Original Research Article

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Interrogating the chemical mechanism for carbon dioxide (CO_2) reactivity in aqueous tertiary amine solutions: Can a simple parallel hydration reaction mechanism work?

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Abstract: In this study, the kinetics of CO_2 absorption into tertiary amine methyldiethanolamine (MDEA) was studied intensively using both experimental and theoretical approaches. The experimental work measured the kinetics of $CO_{2(aq)}$ react with MDEA over a range of concentrations including dilute (0.5–10.0 mM) and concentrated (0.5–2.5 M) solutions via stopped-flow spectrophotometric at 25.0°C. The resulting kinetic data has been theoretically evaluated using three chemical reaction mechanism variants including the complete base catalysis mechanism, the simplified base catalysis mechanism, and the parallel CO_2 hydration mechanism. Results showed that the simplified base catalysis mechanism in the absence of the kinetic pathways for CO_2 via hydroxide and water is insufficient to predict the measured kinetic data while the complete base catalysis mechanism and parallel hydration mechanisms can accurately predict the kinetics of CO_2 absorption into MDEA solutions. In particular, the experimental data of reversibility of the hydration reactions at low pH was in poor agreement with the simplified model predicted results. Given the simplicity of the parallel hydration mechanism with no requirement for determination of rate constants of the base catalysis reaction unlike the complete base catalysis mechanism, the parallel hydration mechanism can be considered the simplest and preferred mechanism describing the reaction between tertiary amine MDEA and CO_2. © 2022 Society of Chemical Industry and John Wiley & Sons, Ltd.

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Keywords: tertiary amine; base catalysis; parallel hydration; CO_2 capture

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Introduction

Global warming is becoming a critical issue in 21st century therefore ways to exploring alternative clean energy and reducing greenhouse gases emissions are emerging in recent years.[1–3] Cyclic chemical absorption/regeneration process is the most mature and widely utilized treatment and separation technology for the removal of carbon dioxide (CO_2) from industrial exhaust gas streams for the purpose of reducing greenhouse gas emission.[4–7] The alkanolamine solutions are used frequently for the chemical absorption-based CO_2 capture process in fossil-fuel-fired power industry.[8–12] The large amount of energy required to regenerate the solvent is one of the key characteristics that hindered the wide application of the amine-based CO_2 capture system.[13]

Industrially important amines are normally divided into three main catalogues, primary, secondary, and tertiary amines. Compared with primary/secondary amines, the reactivity of tertiary amines is typically several magnitude lower since they cannot react with CO_2 directly due to the lack of α-H atom.[14–16] But on the other hand, tertiary amines have gained increasing attention this year as promising candidates for CO_2 absorption because of the noticeable less energy requirement for solvent regeneration.[17,18] In addition, blending a small portion of rate promoting amine into conventional tertiary amine solutions can increase the rate of absorption of CO_2 to a large extent with minimum effect on the solvent regeneration characteristics.[6,19] Therefore, a comprehensive understanding of the reaction mechanism between CO_2 and tertiary amines is of great importance for the development of cost-effective sole tertiary and tertiary amine blended amine solvents.

Over the last few decades, plenty of research effort have been carried out to reveal the reaction mechanism of CO_2 absorption into aqueous tertiary amine solutions. N-methyldiethanolamine (MDEA), due to its low solvent regeneration energy, low degradation and corrosion rate, has been considered as one of the most promising tertiary amine candidates for CO_2 capture. Therefore, in this study, MDEA was chosen as the example tertiary amine to validate the kinetics reaction mechanism for CO_2 absorption. A number of different chemical mechanisms have been suggested for describing the CO_2 reaction mechanism in MDEA solutions. The most commonly discussed mechanism, the complete base catalysis mechanism, was initially developed by Donaldson and Nguyen (1980).[20] It was suggested that three molecules including amine, water, and CO_2 are involved in an overall reaction where a complex formed from tertiary amine and water first. The formed complex then acted as a "catalyst" to facilitate the hydration of CO_2 to form bicarbonate.[16,21–23] Bicarbonate can also form from the direct reaction of CO_2 with water, and hydroxide ions, depending on the pH of the solution. Hydroxide ions are initially present in tertiary amines solutions due to the protonation of water in the presence of the tertiary amine bases. Overall, a complete base-catalysis mechanism is formulated by combining the reversible CO_2 absorption pathways via reaction with water and hydroxide in Eqns (1) and (2), based-catalyzed CO_2 hydration reaction in Eqn (3), and all involved instantaneous equilibria of protonation of carbonate and bicarbonate in Eqns (4) and (5), protonation of water in Eqn (6), protonation of the amine in Eqn (7).

