consumption per unit of absorbed CO$_2$.

An additional advantage of fundamental understanding is the possibility of rational design of new chemicals such as amines or parts of the process conditions such as concentrations, temperature profiles, and addition of supporting chemicals such as acids and bases.


(3) Martell, A. E.; Smith, R. M.; Motekaitis, R. J. In *NIST Std. Ref. database* 2001; Vol. 46.


(14) Ermatchkov, V.; Pérez-Salado Kamps, Á.; Maurer, G. *Journal of Chemical Thermodynamics* 2003, 35, 1277-1289.


The Activity of “piperazine” and the formation of carbamate(s) from the reaction(s) with CO$_2$(aq) in aqueous solution at 25.0 °C for post combustion capture processes

Fernandes Debra, Conway William, Wang Xiaoguang, Burns Robert, Lawrance Geoffrey, Maeder Marcel and Puxty Graeme

This manuscript will be submitted to a journal shortly
The activity of piperazine and the formation of carbamate(s) from the reaction(s) with CO$_2$(aq) in aqueous solution at 25.0 °C for post combustion capture processes

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Abstract

Piperazine (PZ) is widely recognised as a promising absorbent for the capture of CO$_2$ from combustion flue gases. We report here the results of the first complete and comprehensive kinetic investigation into the homogeneous formation of piperazine carbamates/carbamic acids from all reactive forms of PZ [free piperazine (PZ), mono-carbamate (PZCO$_2^-$), and mono-protonated piperazine (PZH$^+$)] at 25.0 °C and 0.0 M ionic strength. Global analysis of stopped-flow spectrophotometric kinetic measurements has revealed the complete set of rate and equilibrium constants for all possible reaction pathways, together with estimations for the protonation constants of the piperazine carbamates/carbamic acids. The second order rate constant for the formation of the mono-carbamic acid (PZCO$_2$H) (1.2 x 10$^4$ M$^{-1}$ s$^{-1}$) is approximately a factor of two higher than the corresponding value for MEA (4.9 x 10$^3$ M$^{-1}$ s$^{-1}$) at 25.0 °C and is consistent with the Bronsted reactivity of other cyclic, and acyclic amines we have investigated. The reactions of CO$_2$ with mono-carbamate (PZCO$_2^-$) to form the di-carbamate, and protonated piperazine (PZH$^+$) to form the mono-carbamic acid (PZCO$_2$H$^+$), are substantially slower than the reaction with free piperazine (PZ). Despite the theoretical capacity of PZ to absorb up to 1 mole of CO$_2$ per mole of PZ, the buffer capacity of PZ and the mono-carbamate limits the capacity of PZ solutions to that
of typical carbamate forming mono-aamines (0.5 mole CO₂ / mole amine) at the pH conditions (10 - 8) which correspond to those encountered in the industrial process.

**Introduction**

In recent years, the onset of climate change and the recognition of issues relating to CO₂ emissions from coal-fired electricity production has driven a corresponding investment in research and technologies to improve the environmental impact of electricity generation and diminish the associated emissions from such technologies. Post Combustion Capture (PCC) of CO₂ using aqueous amines as an absorbent has been proposed to accomplish the required reductions. Currently, the standard monoethanolamine (MEA) solvent suffers in the exhaustive additional energy input from the power station to drive the regeneration swing to higher temperature in the stripper for the release of pure CO₂. Although this capture system has seen significant investigation there is still a requisite for refinement and scope for the development of more efficient, alternative, solvent systems to ensure the capture process is sustainable and the highest capture efficiencies are maintained.

To address these concerns requires a fundamental understanding of the process at the molecular level where CO₂ is in contact with the amine. Currently, the limited availability of experimentally determined parameters, aside from those which have been determined for the basic common amine systems, are partial in their ability to describe/predict the amine behaviour of novel absorbents. Additionally, the CO₂-amine interactions for highly complex systems are less investigated and remain fundamentally unsolved. The cyclic di-amine piperazine is one such example which has seen extensive use in CO₂ capture applications, particularly as a rate promoter for CO₂ absorption in carbonate and tertiary amine solutions. The well established carbamate/carbamic acid mechanism for the aqueous reactions of CO₂(aq) in amine solutions are directly applicable to the piperazine system, however the corresponding mechanism for piperazine is significantly more complex and requires additional reaction pathways and protonation equilibria ensuing from the second amine moiety. In light of the determination of equilibrium speciation and CO₂ solubility from ¹H NMR spectroscopic and gas-liquid VLE/partial pressure measurements across a range of temperatures and
CO₂ loadings,¹⁻³ previous attempts to quantitatively describe the kinetic reactions are markedly conflicting and incomplete.⁴⁻¹²

To expand the scope for the CO₂-piperazine system we have focussed on determining the complete set of kinetic and equilibrium constants for the reversible formation of carbamic acid/carbamate species in the absence of gas-liquid mass-transfer processes. Stopped-flow spectrophotometric measurements at 25.0 °C, coupled with coloured acid-base indicators were employed to follow the pH changes and establish the kinetics during the reactions of CO₂(aq) with the reactive piperazine species; free piperazine (PZ), mono-carbamate (PZCO₂⁻), and protonated piperazine (PZH⁺). The rate and equilibrium constants for each of the individual reaction pathways, together with estimates for the corresponding protonation constants of piperazine carbamate/carbamic acid species, have been determined.

Mechanism/reactions: A number of reactive piperazine species, specifically the free piperazine (PZ), mono-carbamate (PZCO₂⁻), and the monoprotonated piperazine (PZH⁺) compete for CO₂ in aqueous solution, the reactions of which are strongly dependent on the pH of the solution and the intrinsic CO₂ loading (α = mole CO₂ / mole amine). A general model to describe the reactions of CO₂(aq) with all reactive piperazine species, together with protonation equilibria for the amine, and piperazine carbamate/carbamic acid species, is shown in Figure 1, with the corresponding formal reactions listed in equations (1) to (15).
Figure 1. General reaction scheme to describe the interactions of CO$_2$(aq), and protons (H$^+$), with piperazine species in aqueous solution.

The free piperazine (PZ) is the dominant reactive species at high pH and low CO$_2$ loadings ($\alpha \leq 0.01$) which reacts with CO$_2$(aq) to form the mono-carbamic acid as in equation (1).

$$\text{A} + \text{CO}_2(\text{aq}) \xrightarrow{k_7 \text{, } k_{-7}} \text{ACO}_2\text{H} \tag{1}$$

At intermediate and high loadings ($\alpha = 0.0 - 1.0$) accumulated mono-carbamate (PZCO$_2^-$) can react with a second molecule of CO$_2$ to form the di-carbamic acid/carbamate species, equation (2).

$$\text{ACO}_2^- + \text{CO}_2(\text{aq}) \xrightarrow{k_9 \text{, } k_{-9}} \text{A(CO}_2\text{)}^2\text{H}^- \tag{2}$$
Correspondingly, at intermediate and high CO₂ loadings, which correspond to lower solution pH, protonated piperazine (PZH⁺) is able to react with CO₂ to form the di-protonated mono-carbamic acid (PZCO₂H₂⁺), equation (3).

\[
\text{AH}^+ + \text{CO}_2^{\text{(aq)}} \rightleftharpoons \text{ACO}_2\text{H}^+ + \text{CO}_2 \quad \text{equation (3)}
\]

Typically, the proton released from the amine group upon absorption of CO₂ is nominally located on the carbamate oxygen, however, the second amine group in piperazine is a stronger lewis base (than the carbamate oxygen) and will absorb the proton more readily. Since the location of the proton on the mono-carbamic acid cannot be explicitly assigned due to the fast proton exchange, the term for the protonation constant of the carbamate, equation (4), represents a sum over the contributions of the two possible protonation sites.

\[
\text{ACO}_2^+ + \text{H}^+ \rightleftharpoons \text{ACO}_2\text{H} \quad \text{equation (4)}
\]

\[
\text{ACO}_2^+ + 2\text{H}^+ \rightleftharpoons \text{ACO}_2\text{H}_2 \quad \text{equation (5)}
\]

\[
\text{A(CO}_2\text{)}^{2-} + \text{H}^+ \rightleftharpoons \text{A(CO}_2\text{)H}^- \quad \text{equation (6)}
\]

\[
\text{A(CO}_2\text{)}^{2-} + 2\text{H}^+ \rightleftharpoons \text{A(CO}_2\text{)H}_2 \quad \text{equation (7)}
\]

