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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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, CO₂(aq), with water and hydroxide ions to reversibly form carbonic acid and bicarbonate:

\[
\begin{align*}
H₂O + CO₂(aq) & \rightleftharpoons H₂CO₃ \\
OH^- + CO₂(aq) & \rightleftharpoons HCO₃^-
\end{align*}
\]
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\text{-NH}_2 + H^+ & \rightleftharpoons R\text{-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:

\begin{align*}
H_2O + CO_3^{(aq)} & \rightleftharpoons H_2CO_3 \\
H_2CO_3 + \text{R-NH}_2 & \leftrightarrow HCO_3^- + \text{R-NH}_3^+
\end{align*}

It is important to note that it is a 1:1 interaction between CO\textsubscript{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\textsubscript{2}/carbonates. Carbamate formation is formally a simple reaction:

\begin{align*}
\text{RNH}_2 + \text{CO}_2 & \rightleftharpoons \text{RNHCOO}^- + H^+
\end{align*}

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

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

The unfavorable CO\textsubscript{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\textsubscript{2} and R-NH\textsubscript{3}\textsuperscript{+}) must react with one molecule of the CO\textsubscript{2}/carbonate family (CO\textsubscript{2}(aq), H\textsubscript{2}CO\textsubscript{3}, HCO\textsubscript{3}\textsuperscript{−}, and CO\textsubscript{3}\textsuperscript{2−}). The reaction is essentially a Lewis acid-base reaction where the amine is the Lewis base and the CO\textsubscript{2} species (CO\textsubscript{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\textsubscript{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*}
\text{RNH}_2 + H_2CO_3 & \rightleftharpoons \text{RNHCOOH} + H_2O \\
\text{RNH}_2 + HCO_3^- & \rightleftharpoons \text{RNHCOO}^- + H_2O \\
\text{RNH}_2 + CO_2(aq) & \rightleftharpoons \text{RNHCOOH}
\end{align*}
Also, the protonation equilibrium of the carbamic acid needs to be included:

\[ \text{RNHCOO}^- + \text{H}^+ \rightleftharpoons \text{RNHCOOH} \]  

An overall reaction scheme which contains all relevant processes is best represented graphically (recall we use \( \rightleftharpoons \) for protonation equilibria and \( \longrightarrow \) 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.\(^5\)\(^-\)\(^10\) 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 carbamate 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.\textsuperscript{14}

(d) For fast reactions, the only option is stopped-flow with UV-Vis absorption measurement or conductometry\textsuperscript{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.\textsuperscript{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

\textsuperscript{1}H-NMR data were acquired for two types of experiments: \textsuperscript{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\textsubscript{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: Typical \textsuperscript{1}H-NMR spectrum. The multiplet at 2.8ppm arises from the N-CH\textsubscript{2} group of MEA, at 3.1ppm from the N-CH\textsubscript{2} of the carbamate, at 3.5ppm from the O-CH\textsubscript{2} group of the carbamate and at 3.6ppm from the O-CH\textsubscript{2} group of the amine.](image-url)
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 CO$_2$ could not be observed in our data sets as the concentration of CO$_2$(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.,$^{19}$ No information is given about the reverse reaction.

Table 1 contains all relevant published rate and equilibrium constants, the table includes the reactions of CO$_2$(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 1: Published rate and equilibrium constants for the reactions of CO$_2$ in water and relevant constants for the protonation of MEA and the ionic product of water.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetics</th>
<th>equilibrium</th>
<th>References</th>
</tr>
</thead>
</table>
| CO$_2$(aq) + H$_2$O $\rightleftharpoons$ H$_2$CO$_3$ | $k_1 = 3.7 \times 10^7$ s$^{-1}$  
$k_2 = 18$ s$^{-1}$  
$k_1 = 18$ s$^{-1}$  
$k_2 = 2.4 \times 10^4$ s$^{-1}$  
$k_3 = 8.5 \times 10^4$ M$^{-1}$s$^{-1}$  
$k_4 = 8.5 \times 10^4$ M$^{-1}$s$^{-1}$ | $K_1 = 2.06 \times 10^4$  
log $K_1 = 2.69$  
$K_2 = 3.57 \times 10^3$  
log $K_2 = 3.57$ | Pocker et al.$^2$

| CO$_2$(aq) + OH$^-$ $\rightleftharpoons$ HCO$_3^-$ | $K_5 = 1.0 \times 10^{-14}$  
$log K_5 = 14.00$ | Stumm and Morgan$^{23}$

| CO$_3^{2-}$ + H$^+$ $\rightleftharpoons$ HCO$_3^-$ | $K_6 = 1.0 \times 10^{-14}$  
$log K_6 = 14.00$ | Stumm and Morgan$^{23}$

The rate constant for the reaction of CO$_2$ with H$_2$O is defined as the pseudo-first order rate constant

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$_2$CO$_3$ and dissolved CO$_2$ 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>
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<tbody>
<tr>
<td></td>
<td>via kinetics</td>
<td>via titrations</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3 + \text{RNH}<em>2 \xrightleftharpoons[k</em>{-2}]^{k_2} \text{RNHCOOH} + \text{H}_2\text{O}$</td>
<td>$k_2 = 1.02(5) \times 10^3 \text{M}^{-1}\text{s}^{-1}$</td>
<td>log $K_7 = 5.12(4)$</td>
</tr>
<tr>
<td></td>
<td>$k_{-2} = 7.8(5) \times 10^3 \text{s}^{-1}$</td>
<td></td>
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<tr>
<td>$\text{HCO}_3^- + \text{RNH}<em>2 \xrightleftharpoons[k</em>{-3}]^{k_3} \text{RNHCOO}^- + \text{H}_2\text{O}$</td>
<td>$k_3 = 3.8(6) \times 10^{-4} \text{M}^{-1}\text{s}^{-1}$</td>
<td>log $K_8 = 1.28(7)$</td>
</tr>
<tr>
<td></td>
<td>$k_{-3} = 2.0(4) \times 10^{-5} \text{s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\text{RNHCOO}^- + \text{H}^+ \xrightleftharpoons[k_9]{k_9} \text{RNHCOOH}$</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 $\text{CO}_2$/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 $\text{CO}_2$ 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 $\text{CO}_2$.

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