$$CO_{2(aq)} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2CO_3 \tag{1}$$

$$CO_{2(aq)} + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2CO_3 \tag{2}$$

$$CO_{2(aq)} + H_2O + R_3N \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HCO_3^- + R_3NH^+ \tag{3}$$

$$CO_3^{2-} + H^+ \overset{K_4}{\longleftrightarrow} HCO_3^- \tag{4}$$

$$HCO_3^- + H^+ \overset{K_5}{\longleftrightarrow} H_2CO_3 \tag{5}$$

$$OH^- + H^+ \overset{K_6}{\longleftrightarrow} H_2O \tag{6}$$

$$R_3N = H^+ \overset{K_7}{\longleftrightarrow} R_3NH^+ \tag{7}$$

However, in some publications, simplified base catalysis mechanism is applied for the data interoperation in which the reaction between H_2O and OH^- with CO_2 are considered negligible.[15,23–29] Another simple mechanism describing the reactions during CO_2 absorption into aqueous tertiary amine solutions is the parallel hydration mechanism where the base-catalyzed water hydration (Eqn (3)) was eliminated from the complete base catalysis mechanism.[30] In this mechanism, the tertiary amine

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acts only as a base to absorb protons (either to buffer pH or generate OH^-) during the reaction of CO_2 with water and OH^-. The main difference between parallel reaction mechanism with the above-mentioned reaction mechanisms is that the application of the parallel mechanism does not require the determination of kinetic constants for each tertiary amine while the protonation constant is the only parameter needed to complete the reaction mechanism.

However, application of the simple parallel mechanism has not been thoroughly evaluated alongside the complete/simplified base catalysis mechanism in a single consistent study over a wide range of concentrations using rapid stopped-flow kinetics. Stopped-flow spectrophotometer offers a way to measure the fundamental reaction kinetics between dissolved CO_2 and MDEA solutions which eliminates the mass transfer during the conventional kinetics measurements of CO_2 absorption into aqueous amine solutions. Therefore, this work focuses on the investigation of the kinetic interaction of CO_2 with MDEA solutions via stopped-flow spectrophotometric measurements at 25.0°C. The effect of amine concentration from 0.001–2.5 M, and CO_2(aq) concentrations from 0.002–0.0089 M, has been investigated and the resulting kinetic data were evaluated using the three different reaction mechanisms. Potential catalytic effects of the amine on the reversible pathways via decomposition of carbonic acid at low pH has also been investigated experimentally. Analysis of the measurement data using each of the mechanism variants is compared and discussed herein.

Experimental

Chemicals

N,N-dimethyletehylenediamine (99%, Sigma-Aldrich), potassium bicarbonate (>99%, Sigma-Aldrich), hydrochloric acid (Sigma Aldrich), thymol blue sodium salt (Sigma-Aldrich), Alizarin Red S sodium salt (BDH), methyl orange sodium salt (SELBY), and alizarin yellow GG (50% dye content, Sigma Aldrich) were all used as obtained without further purification. High-purity CO_2 gas (BOC) and N_2 gas (Coregas) were used to prepare aqueous CO_2 solutions. Ultra-high-purity Milli-Q water was boiled to remove dissolved CO_2 and was used to prepare all solutions for the stopped-flow measurements.