The corresponding protonation constants of the remaining carbamate species are listed in equations (5) - (7) while the first and second protonation constants of piperazine, \(P_1 = 9.77 \text{ M}^{-1}\) and \(P_2 = 5.60 \text{ M}^{-1}\), at 25.0 °C respectively, equations (8) and (9), have been determined via potentiometric titrations by Fernandes et al.\(^\text{13}\)

\[
\text{A} + \text{H}^+ \rightleftharpoons \text{AH}^+ \quad \text{equation (8)}
\]

\[
\text{AH}^+ + \text{H}^+ \rightleftharpoons \text{AH}^{2+} \quad \text{equation (9)}
\]

The reactions of CO₂(aq) with H₂O and OH⁻, equations (10) - (11), as well as the associated protonation constants of the hydroxide and carbonate species, equations (12) - (14), do not appear in Figure 1 for simplicity, however, these reactions form an integral part of the absorption chemistry and must be included in the mechanism.
\[
\begin{align*}
\text{CO}_2^{(aq)} + \text{H}_2\text{O} & \rightleftharpoons \frac{k_1}{k_1} \text{H}_2\text{CO}_3 \quad (10) \\
\text{CO}_2^{(aq)} + \text{OH}^- & \rightleftharpoons \frac{k_2}{k_2} \text{HCO}_3^- \quad (11) \\
\text{CO}_3^{2-} + \text{H}^+ & \rightleftharpoons \frac{k_1}{k_1} \text{HCO}_3^- \quad (12) \\
\text{HCO}_3^- + \text{H}^+ & \rightleftharpoons \frac{k_1}{k_1} \text{H}_2\text{CO}_3 \quad (13) \\
\text{OH}^- + \text{H}^+ & \rightleftharpoons \frac{k_1}{k_1} \text{H}_2\text{O} \quad (14)
\end{align*}
\]

From equations (1) - (14) above, a total of nineteen (19) constants are required to completely quantify the aqueous CO$_2$ - piperazine system, excluding the mass transfer of CO$_2$(g) to CO$_2$(aq) into the aqueous phase. The application of microscopic reversibility allows the determination of $k_{-8}$ based on other constants in a loop as $k_{-8} = \frac{(k_8 k_{-7} P_1)}{(P_4 k_7)}$, while published values for the hydration reactions of CO$_2$, equations (10) - (14), and the protonation constants of the free amine, equations (8) - (9), reduces the total number of parameters to be determined in the fitting to ten (10).

**Experimental section**

**Chemicals** High purity CO$_2$ gas (BOC), N$_2$ (core gas), potassium bicarbonate (BDH), sodium hydroxide (Merck), piperazine (Sigma-Aldrich), potassium hydrogen phthalate (AJAX), hydrochloric acid (AJAX), thymol blue sodium salt (Sigma-Aldrich), alizarin red S (BDH), methyl orange (SELBY) were all used as obtained. Piperazine, NaOH, and HCl solutions were standardised by potentiometric titrations. Ultra-high purity Milli-Q water was boiled to remove CO$_2$ gas and used to prepare all solutions. All samples and solutions were prepared inside a CO$_2$ free atmosphere glove bag.

**Stopped flow measurements** All kinetic reactions were performed on an Applied Photophysics DX-17 spectrophotometer equipped with a J&M Tidas MCS 500-3 diode-array detector, observing the pH changes over the wavelength range 400-700 nm via coupling to the coloured acid-base indicators. Samples were thermostatted at 25.0 (± 0.1) °C and the exact temperature reported by a thermocouple located in the stopped-flow.
Reversible formation of piperazine carbamates from PZ and CO$_2$(aq) The formation of piperazine carbamates/carbamic acids (mono and di) were studied by mixing equal volumes of a CO$_2$ (aq) solution ([CO$_2$]$_0$ = 4.35 mM) with a series of piperazine solutions ([PIPZ]$_0$ = 1.0 – 6.0 mM), containing thymol blue ($\log_{10} K_{\text{IND}} = 9.05$ at 25.0 °C) indicator, in the stopped flow at 25.0 °C. The reversibility of the reactions was studied by observing the decomposition of an equilibrated solution of piperazine carbamate. To do so, a piperazine carbamate solution containing 0.15 M HCO$_3^-$ and 0.05 M piperazine was firstly prepared and equilibrated at 25.0°C for 24 hours. The concentrations of the carbamate species were determined quantitatively by $^1$H NMR spectroscopy at 25.0°C, Figure 2, and applied directly in the fitting. The equilibrated solution was then transferred to one of the stopped flow syringes and equal volumes of the equilibrated piperazine carbamate solution, and a hydrochloric acid solution in the second syringe ([HCl]$_0$ = 90.0 – 100.0 mM) containing 0.05 mM methyl orange, and 0.1 mM alizarin red S indicators, were mixed at 25.0 °C.

Figure 2. $^1$H NMR spectrum of an equilibrated HCO$_3^-$/PZ solution at 25.0 °C containing 7.0 mM piperazine monocarbamate, and 2.4 mM piperazine di-carbamate, 65.6 mM HCO$_3^-$, and 15.6 mM piperazine. (Peak integrals and chemical shifts not shown for clarity).
Reversible formation of carbamates from PZH$^+$ and CO$_2$(aq) The pH of a piperazine solution was adjusted down by addition of H$^+$, to observe the reversible formation of piperazine mono-carbamaic acid from protonated piperazine and CO$_2$(aq). The kinetics were established by mixing equal volumes of a CO$_2$(aq) solution ([CO$_2$]$_0$ = 5.1 mM) with a series of protonated piperazine solutions([PZH$^+$] = 1.0 – 3.0 mM), containing 25.0 µM thymol blue, in the stopped flow at 25.0 °C. The protonated piperazine solution was generated by sequential addition of hydrochloric acid ([HCl] = 1.0 – 3.0 mM) to a stock solution of free piperazine (4.0 mM), respectively.

Results

The measurement and calculated curves for the reactions of CO$_2$(aq) with free and mono-protonated piperazine, PZ, and PZH$^+$ respectively, together with concentration profiles for the reactions, are shown in Figures (3) and (4) respectively. The pH change during the reactions in the right of Figure (3) and (4) is 10.6 -8.8 , and 10.2 -8.3 , respectively. From the right of Figure 3, the fast initial stage of the reaction (25ms) of CO$_2$(aq) with PZ is dominated by the formation of the mono-carbamate (PZCO$_2^-$), with free piperazine acting as the dominant base accepting protons from the mono-carbamic acid formed. Significant amounts of the mono-carbamic acid (PZCO$_2$H) begin to form after some 50ms. An explanation lies in the pH and the competition for protons among the free piperazine and the mono-carbamate bases. Free PZ (~90%) is consumed quickly in the early stages of the reaction, hence the relative basic species after a reaction time of 50ms, and at a solution of pH 9, are now the mono-carbamate (PZCO$_2^-$) and protonated piperazine (PZH$^+$). Since the protonation constant of PZH$^+$ is orders of magnitude lower it does not play a role in the buffering of pH above pH ~7.5, hence the mono-carbamate becomes the dominant active base. Any further reaction with CO$_2$ must proceed by a reaction with free piperazine (which is now present only as PZH$^+$), or the formation of the di-carbamate/carbamic acid species, stemming from a reaction with the mono-carbamate/carbamic acid. This is in fact observed in a slower second phase (> 50ms) in the right of Figure 3 where the concentration of the mono-carbamate declines, a result of the buffer activity (of the mono-carbamate/carbamic acid) and the slow formation of the di-carbamate/carbamic acid.
Despite the theoretical capacity of PZ to consume 1 mole of CO$_2$ per molecule of amine, a significant amount of free CO$_2$(aq) remains at the end of the reaction. Again, an explanation lies in the pH and the buffer activity of the basic species, specifically free piperazine and mono-carbamate. After a reaction time of 50ms, the majority of the free piperazine has been converted to PZCO$_2^-$, PZH$^+$ and PZCO$_2$H. The latter two species are unreactive towards CO$_2$ at high pH (10-8), hence, the buildup of such species is detrimental to the process. Hence, the overall absorption of CO$_2$ is similar to that of typical carbamate forming mono-amines in the pH region 10-8 which corresponds to the PCC process.

**Figure 3.** (left) absorbance traces at 590 nm in the reaction of 4.35 mM CO$_2$(aq) with 1.0 – 4.0 mM CO PZ in the presence of 12.5 µM thymol blue indicator; (right) concentration profile for the reaction of 4.0 mM PZ + 4.35 mM CO$_2$(aq)

**Figure 4.** (left) absorbance traces at 590nm in the reaction of 5.10 mM CO$_2$(aq) with 1.0 – 3.0 mM PZH$^+$ in the presence of 12.5 µM thymol blue indicator; (right) concentration profile for the reaction of 1.0mM PZH$^+$ with 5.1 mM CO$_2$(aq)
The corresponding decomposition reaction is shown in Figure (5).

![Graph showing absorbance traces at 550 nm in the decomposition of 7.0 mM piperazine monocarbamate, and 2.4 mM piperazine di-carbamate, in the presence of 65.6 mM HCO₃⁻, 15.6 mM piperazine, 0.5 mM ARS, 0.025 methyl orange, with 90.0 – 100.0 mM HCl; (right) concentration profile in the dissociation of carbamate solution with 90.0 mM HCl (0.5 secs, 5 secs).](image)

**Figure 5.** (left) absorbance traces at 550 nm in the decomposition of 7.0 mM piperazine monocarbamate, and 2.4 mM piperazine di-carbamate, in the presence of 65.6 mM HCO₃⁻, 15.6 mM piperazine, 0.5 mM ARS, 0.025 methyl orange, with 90.0 – 100.0 mM HCl; (right) concentration profile in the dissociation of carbamate solution with 90.0 mM HCl (0.5 secs, 5 secs).

The complete set of rate and equilibrium constants from the global analysis of the kinetic measurements is shown in Table 1, together with standard deviations for the parameters in parenthesis. In favour of maintaining constant ionic strength in the solutions, a Debye-Hückel approximation for the species charges was applied during the fitting, hence, all constants are reported as 0.0 M ionic strength.
Table 1. Rate and equilibrium constants for the reactions of CO$_2$(aq) with piperazine species at 25.0 °C, including the protonation constants of the carbamic acid species. Numbers in brackets represent the error in the last digit.

<table>
<thead>
<tr>
<th>reaction</th>
<th>constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + CO$_2$(aq) $\overset{k_7}{\underset{k_7^{-1}}{\rightleftharpoons}}$ ACO$_2$H</td>
<td>$k_7$ [M$^{-1}$ s$^{-1}$] 11.6(8)×10$^3$</td>
</tr>
<tr>
<td>$k_7$ [s$^{-1}$] 3.3(5)</td>
<td></td>
</tr>
<tr>
<td>$K_7$ [M] 3.7(7) × 10$^3$</td>
<td></td>
</tr>
<tr>
<td>AH$^+$ + CO$_2$(aq) $\overset{k_8}{\underset{k_8^{-1}}{\rightleftharpoons}}$[ACO$_2$H$_2$]$^+$</td>
<td>$k_8$ [M$^{-1}$ s$^{-1}$] 1.1(3) × 10$^2$</td>
</tr>
<tr>
<td>$k_8$ [s$^{-1}$] 60(20)</td>
<td></td>
</tr>
<tr>
<td>$K_8$ [M] 1.9(5)</td>
<td></td>
</tr>
<tr>
<td>ACO$_2^+$ + CO$_2$(aq) $\overset{k_9}{\underset{k_9^{-1}}{\rightleftharpoons}}$ [A(CO$_2$)$_2$H]</td>
<td>$k_9$ [M$^{-1}$ s$^{-1}$] 1.4(4) × 10$^2$</td>
</tr>
<tr>
<td>$k_9$ [s$^{-1}$] 1.0(5) × 10$^2$</td>
<td></td>
</tr>
<tr>
<td>$K_9$ [M] 1.8(7)</td>
<td></td>
</tr>
<tr>
<td>ACO$_2^-$ + H$^+$ $\underset{P_3}{\overset{P_3}{\rightarrow}}$ ACO$_2$H</td>
<td>log$_{10}$ $P_3$ 8.83(1)</td>
</tr>
<tr>
<td>ACO$_2$H + H$^+$ $\underset{P_4}{\overset{P_4}{\rightarrow}}$[ACO$_2$H$_2$]$^+$</td>
<td>log$_{10}$ $P_4$ 6.5(1)</td>
</tr>
<tr>
<td>[A(CO$_2$)$_2$]$^2$ + H$^+$ $\underset{P_5}{\overset{P_5}{\rightarrow}}$[A(CO$_2$)$_2$H]$^+$</td>
<td>log$_{10}$ $P_5$ 6.5(1)</td>
</tr>
<tr>
<td>[A(CO$_2$)$_2$H]$^-$ + H$^+$ $\overset{P_6}{\underset{P_6^{-1}}{\rightleftharpoons}}$ A(CO$_2$)$_2$H$_2$</td>
<td>log$_{10}$ $P_6$ 8.0(3)</td>
</tr>
</tbody>
</table>

Discussion

The homogeneous kinetics of the reactions of CO$_2$(aq) with three reactive forms of piperazine, these being; free piperazine (PZ), piperazine mono-carbamate (PZCO$_2^-$), and protonated piperazine (PZH$^+$), were investigated using the fast stopped-flow spectrophotometry technique at 25.0°C. In this way, the analysis of the absorption
process is simplified and the kinetics are observed in the absence of mass transfer phenomena, eliminating the constraint of pseudo-first order conditions, and the possible errors associated with the approximation of physical parameters used in the analysis of such measurements.

**Mechanism validation:** We have developed a comprehensive model, equations (1) – (14), to describe the complete family of possible reactions in piperazine/CO₂/H₂O solutions. In this way, the significance of each of the reaction pathways to the overall absorption can be assessed. Global analysis of the measurement data using the complete mechanism yielded the rate and equilibrium constants for each of the reaction pathways. The validity of the mechanism and the reliability of the determined kinetic and equilibrium constants is confirmed in the generally good agreement between the measurement and calculated curves.

Considering the complexity of the mechanism and the stopped-flow measurements, a perfect fit is not expected and the slightly increased error estimates for the rate constants are therefore also reasonable. A term for the reaction of the mono-carbamic acid (PZCO₂H) with CO₂(aq), where the carbamic acid proton resides on the amine group e.g. PZH₂⁺CO₂⁻ was excluded from the chemical model during the fitting procedure. Since the protonated amine group (e.g. NH₂⁺ for a secondary amine) is unreactive towards CO₂, insertion of a term for this reaction into the chemical model had little effect on the calculated ssq during the data fitting. Despite this, the regressed value for the inserted rate constants did converge towards an approximate value of zero which is further substantiation of the robustness of the mechanism and the fitting procedure.

**Reaction pathways and rate/equilibrium constants** Can we justify the enormous mechanism? From the constants the pathways for the reaction of CO₂(aq) with PZH⁺ and PZCO₂⁻ are orders of magnitude slower and kinetically less significant than the reaction of CO₂ with free piperazine. However, the contributions of the aforementioned reactions are far from insignificant; hence the use of the complete mechanism including these reactions can be justified in the analysis of the measurement data. Such a mechanism will be particularly relevant at higher amine concentrations similar to those
encountered in an industrial process where concentrations of the minor species are correspondingly much higher. Although the model was evaluated here at low concentrations, we cannot guarantee that the model is expected to fit data at significantly higher concentrations and CO₂ loadings. A discussion of the individual reaction pathways follows.

**PZ + CO₂(aq)** Several rate constants are published which describe the reaction of piperazine with CO₂(aq), the values for which are presented in table 2 together with the value determined here in this work. The published values cover some two orders of magnitude, the majority of which are substantially higher than the value determined in this work. This is not surprising considering the diverse assortment of analysis and measurement techniques used to acquire the data.

The reversibility of the reactions is often not considered in mass transfer equations and the reactivity of charged species is assumed not to influence the reaction rate or mass transfer process, both of which are considered in the current study. Furthermore, physical properties of the solutions e.g. diffusion co-efficients/diffusivity are typically unknown and estimated based on other “similar” amines, or assumed to be identical to amines under similar conditions, which can contribute to the differences in the constants between the studies.
The equilibrium constants for each of the reaction pathways are also important. The equilibrium constant here \((3.7(7) \times 10^3 \text{ M}^{-1})\) for the formation of carbamic acid from free piperazine and \(\text{CO}_2(\text{aq})\) is substantially higher than other cyclic and acyclic amines, the highest previously determined value belonging to piperidine \((6.2(3) \times 10^2 \text{ M}^{-1})\). Several published values for the formation of piperazine carbamic acid are available for comparison. Derks et al.\(^9\) presented values for the formation of piperazine monocarbamic acid using equilibrium data from Ermatchkov et al.\(^2\) \((1.48 \times 10^{-5}, 9.4 \times 10^{-6} \text{ at } 25 \text{ and } 40^\circ \text{C respectively})\), which does not incorporate the contribution of the base to the deprotonation of the carbamic acid. It was then assumed by Derks et al. that the free piperazine is the prevailing base for the removal of the carbamic acid proton which yielded equilibrium constants for the formation of carbamic acid from \(\text{CO}_2\) and