Stopped-flow measurements

Kinetic measurements were performed using an applied photophysics SX-20 stopped-flow spectrophotometer equipped with a J&M TIDAS 3-dioide array detector. Absorbance of the solutions, corresponding to changes in pH in the presence of colored acid-base indicators, was monitored over the wavelength range from 400–700 nm. The temperature of the stopped-flow was monitored via a thermocouple located within the cell block and the solution temperatures were maintained at 25.0°C using a circulating Julabo F20 waterbath.

The reaction of CO_2 with MDEA was investigated by mixing equimolar solutions of the amines with aqueous CO_2 solutions in the stopped-flow technique. Initially CO_2 solutions were prepared by bubbling CO_2 into a temperature-controlled syringe reservoir containing milli-Q water and the desired CO_2 concentration provided by adjusting the ratio between Bronkhorst mass flow controllers for CO_2 and N_2. Published saturation constants were used to determine the initial [CO_2(aq)] in the solutions. A series of amine concentrations was investigated here. The reported solution concentrations expressed herein represent the concentrations after mixing in the stopped flow (i.e., initial concentrations are halved when mixed with CO_2 in the stopped-flow).

The series of solutions investigated in this work are outlined in Table 1. The concentration of amine in series 1 and 2 was varied over the reported range while maintaining the concentration of $CO_{2(aq)}$ in syringe 2, respectively. Additionally, the reversibility of the hydration reactions was investigated in series 3 by following the decomposition of carbonic acid at low pH. To do so, a range of pH conditions was investigated by varying the concentration of HCl in syringe 2 while maintaining a fixed $KHCO_3$ concentration in syringe 1. Due to the large changes in pH during the reactions in series 1 and in the decomposition reactions in series 3, a combination of indicators was used to monitor the kinetics. All indicator concentrations were fixed at the reported concentrations for each of the solutions investigated.

Kinetic mechanism variants: Simplified and complete base catalysis versus parallel hydration

A number of mechanism variants were evaluated here and each of the mechanisms are described below.

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Table 1. Solution concentrations for the stopped-flow kinetics measurements.

Measurement	Syringe 1	Syringe 2
Series 1 - Low concentration	[Amine] 0.5–10.0 mM [Thymol blue] 0.0000125 mM [Bromothymol blue] 0.0000125 M	[CO_2(aq)] 2.45 mM
Series 2 -High concentration	[Amine] 0.5–2.5 M [Alizarin yellow R] 0.0000375 mM	[CO_2(aq)] 8.9 mM
Series 3 - Reversibility of the hydration reactions	[Amine] 0.025M [$KHCO_3$] 0.05 M	[HCl] 45–55 mM [Alizarin Red S] 0.00005 [methyl orange] 0.000025

Initially the simplest mechanism variant, termed the parallel hydration mechanism, which excludes any base catalysis reactions, was evaluated. The mechanism includes only the system of CO_2 hydration reactions, Eqns (1), (2) and (4)–(6), and the protonation of amine, Eqn (7). Second, the "simplified base catalysis" mechanism was evaluated whereby the kinetic pathways for CO_2 reacting with water and hydroxide in Eqns (1) and (2) are excluded and only the base catalysis pathway for CO_2 in Eqn (3), all instantaneous equlibria, Eqns (4) to (6), and protonation of the amine, Eqn (7), remain. Third, the water and hydroxide pathways were reintroduced to the simplified base catalysis mechanism and termed as the complete base catalysis mechanism herein (Eqns (1)–(7)). For the three different mechanisms, all the reactions between CO_2 and water system including reactions of Eqns (1), (2) and (4–(6) are treated equally, in which the same rate constants and equilibrium constants are used for the development of models. Same values for the pKa of 8.65 for MDEA were used for the three reaction mechanisms.