<table>
<thead>
<tr>
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<th>Rate constant ((\text{M}^{-1} \text{ s}^{-1}))</th>
<th>Temp ((^\circ \text{C}))</th>
<th>Technique</th>
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<tr>
<td></td>
<td>(11.6 \times 10^3)</td>
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<tr>
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<td>Seo / Hong(^6)</td>
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<td>30</td>
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<td>Bougie et al.(^13)</td>
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<tr>
<td></td>
<td>141.613 \times 10^3</td>
<td>40.15</td>
<td></td>
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</table>
piperazine of $8.0 \times 10^4$ m$^{-1}$ and $2.2 \times 10^4$ m$^{-1}$ at 25.0 and 40.0 °C respectively. The corresponding value using the protonation constant determined by Ermatchkov is $4.1 \times 10^4$ M$^{-1}$ at 25.0 °C. A similar value ($-4.0 \times 10^4$) is obtained from the equilibrium data of Bishnoi and Rochelle at 25.0°C.\(^5\)

The corresponding value from Fernandes et al. is $1.47 \times 10^4$ M$^{-1}$ at 25.0 °C. Although the above mentioned published values are substantially larger than the corresponding value determined in this work, there is a general agreement that piperazine has a substantially higher equilibrium constant than that of other cyclic and acyclic amines. It is also interesting to note the sizeable difference in the equilibrium constants of piperazine ($3.7(7) \times 10^3$ M$^{-1}$) and a piperazine “model” compound n-methylpiperazine ($1.51(5) \times 10^2$ M$^{-1}$). The substantial differences in the constants imply that that the activity of the second nitrogen in piperazine plays a role in the intermediate and transition state carbamic acid products. The steric hindrance around the N-methyl nitrogen of N-MPIPZ may also play a role in the reduced equilibrium constant compared to piperazine here.

**PZH$^+$ + CO$_2$(aq)** The kinetics of the reaction between CO$_2$(aq) and protonated piperazine are less investigated. Here, the rate constant for the formation reaction, $k_8$, is significantly lower ($1.1(3) \times 10^2$ M$^{-1}$ s$^{-1}$) than the reaction of CO$_2$(aq) with free piperazine, $k_7 = 11.6(8) \times 10^3$ M$^{-1}$ s$^{-1}$. This is not surprising considering the differences in the base strength of the two amine molecules. Recently, Derks et al. investigated the same reaction using a stirred cell reactor and determined a value of $2.8(1) \times 10^2$ (M$^{-1}$ s$^{-1}$) which is comparable to the value determined in this work. The equilibrium constant presented by Derks et al. (1.6 m$^{-1}$) using the data of Ermatchkov, again making the assumption that protonated piperazine is the proton accepting base, is in excellent agreement with the value determine here (1.9(5) M$^{-1}$).

**PZCO$_2^-$ + CO$_2$(aq)** Only one previously determined rate constant for the formation of the di-carbamate from mono-carbamate. It is difficult to determine. The concentration of the di-carbamate is typically low, hence the reaction is often not considered in the analysis. The kinetic constant determined by Samanta (59,500 M$^{-1}$ s$^{-1}$) is significantly higher than that estimated in this work.
**carbamate protonation constants** $\log P_3 - \log P_6$ Values for the protonation constants of piperazine carbamates, $\log_{10} P_3$ to $\log_{10} P_6$ are reported here in Table 1. A definitive understanding of each protonation constant is difficult. Nevertheless, the protonation constants for the mono-carbamic acid, $\log_{10} K_8 = 8.83(1)$ here, is in good agreement with the value determined by Bishnoi and Rochelle (9.15 at 25.0 °C), Ermatchkov (9.444 at 25.0 °C), Fernandes et al (9.02 at 25.0 °C), and Cullinane 2005 (9.52 at 25.0°C). The magnitude of the protonation constant for the mono-carbamate is much larger than those of other amines with similar or higher parent amine base strength. Since the piperazine carbamate has two possible protonation sites, the observed protonation constant is consistent with the suggestion that the first protonation of the carbamate is occurring on the second amine group, rather than the traditional carbamic acid oxygen group. Furthermore, the estimation for the second protonation constant of the mono-carbamic acid (carbamic acid oxygen site), $\log_{10} P_4$, is more consistent with other typical carbamic acid protonation constants we have determined.

**Bronsted correlations** we have recently proposed a Bronsted correlation for the reactivity of amines with CO₂ as a function of the base strength (protonation constant). The kinetic rate constants for the reaction of free piperazine (PZ), $\log k_7$, and protonated piperazine (PZH⁺), $\log k_8$, with CO₂(aq), together with additional data for cyclic and acyclic amines as a function of the protonation constants of the amine is shown in Figure 6.
Figure 6. Bronsted trend for amines

The data is in good agreement with the trend for the other amines. Surprisingly, the kinetic correlation extends to the protonated piperazine (PZH$^+$) which is significantly lower in base strength than the other amines. However, the Bronsted dependence does not extend to the formation of the di-carbamate from mono-carbamate and CO$_2$(aq). The di-carbamate appears kinetically limited, the effect of which is likely related to steric effects of the mono-carbamate group and the hindered approach of CO$_2$ to the second amine group.

Conclusions

All PZ is consumed in early stages of reaction and main species are PZCO$_2^-$, PZH$^+$, and PZCO$_2$H. The latter two species are unreactive towards CO$_2$ and the mono-carbamate is kinetically limited based on the rate constant. From concentration profiles the reactivity of PZ with CO$_2$ is similar to that of carbamate forming mono-amines at pH 10-8 which corresponds to the industrial process conditions.

Acknowledgements
References

Towards the Understanding of the Kinetic Reaction of CO$_2$(aq) with Amines for Post Combustion Capture Processes: Structural Modification of Primary amines and the effect of Steric Hindrance

Conway William, Wang Xiaoguang, Fernandes Debra, Burns Robert, Lawrance Geoffrey, Maeder Marcel and Puxty Graeme

Submitted to Environmental Science and Technology
(June 2012)
Towards the Understanding of Chemical Absorption Processes for Post Combustion Capture of Carbon Dioxide: Electronic and Steric Considerations from the Kinetics of Reactions of CO₂(aq) with Sterically-hindered Amines

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Abstract

The present study reports (a) the determination of both the kinetic rate constants and equilibrium constants for the reaction of CO₂(aq) with sterically-hindered amines and (b) an attempt to elucidate a fundamental chemical understanding of the relationship between the amine structure and chemical properties of the amine that are relevant for post-combustion capture of CO₂ (PCC) applications. The reactions of CO₂(aq) with a series of linear and methylated primary amines and alkanolamines has been investigated using stopped-flow spectrophotometry and ¹H-NMR measurementsat
25.0 °C. The specific mechanism of absorption for each of the amines, that is \( \text{CO}_2 \) hydration and/or carbamate formation, is examined and, based on the mechanism, the kinetic and equilibrium constants for the formation of carbamic acid/carbamates, including protonation constants of the carbamate, are reported for amines that follow this pathway. A Brønsted correlation relating the kinetic rate constants and equilibrium constants for the formation of carbamic acid/carbamates with the protonation constant of the amine is reported. Such a relationship facilitates an understanding of the effects of steric and electronic properties of the amine towards its reactivity with \( \text{CO}_2 \). Further, such relationships can be used to guide the design of new amines with improved properties relevant to PCC applications.

**Introduction**

The coal-fired power generation sector has been identified as the most logical target for the reduction of runaway atmospheric \( \text{CO}_2 \) emissions. Carbon capture and storage (CCS), incorporating post-combustion capture (PCC), is the best placed option for the abatement of \( \text{CO}_2 \) emissions, where reversible capture and release of \( \text{CO}_2 \) using aqueous amine solvents is at present the frontline commercial technology. However, the high capital cost associated with the requirement for stainless steel absorber/stripping columns and the high cost of energy (COE) associated with the regeneration of \( \text{CO}_2 \) in the stripping process demands improvements to facilitate the upscale and successful deployment to a large-scale industrial process.\(^1\)

Significant advances can be made via insights into the fundamental chemical aspects of the absorption and desorption processes. Since the physical size and footprint of both the absorber and stripper columns is directly influenced by the solution chemistry of the amine, the outcomes of chemical investigations will lead to the identification of amines that can provide faster absorption rates, smaller equipment sizes, reductions in the overall energy demand and, ultimately, lower \( \text{CO}_2 \) capture costs.

A crucially important property of an amine for PCC applications is its ability to form a carbamate. Interestingly, carbamate formation has distinct advantages as well as disadvantages, and thus the determination of the overall suitability of a particular amine is a non-trivial evaluation of many aspects, including the above apparent paradox.
Sterically-hindered amines and in particular tertiary amines do not form carbamates. Their reactivity in PCC involves the absorption of the proton released from carbonic acid, which is formed from the reaction between CO₂ and water. Note also that bicarbonate is formed via the direct reaction of hydroxide with CO₂. This second reaction becomes faster with increasing pH and eventually surpasses the reaction with water at a pH higher than 8.5. Thus amines with high protonation constants under the same conditions will result in higher pH and consequently faster reactivity towards CO₂. A more important property of non-carbamate forming amines is the fact that they react in a 1:1 ratio with CO₂; the net reaction is given in equation (1), where RNH₂ represents an amine.