Data analysis

Kinetic absorbance data was evaluated using Reactlab kinetics (www.jplusconsulting.com) and in house extensions of the software written in MATLAB to incorporate ionic strength corrections. Species charges and activity coefficients can influence the kinetic constants. Hence, in favor of concentrations, the Debye-Hückel equation was used for the estimation of the activity coefficients of all ionic species, as shown in Eqn (8).

$$\log \gamma_x = \frac{-Az_x^2\sqrt{\mu}}{1+\sqrt{\mu}}\,. \tag{8}$$

In this Eqn, γ_x is the activity coefficient of the species x, z_x is the charge of the species x and μ is the ionic strength of the solution. The parameter A is taken from Manov *et al.*[31]

Results and discussion

Despite the large number of reported kinetic studies to quantify the bulk kinetics of CO_2 absorption into aqueous MDEA solutions, there is still no agreement on the chemical mechanism. Discrepancies can be found between various publications for which available reaction rate data for k_3 in Eqn (3), for MDEA, has been collected and presented in Table S1. Among the studies, varying concentrations, techniques, sample quality, and mechanisms are purported as explanations for the discrepancies. As can be found in Table S1, the literature published reaction rate constant for the base catalyzed CO_2 hydration in Eqn (3), k_3, are all over the place for MDEA solutions ranging from 2.35 to 15.0 $M^{-1}\cdot s^{-1}$.

Series 1: Low MDEA concentrations

The effect of varying k_3 values on predicted kinetic absorbance traces for reaction kinetics of CO_2 reacting with low MDEA concentration is studied herein. Three k_3 values covering the lowest (2.35 $M^{-1}\cdot s^{-1}$)[22], highest (15 $M^{-1}\cdot s^{-1}$)[27], and intermediate (7.8 $M^{-1}\cdot s^{-1}$) ranges were selected and employed in the calculations. The simplified and complete base catalysis mechanism predicted together with the experimental absorbance traces of the small amount of acid-base indicator representing the reaction kinetics between 2.45 mM $CO_{2(aq)}$ and 2 mM MDEA are shown in Fig. 1(A) and (B).

First, from the data in Fig. 1(A) and (B) the kinetic traces can be broken down into two regions:

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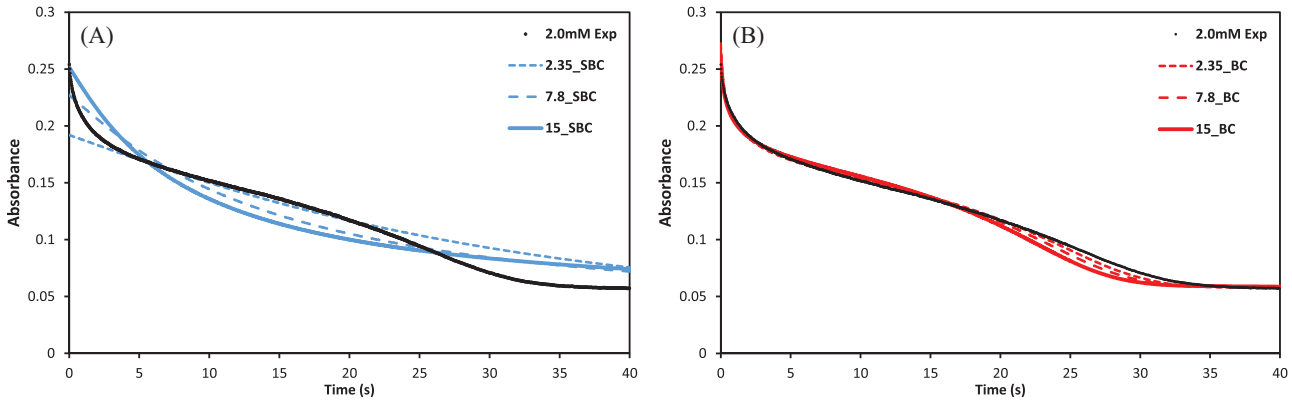

Figure 1. Effect of varying k_3 values for Eqn (3) on the predicted kinetic traces for measurements of 2.45 mM $CO_{2(aq)}$ reacting with low MDEA concentration at 2 mM at 590 nm using the simplified (A) and complete base catalysis (B) mechanisms. Solid points (•) represent measured absorbance data; solid (–) and dashed lines (- - -, - -) represent calculated absorbance traces with different k_3 values.