On the other hand, the crucial advantage of the carbamate-forming or reactive amines is the fact that their reaction with CO₂ is generally much faster than the reaction with water/hydroxide. Fast reactions result in a significant advantage as they allow a smaller physical size for the absorber column, and hence deliver cost advantages. While the rate of this reaction is not the sole determinant of the size of the absorber column, it is one of many important characteristics. A clear disadvantage of carbamate formation is the 2:1 stoichiometry of the interaction of the amine with CO₂. This stems from the fact that the initially formed carbamic acid is relatively acidic and, under relevant conditions, a second amine absorbs the released proton. Equation (2) represents this situation.

\[
\text{CO}_2(aq) + H_2O + \text{RNH}_2 \rightleftharpoons \text{HCO}_3^- + \text{RNH}_3^+ \tag{1}
\]

\[
\text{CO}_2(aq) + 2\text{RNH}_2 \rightleftharpoons \text{RNHCO}_2^- + \text{RNH}_3^+ \tag{2}
\]

Apart from the basicity of the amine which defines the pH and thus the rate of the reaction of CO₂ with OH⁻, the capacity to form carbamates is the distinguishing factor between the amines.

The reaction between CO₂ and the amine is a Lewis acid-base interaction and thus Lewis basicity is an important property of the amine. It will influence the rate as well as the equilibrium constant for the reaction with CO₂. The simplest approximation for the Lewis basicity of the amine is the Brønsted basicity which is straightforwardly defined by the protonation constant. However, this approximation is of limited value as
the proton is much smaller than a CO$_2$ molecule and thus any steric interaction needs to be taken into account.

To date, the majority of PCC chemical research has focussed on monoethanolamine (MEA); however the prospect of significant improvements has inspired a view to alternative capture solvents, in particular sterically-hindered amines which aim to combine the fast kinetics of the carbamate-forming amines with the favourable stoichiometry of tertiary amines. The most widely recognised of the sterically hindered family of amines is 2-amino-2-methyl-1-propanol (AMP). Despite substantial efforts towards the quantification of the kinetic relationship of AMP with CO$_2$, the fundamental mechanism and reactive pathways for CO$_2$ in sterically-hindered amines is evidently not as clear as that for MEA.$^{3-13}$

The present study investigates the relationship between electronic effects on amine reactivity, which are measured by the protonation constant, and steric effects which are defined by the difference in Lewis basicity towards a proton and the CO$_2$ molecule. The overall aim is to work towards an understanding of the relationship between the molecular structure of an amine and its usefulness for PCC applications. This in turn will guide the development of novel amines with improved properties that are relevant for PCC applications.

In this study we report the results of stopped-flow spectrophotometric measurements at 25.0 $^\circ$C for the reaction of CO$_2$(aq) with the series of sterically-hindered, substituted MEA derivatives: 1-amino-2-propanol (1-AP), 2-amino-1-propanol (2-AP), 2-amino-2-methyl-1-propanol (AMP) and 2-amino-1,3-propanediol (BIS), as well as a series of alkylamines and alkanolamines: $n$-propylamine (PA), $n$-butylamine (BA), tertiary-butylamine (TBA), isobutylamine (IBA), sec-butylamine (SBA) and 3-amino-1-propanol (MPA). In particular, the rate constant, $k_7$, for the direct reaction between the amine and CO$_2$ to form the carbamic acid (see Figure 1), as well as the equilibrium constant, $K_7$, for the same reaction have been determined and related to the protonation constants, $K_6$, of the reactive amines. Such Brønsted relationships reveal useful insight into the properties of amines that are relevant for PCC applications. The chemical pathways, kinetic behaviour, carbamate stability, and the role of the
protonation constant in the maintenance of pH and in the kinetics reactions of sterically-hindered amines with CO\textsubscript{2} are discussed throughout.

\textit{CO\textsubscript{2} hydration/carbamate formation mechanism}

We have established a general reaction mechanism that encompasses all reactions of CO\textsubscript{2} in aqueous amine solutions, as illustrated in Figure 1.\textsuperscript{14-16}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{reaction_diagram}
\caption{The chemical reaction set for reactive amines interacting with CO\textsubscript{2}(aq), including the parallel reaction(s) of CO\textsubscript{2}(aq) with water and hydroxide, as well as the associated protonation equilibria for the carbonate species, amine, and carbamate.}
\end{figure}

The formal equations for the reactions of CO\textsubscript{2}(aq) with water, hydroxide, including the protonation reactions of carbonate, bicarbonate and hydroxide, are listed in equations (3) to (7):

\begin{align*}
\text{CO}_2\text{(aq)} + \text{H}_2\text{O} & \rightleftharpoons \frac{k_1}{k_1^{-1}} \text{H}_2\text{CO}_3 \quad (3) \\
\text{CO}_2\text{(aq)} + \text{OH}^- & \rightleftharpoons \frac{k_2}{k_2^{-1}} \text{HCO}_3^- \quad (4) \\
\text{CO}_3^{2-} + \text{H}^+ & \rightleftharpoons \frac{k_3}{k_3^{-1}} \text{HCO}_3^- \quad (5) \\
\text{HCO}_3^- + \text{H}^+ & \rightleftharpoons \frac{k_4}{k_4^{-1}} \text{H}_2\text{CO}_3 \quad (6) \\
\text{OH}^- + \text{H}^+ & \rightleftharpoons \frac{k_5}{k_5^{-1}} \text{H}_2\text{O} \quad (7)
\end{align*}
while the reactions leading to the formation of the carbamic acid/carbamate are listed in equations (8) to (11):

\[
\text{RNH}_2 + H^+ \stackrel{k_6}{\rightleftharpoons} \text{RNH}_3^+ \quad (8)
\]

\[
\text{RNH}_2 + \text{CO}_2\text{(aq)} \stackrel{k_7}{\rightleftharpoons} \text{RNHCO}_2\text{H} \quad (9)
\]

\[
\text{RNHCO}_2^- + H^+ \stackrel{k_8}{\rightleftharpoons} \text{RNHCO}_2\text{H} \quad (10)
\]

\[
\text{RNH}_2 + \text{HCO}_3^- \stackrel{k_9}{\rightleftharpoons} \text{RNHCO}_2^- + \text{H}_2\text{O} \quad (11)
\]

Note that in the above equations two-way arrows represent kinetically measurable rate constants, while a double-headed arrow represents an equilibrium reaction.

We have previously introduced this mechanism and the reactions for the kinetic and equilibrium study of the reversible formation and decomposition of carbamates in amine solutions for several amines including MEA, ammonia and a series of cyclic secondary amines.\textsuperscript{14-18}

**Experimental section**

**Chemicals.** All chemicals including \textit{n}-propylamine (PA, 99%), \textit{n}-butylamine (BA, >99%), \textit{tertiary}-butylamine (TBA, 99%), isobutylamine (IBA, 99%), \textit{sec}-butylamine (SBA, 99%), 2-amino-2-methyl-1-propanol (AMP, 95%, ~5% water), 1-amino-2-propanol (1-AP, 99%), 2-amino-1-propanol (2-AP, 93%), 2-amino-1,3-propandiol (BIS, 99%), 3-amino-1-propanol (MPA, 99%), thymol blue-sodium salt (TB), alizarin red S (ARS), and methyl orange (MO) were purchased from Sigma-Aldrich and were used without further purification. Representations of the amines, together with their protonation constants at 25.0 °C, are collected in Table 1. All amine solutions for the stopped-flow and \textsuperscript{1}H NMR studies, including all stock solutions of amine, amine-carbamate, indicator, HCl, and HCO\textsubscript{3}^- were prepared using de-ionised water that had been boiled to remove dissolved CO\textsubscript{2}. The solutions were stored in a glove-bag that was purged constantly with nitrogen.

**Table 1.** Chemical names, abbreviations, structures, and protonation constants of the amines at 25.0 °C.
<table>
<thead>
<tr>
<th>Amine</th>
<th>Abbreviation</th>
<th>Structure</th>
<th>log $K_a$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-Propylamine</td>
<td>PA</td>
<td>$\text{H}_2\text{N}$</td>
<td>10.566*</td>
</tr>
<tr>
<td>$n$-Butylamine</td>
<td>BA</td>
<td>$\text{H}_2\text{N}$</td>
<td>10.640*</td>
</tr>
<tr>
<td>Iso-butylamine</td>
<td>IBA</td>
<td>$\text{H}_2\text{N}$</td>
<td>10.48*</td>
</tr>
<tr>
<td>Sec-Butylamine</td>
<td>SBA</td>
<td>$\text{H}_2\text{N}$</td>
<td>10.57*</td>
</tr>
<tr>
<td>Tertiary-butylamine</td>
<td>TBA</td>
<td></td>
<td>10.685*</td>
</tr>
<tr>
<td>1-amino-2-propanol</td>
<td>1-AP</td>
<td>$\text{H}_2\text{N}$</td>
<td>9.50*</td>
</tr>
<tr>
<td>2-amino-1-propanol</td>
<td>2-AP</td>
<td>$\text{H}_2\text{N}$</td>
<td>9.52*</td>
</tr>
<tr>
<td>2-amino-1,3-propanol</td>
<td>BIS</td>
<td>$\text{H}_2\text{N}$</td>
<td>8.81*</td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol</td>
<td>AMP</td>
<td>$\text{H}_2\text{N}$</td>
<td>9.67*</td>
</tr>
<tr>
<td>3-amino-1-propanol</td>
<td>MPA</td>
<td>$\text{H}_2\text{N}$</td>
<td>10.088*</td>
</tr>
</tbody>
</table>

*IUPAC Stability Constants Database.*¹⁹b Fernandes et al.¹⁷

**1H-NMR Measurements.** The existence of carbamate was investigated for each amine by $^1$H-NMR measurements. Solutions containing $\text{HCO}_3^-$ (0.1 M) and amine (0.05 M) were equilibrated for 24 hours prior to the $^1$H-NMR measurement. Carbamate formation results in additional peaks for selected $\text{–CH}_2$ or $\text{–CH}_3$ groups of the amine. The carbamate concentration was determined by analysis of the peak integrals which were then related to the known total concentration of the amines. The equilibrium
concentrations were used for the analysis of the kinetic investigation of their reactivity at low pH values in the decomposition reactions. Carbamates were observed for PA, BA, IBA, SBA, 2-AP, 1-AP and MPA.

**Stopped-flow measurements.** Kinetic measurements were performed on an Applied Photophysics SX-20 stopped-flow spectrophotometer coupled to a J & M TIDAS MCS-500 3-diode array detector, measuring the absorbance of the solutions over the wavelength range 400-700 nm. Solutions were thermostatted in the stopped-flow instrument at 25.0 ±0.1 °C using a Julabo F20 circulating water bath.

(i) **CO₂(aq) + amine reactions:** Each of the amines was investigated for carbamate formation by reacting a CO₂(aq) solution with each amine solution, in the presence of indicator, using the stopped-flow spectrophotometer. The kinetics of the reactions were established by monitoring changes in the absorbance of the indicator(s) over time, which occurred as a result of pH changes from the release of protons from the carbamic/carbonic acid formed during the reactions.

(ii) **Acid decomposition reactions:** The decompositions of the amine-carbamates were investigated by the reactions of equilibrated carbamatesolutions with hydrochloric acid, in the presence of 0.05 mM alizarin red S and 0.025 mM methyl orange indicators, in the stopped-flow spectrophotometer. Carbamate solutions containing 0.05 M amine and 0.1 M HCO₃⁻ were first prepared and equilibrated at 25.0 °C for 24 hours. The composition of the carbamate solution was quantitatively evaluated by ¹H-NMR spectroscopy based on the intensities of the –CH₃ or –CH₂– signals of the species in solution. Species concentrations were used directly in the subsequent data fitting procedures.

**Data Analysis.** All analyses were performed with ReactLab (www.jplusconsulting.com) and in-house written extensions. The calculations include estimates of all activity coefficients based on Debye-Hückel approximations. All kinetic measurements were analysed globally, i.e. all wavelengths and data sets were fitted as one. For more detail see reference 16. All measurements were repeated five times, resulting in five complete data sets. This in turn results in well-founded error estimates for the fitted parameters.

**Results**
A selection of the absorbance measurements and calculated fitted traces are available in Figures S1 and S2 of the Supplementary material. Global analyses of the measured data for the reactions of CO$_2$(aq) with the selected amines at 25.0 °C, as well as the acid-catalysed decomposition reactions, resulted in rate and equilibrium constants for the reversible formation of carbamate, i.e. $k_7$, $k_{-7}$, the corresponding equilibrium constant, $K_7$, as well as protonation of the carbamate, which is reported as log $K_8$. All of the parameters, together with the calculated values for the equilibrium constant that describes the formation of carbamate from HCO$_3^-$ and amine, $K_9$, are listed in Table 2. The application of microscopic reversibility allowed the calculation of the equilibrium constant for the reaction of bicarbonate with amine, $K_9$, as $K_9 = K_7 K_4 / K_1 K_8$. We have previously used this approach where the calculated values correlate with those determined by direct $^1$H-NMR spectroscopic methods.$^{16,18}$ Standard deviations (shown in parenthesis in the table) represent the error in the last digit of the parameters and were calculated based on the complete analysis of five measured data sets as indicated above.
Table 2. The rate and equilibrium constants for the reactions of amine with CO$_2$(aq) and bicarbonate, HCO$_3^-$, including the protonation constants of the carbamate, at 25.0°C. The numbers in parentheses represent the standard deviation in the last digit.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constant</th>
<th>PA</th>
<th>BA</th>
<th>IBA</th>
<th>SBA</th>
<th>1-AP</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNH$_2$ + CO$_2$(aq) $\xrightleftharpoons{K_7}$ RNHCO$_2$H</td>
<td>$k_7$, M$^{-1}$ s$^{-1}$</td>
<td>$(10.0 \pm 0.9) \times 10^3$</td>
<td>$(11.8 \pm 1.0) \times 10^3$</td>
<td>$(11.8 \pm 1.3) \times 10^3$</td>
<td>$(2.36 \pm 0.3) \times 10^3$</td>
<td>$(5.3 \pm 0.6) \times 10^3$</td>
</tr>
<tr>
<td>RNHCO$_2$ + H$^+$ $\xrightleftharpoons{K_8}$ RNHCO$_2$H</td>
<td>log $K_8$</td>
<td>2.40(4)</td>
<td>2.30(5)</td>
<td>2.46(2)</td>
<td>2.01(1)</td>
<td>2.0(2)</td>
</tr>
<tr>
<td>RNH$_2$ + HCO$_3^-$ $\xrightleftharpoons{K_9}$ RNHCO$_2$</td>
<td>log $K_9^{a}$</td>
<td>6.7(2)</td>
<td>7.1(5)</td>
<td>6.91(2)</td>
<td>7.11(1)</td>
<td>6.8(2)</td>
</tr>
</tbody>
</table>

$^a$ $K_9$ calculated by $K_9 = K_7 K_4 / K_1 K_8$. 


Discussion

Assessing carbamate formation

For PA, BA, IBA, SBA, 1-AP, 2-AP and MPA carbamate formation was observed as a result of the analysis of the $^1$H-NMR spectral studies. Note, however, that these studies were performed at relatively low concentrations (0.05 M amine, 0.1 M HCO$_3^-$). No carbamate formation was observed for TBA, BIS and AMP. In the case of AMP, carbamate formation has been detected by $^{13}$C-NMR at much higher total concentrations (30 wt% amine solution), and the equilibrium constant for the reaction between HCO$_3^-$ and amine, $K_9$, was reported as 0.47. This equilibrium constant allows the calculation of the expected carbamate concentration under our conditions to be approximately 0.28 mM which amounts to a $^1$H signal integrated intensity of about 0.5 % of the total amine concentration (corrections for activity coefficients are not expected to be substantial). This value is below the peak integrals expected for the $^{13}$C satellites of the –CH$_2$ and –CH$_3$ $^1$H-NMR signals. Thus the carbamate concentration was too small to be observed under our reaction conditions. Similar conclusions can be made for all other non-carbamate forming amines, and higher concentrations may indeed reveal limited carbamate formation in one or more cases. Indeed, the formation of a carbamate of TBA has been reported using precipitation methods, although this was performed at 18°C.

The kinetics of the reversible carbamate forming reaction between CO$_2$(aq) and the amine is defined by the rate constants $k_7$ and $k_{-7}$. The determination of these values, together with the determination of the protonation constant, $K_8$, of the carbamate to form the corresponding carbamic acid, is well established. Selected fits to the experimental data are shown in the Supplementary material in Figures S1 and S2. The resulting rate constants as well as the protonation constants are listed in Table 2. This table also lists the derived equilibrium constants log $K_7$ and log $K_9$. The latter is the equilibrium constant for the formation of the carbamate from the amine and bicarbonate. This path has been identified and confirmed experimentally for MEA, DEA, and the cyclic amines morpholine, thiomorpholine, piperidine, 4-piperidinemethanol, 1-methylpiperazine and pyrrolidine. Here we only report the calculated equilibrium constant.
Recently, we have observed the intermediate formation of carbamate with ammonia under experimental conditions very similar to those existing in the present study. Indeed, ammonia reacts quickly with CO$_2$(aq) to form an intermediate carbamate that decomposes subsequently on a time scale of seconds. Thus under the equilibrium conditions no carbamate was observed. We have also investigated this potential pathway in the analysis of the non-carbamate forming amines. However, no improvement in the calculated fits to the reactions profiles could be established by inclusion of this pathway. Thus the kinetic analysis is consistent with the $^1$H-NMR results for all amines. Model calculations demonstrate that intermediate carbamate formation would straightforwardly be detected in the analysis of the kinetic data. Perfect fits for the reduced model and the lack of any improvement of fit after the addition of the carbamate forming reactions indicates that carbamate formation in these cases does not play a significant role in the reaction of the amine with CO$_2$(aq).

**Investigation of electronic and steric effects**

A major goal of the present research is the rationalisation of the values for the rate constants, $k_7$, and equilibrium constants, $K_7$, for carbamate formation. As carbamate formation is a Lewis acid-base reaction it makes chemical sense to relate the Lewis basicities of the amines towards the Lewis acids CO$_2$ and H$^+$. In view of the negligible size of the proton, steric effects are minimal and thus the Brønsted and Lewis basicities towards H$^+$ should be very similar. Thus $k_7$ and $K_7$ represent a direct measure of the electronic contribution towards the Lewis basicity of the amine in its reaction with CO$_2$. Any steric effects present during the reaction would manifest themselves in a difference between the Brønsted and Lewis basicities.
Figure 2. Plots of log $k_7$ and log $K_7$ vs log $K_6$ for the amines reported here (●) as well as a series of cyclic secondary amines (◊) and a selection of other important amines (MEA, DEA, NH$_3$).

The Figures 2(a) and (b) display the Brønsted relationships between the protonation constant, log $K_6$, and the rate constant, log $k_7$, in part (a) and the equilibrium constant, log $K_7$, in part (b). The figures include the amines reported here (●), a series of unhindered cyclic secondary amines (◊) [morpholine, thiomorpholine, piperidine, 4-piperidinemethanol, 1-methylpiperazine and pyrrolidine] as well as a collection of important other amines including MEA (◊), DEA (◊) and ammonia (□). Both relationships feature a clear correlation for the sterically unhindered amines, which is indicated by the dashed line. The slope of the line in Figure 2(a) for the correlation of the kinetics is slightly larger than the slope of the line in Figure 2(b) for the equilibrium. Thus the Brønsted basicity, represented by log $k_7$ and log $K_7$, is a direct measure of Lewis basicity towards CO$_2$, with a larger effect on the kinetics than on the equilibrium. Both NH$_3$ and DEA fall below the lines in both plots. Clearly, ammonia is not sterically hindered; however its unique solvation properties in aqueous solution presumably accounts for its deviation from the line. Similarly, DEA is a secondary amine but sterically not restrained in the same way as the cyclic amines. The two –CH$_2$-CH$_2$-OH groups are highly fluctional and restrict access for CO$_2$ to the amine nitrogen atom, thus resulting in lower $k_7$ and $K_7$ values.

All linear amines and alkanolamines are reactive towards carbamate formation and their Lewis basicities are in accord with their Brønsted basicities, that is they fall on the dashed lines in Figure 2(a) and (b). However, the position of an attached –CH$_3$ or related group, to give a branched hydrocarbon chain, can have a major effect in both relationships. However, this depends on the location of these groups. Both 1-AP and IBA have a –CH$_3$ group located on the β-carbon, which results in no discernible steric hindrance. These two amines are thus located on the dashed lines in Figure 2(a) and (b), as might be expected. Three amines do not form carbamates, TBA, AMP and BIS. These amines feature two –CH$_3$ groups located on the carbon α to the amine nitrogen (TBA and AMP) or an even more sterically demanding –CH$_2$OH group (BIS); their interaction with CO$_2$ is too weak to be observed under our reaction conditions. Note, however, that AMP
has been reported to form a carbamate at higher concentrations, as has been noted above,
while TBA has also been reported to form a carbamate. (reference 21 here)

Now, both 2-AP and SBA only feature one –CH$_3$ group located on the carbon $\alpha$ to
the primary amine group and both exhibit significantly reduced $k_7$ values by some 0.8
logarithmic units less than expected, based on their log $k_6$ values. Both amines sit clearly
below the line found for the sterically unhindered amines in Figure 2(a). The effect on
the equilibrium constant, as shown in Figure 2(b) is less pronounced. The decrease in
log $K_7$ is larger for 2-AP (~0.8 logarithmic units less than predicted) than for SBA (~ 0.5
units). Note also that the scatter about the linear correlation is greater for the
equilibrium relationship, and this also might explain the modest inconsistencybetween
2-AP and SBA of the steric effect in this case.

The twocorrelations in Figure 2(a) and (b) render strongly basic amines (high log
$K_6$ values) potentially interesting for PCC applications. Firstly, such amines feature fast
carbamate formation (high log $k_7$ values) and secondly they result in a high pH and thus
support the reaction of CO$_2$ with OH$^-$ via $k_2$. Thus, if a sterically-hindered amine (in the
manner of 2-AP and SBA) can be synthesised, which is also strongly basic then
carbamate formation would be suppressed. Such an amine will have the advantage of
fast kinetics (comparable to, say, MEA) and will also exhibit a more favourable CO$_2$
absorption capacity from an equilibrium aspect.

While the rate constant for the carbamate formation, $k_7$, is important, it is only
one of several parameters that define the suitability of an amine for PCC applications.
The enthalpy of protonation has been identified as an important component for the
overall energy requirement in the stripper.$^{22}$ We are in the process of analysing this
value as a function of amine structural properties, similarly to the efforts presented
here.$^{17}$

An important objective of PCC research is to develop novel and better amines for
improved performance. Such endeavours are guided by the kind of understanding that
results from the investigations discussed here.

Acknowledgements

Supplementary materials section
**Figure S1.** Absorbance traces at 590nm in the reaction of 3.0 mM CO\textsubscript{2} with 2.0 - 8.0 mM IBA in the presence of 0.05 mM alizarin red S and 12.5 µM thymol blue indicators at 25.0 °C. The markers represent the measurements, the lines the fitted curves.

**Figure S2.** Absorbance traces at 550 nm in the decomposition of 2.1 mM SBA carbamate in the presence of 47.9 mM HCO\textsubscript{3}, 22.9 mM IBA, 40.0 - 50.0 mM HCl, 0.05 mM alizarin red S, and 0.025 mM methyl orange indicators at 25.0 °C

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Conclusions

The level of greenhouse gas emissions is enormous and evidence is mounting that climate change is occurring faster than had been previously predicted. Forecasts predict severe consequences for the environment and humans if these emissions are not reduced in the very near future, otherwise it will be much more difficult to bring further warming under control.

The greenhouse gas emissions, particularly CO$_2$ from power plants are enormous. Coal is likely to continue to be a major source of power; at least for the immediate future, hence it is vital to reduce the emissions of CO$_2$ directly into the atmosphere from this stationary source. One promising approach currently under consideration is carbon capture and storage (CCS). The central process prior to storage is the removal of CO$_2$ from the flue gas stream which consists typically of 15 % CO$_2$ and approximately 80% N$_2$. This is achieved by employing chemical absorption separation technology by aqueous amine solutions after the combustion has occurred called the post combustion capture (PCC). Separation of the two gases is crucial for reducing the cost of compression, transportation and storage of CO$_2$.

Post combustion capture (PCC) is a cyclic process whereby the amine solution absorbs CO$_2$ under one set of conditions in the absorber, and releases it under a different set of conditions in the stripper. The amine solution is then recycled through the system to the absorber and the cycle continues. The most relevant aspect for the process is the price per unit of captured CO$_2$ which is dominated by the energy requirement of the cyclic process. Temperature is the most likely candidate for the driving of the cycle. The accurate knowledge of all the chemical reactions that occur in the cyclic process is an invaluable tool.

The chemistry of the complete PCC process can be loosely divided into three components which are interlinked: the kinetics or rates of absorption, the equilibrium or solution composition, and the thermodynamics or energies, including enthalpies and entropies of the reactions as well as those of activation of the reactions. As a result of this project, we now provide knowledge of the chemical reactions of selected amines with CO$_2$ in aqueous solution, the corresponding rate and equilibrium constants for the
reactions, and the energies (activation parameters, enthalpies and entropies) that are crucial for the complete modelling of the absorption and stripping processes.

Papers 1 and 6: Carbamate formation decreases the cyclic capacity of the amine solution; its formation is an undesirable part of the post combustion capture process. We found that increasing steric hindrance of the parent amine, intramolecular hydrogen bonding and electronic effects can all lead to a decrease in the stability of the carbamate. A plot of $\Delta H^\circ_m$-$\Delta S^\circ_m$ showed interesting structural trends for carbamate formation as follows: a) as $\Delta H^\circ_m$ becomes more exothermic (negative), $\Delta S^\circ_m$ also becomes more negative; this is because carbamate formation involves ionic species so that there will be a large amount of solvent reorganisation and ordering of the solvent molecules associated with the negatively-charged HCO$_3^-$ and amine-carbamate species, b) with increasing size of the aliphatic organic group and increasing length of the pendent side chain $\Delta H^\circ_m$ becomes more exothermic, c) in the case of cyclic pyrrolidine and piperidine systems, $\Delta H^\circ_m$ becomes more exothermic on decreasing the ring size, and this is consistent with a greater release of ring strain in pyrrolidine by a change in conformation and accompanying solvent reorganisation, d) For 1-methylpiperazine and piperidine, more positive values for $\Delta S^\circ_m$ result from considerable conformational change produced in their ring structures, and reorientation of the –CH$_3$ substituent in 1-methylpiperazine, on carbamate formation. This must counteract solvent reorganisation. The outstanding amine was ammonia as it had a lower equilibrium constant than the other amines.

Papers 1, 3, 4, 5, 6, 7, 8 and 9: The carbamate/carbamic acid is also involved in a protonation/deprotonation equilibrium. It is difficult to obtain an accurate value, for the protonation/deprotonation of the carbamate/carbamic acid as the concentration of the carbamic acid is always low under any conditions. The protonation of the carbamate requires a pH at which the overall equilibrium favours the release of CO$_2$. Based on the results of this project the protonation constants for the carbamate did not vary much with the temperature.

Paper 2: The energy requirement for the cyclic cooling/heating process is strongly dependent on the enthalpy of protonation of the amine and thus on the
protonation constant. The temperature dependence of the protonation constant provides a measure of the reaction enthalpy that accompanies the change of the base strength of the absorbent with temperature. Based on my work, a plot of $\Delta H_m^\circ - \Delta S_m^\circ$ for the alkanolamines gave linear correlations for the primary, secondary and tertiary mono-, di- and tri- alkanolamines, and the substituted piperidines. Species with a lower positive $\Delta S_m^\circ$ had a more exothermic $\Delta H_m^\circ$, and vice versa. Any addition of –OH to a structure causes a change of +5 kJ/mol leading to a more positive $\Delta H_m^\circ$ and hence to a less efficient heat difference between the absorber and stripper under PCC application. The replacement of –H by an electron donating/withdrawing group like –CH₃ or –CH₂OH or –CH₂CH₂OH on the carbon chain/cyclic ring in case of piperidines may affect the $\Delta H_m^\circ$ and $\Delta S_m^\circ$ by causing one or more changes in a steric effect, intermolecular or intramolecular hydrogen bonding, an inductive effect and solvation effects. Ammonia has the most exothermic $\Delta H_m^\circ$ and the lowest value for $\Delta S_m^\circ$, this is a consequence of the highly solvated environment that ammonia experiences in solution, with considerable hydrogen bonding in both its neutral and protonated forms.

Based on the $\Delta H_m^\circ - \Delta S_m^\circ$ plot the trend observed was alkylamines → ammonia → monoalkanolamine → dialkanolamine → trialkanolamine, and this trend will help guide the selection of suitable amine-based compounds for PCC application.

**Paper 3:** The kinetics of the reversible reactions of CO$_2$(aq) and HCO$_3^-$ at 25 °C with a series of substituted cyclic secondary amines, as well as the non-cyclic secondary amine diethanolamine, has been investigated. In terms of the forward reaction of CO$_2$(aq) with amine, the order with increasing rate constants was: diethanolamine < morpholine < thiomorpholine < 1-methylpiperazine < 4-piperidinemethanol < piperidine < pyrrolidine. A Brønsted correlation for the cyclic amines and some relevant acyclic amines (monoethanolamine, ammonia and diethanolamine) was obtained. The protonation constant of the amine was compared to the rate and the equilibrium constant, which gave linear relationship for the cyclic amines with significantly lower values for most of the acyclic amines. Both 2-piperidinemethanol and 2-piperidineethanol did not form a carbamate, and this could be due to the intramolecular hydrogen bonding as discussed in papers 1 and 2. Based on this work pyrrolidine
represented a good option for the entire capture process across both the absorption and desorption regimes, mainly due to its fast kinetics.

**Papers 4, 5 and 7:** A temperature dependence of the rate and the equilibrium constants for ammonia and monoethanolamine was investigated using stopped flow spectrophotometry and $^1$H NMR spectroscopy. The rate constants for the reaction of CO$_2$(aq) with monoethanolamine was found to increase with increasing temperature, and a similar trend was seen for ammonia. Analysis of the forward kinetic data reveals that aqueous ammonia reacts with CO$_2$(aq) rapidly to form carbamic acid, which at relevant pH values deprotonated instantly to give carbamate. Due to the concomitant pH changes, the equilibrium is reversed and the carbamate eventually decomposes to generate protonated ammonia and bicarbonate. As for monoethanolamine, the reaction proceeds by the fast absorption of CO$_2$(aq) by monoethanolamine and OH$^-$ in combination, producing carbamic acid and bicarbonate, respectively. Monoethanolamine is consumed quickly at approximately twice the rate of CO$_2$ because of the stoichiometry of the reaction and continuous protonation of the amine.

Analysis of the back reaction indicates that the ammonia-derived carbamic acid had a poorer stability than the equivalent monoethanolamine carbamic acid. Based on the kinetic study, the equilibrium constants for ammonia and monoethanolamine were calculated, and for both amines they decreased with increasing temperature. Our results also demonstrate that the equilibrium constants for the carbamate are much lower for ammonia than for monoethanolamine, which indicates that under particular pH conditions, no ammonium carbamate accumulates in the overall reaction, which implies that ammonia has a great advantage over monoethanolamine and other alkanolamines in terms of the overall cyclic capacity of the amine.

An ever increasing interest in possible improvements to the capture rates and efficiencies of the process has inspired a view to selecting alternative absorbents for the capture of CO$_2$. In this project we have also investigated piperazine and some sterically-hindered amines. Piperazine is a cyclic diamine which has been extensively used in CO$_2$ capture applications, particularly as a rate promoter for CO$_2$ absorption in carbonate and tertiary amine solutions. The well-established mechanism for the aqueous reactions of
CO$_2$(aq) in amine solution are directly applicable to piperazine system, however the corresponding mechanism for piperazine is significantly more complex and requires additional reaction pathways and protonation equilibria ensuing from the second amine moiety. To expand the scope for the CO$_2$-piperazine system we have established the kinetics of CO$_2$(aq) with the reactive piperazine species; free piperazine (PZ), monocarbamate (PZCO$_2^-$), and protonated piperazine (PZH$^+$). The rate and the equilibrium constants for each of the individual reaction pathways have been determined, Paper 8 (manuscript in preparation).

Structurally modified and sterically-hindered amines have been considered as a replacement solvent which aims to combine the desired properties of tertiary amines, which have a high capacity of CO$_2$, while maintaining the kinetics characteristics of the fast carbamate forming group of amines. Steric hindrance is achieved by substituting hydrogens at the carbons adjacent to the amine group with bulky groups. In Paper 9 (manuscript in preparation), the kinetic and equilibrium constants for the formation of carbamic acid/carbamates from CO$_2$(aq) and N-propylamine, N-butylamine, 1-amino-2-propanol, 2-amino-1-propanol, iso-butylamine, 2-amino-2-methyl-1-propanol, 2-amino-1,3-propandiol, tertiarybutylamine and sec-butylamine have been investigated at 25 °C.

The outcomes of this thesis, adds to our fundamental understanding of the reaction mechanism and the determination of rate constants, equilibrium constants, protonation constants and the associated thermodynamic constants. The approach and methods employed in this thesis can be used on a number of different amine(s) and amine types in the future to provide values on the kinetic, equilibrium and thermodynamic constants, potentially extending the library of amines for post combustion capture applications.

Such studies are of fundamental importance and aid in the rational design of solvent systems for CO$_2$ capture in the future. It also provides an insight into the concentration and temperature profiles that will help guide the modelling, selection and design of new, novel solvent systems, which along with the physical constants and mass-transfer information will lead to the optimisation of the PCC process without the need for expensive testing at the pilot scale, significantly reducing time and cost.