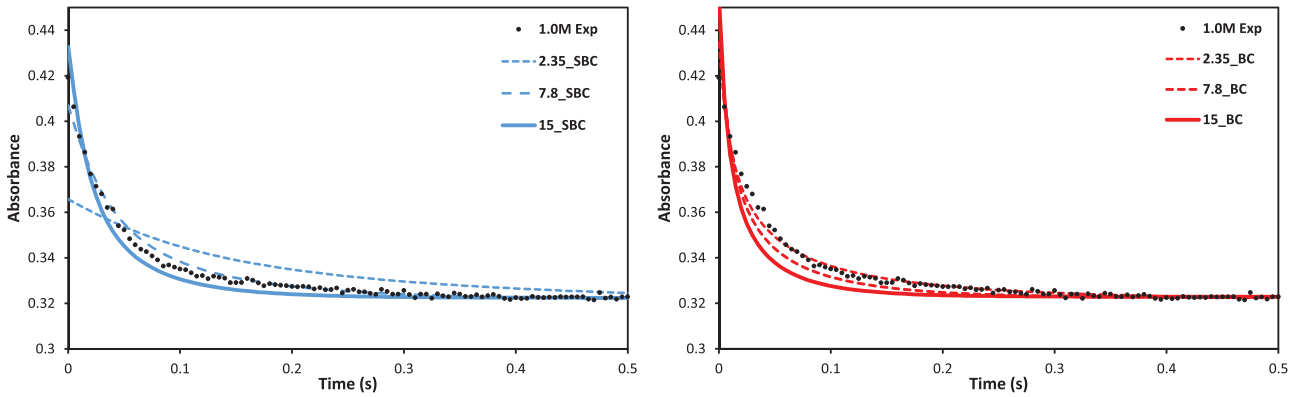

Figure 2. Effect of varying k_3 values for Eqn (3) on the predicted kinetic traces for measurements of 2.45 mM $CO_{2(aq)}$ reacting with 1.0 M MDEA at 590 nm using the simplified (A) and complete (B) base catalysis mechanisms. Solid points (•) represent measured absorbance data; solid (–) and dashed lines (- - -, - -) represent calculated absorbance traces.

0.0 – 5.0 secs representing the rapid kinetic region resulting from $CO_{2(aq)}$ involved reaction, 5.0–40.0 s representing slow kinetics region. As can be seen from Fig. 1(A), the simplified base catalysis mechanism results in poor agreement with the measured kinetic data. The underlying shape of the fast initial kinetic region from 0.0–5.0 s is loosely represented by the largest rate constant, $k_7 = 15.0\ M^{-1}{\cdot}s^{-1}$, while the lowest and intermediate values result in significant under predictions of the kinetics in this region. The possible explanation is that the CO_2 absorption through reacting with OH^-/H_2O are unneglectable under the reaction conditions of low MDEA concentrations.

Conversely, from Fig. 1(B), all predicted kinetic traces result in the general underlying shape of the measured kinetic trace with the lowest k value, 2.35 $M^{-1}{\cdot}s^{-1}$, resulting in the overall best agreement during all regions of the measurement. Both the intermediate and higher k values result in overprediction of the slow kinetic region > 20.0 s but result in the correct final equilibrium position for the measurement. This, again, suggests that under the experimental conditions with low MDEA concentration, the reactions between CO_2 and OH^-/H_2O are unneglectable.

Series 2: High MDEA concentrations

The model predicted and experimental kinetic traces illustrating an typical kinetics measurements of 2.45 mM $CO_{2(aq)}$ react with high MDEA concentration of 1.0 M are shown in Fig. 2(A) and (B). Again, the k_3 values of Eqn (3) varies between 2.35 and 15 $M^{-1}{\cdot}s^{-1}$in both simplified and complete base catalysis mechanism.

Decent agreement is observed from Fig. 2(A) and (B) using both the simplified and complete base catalysis

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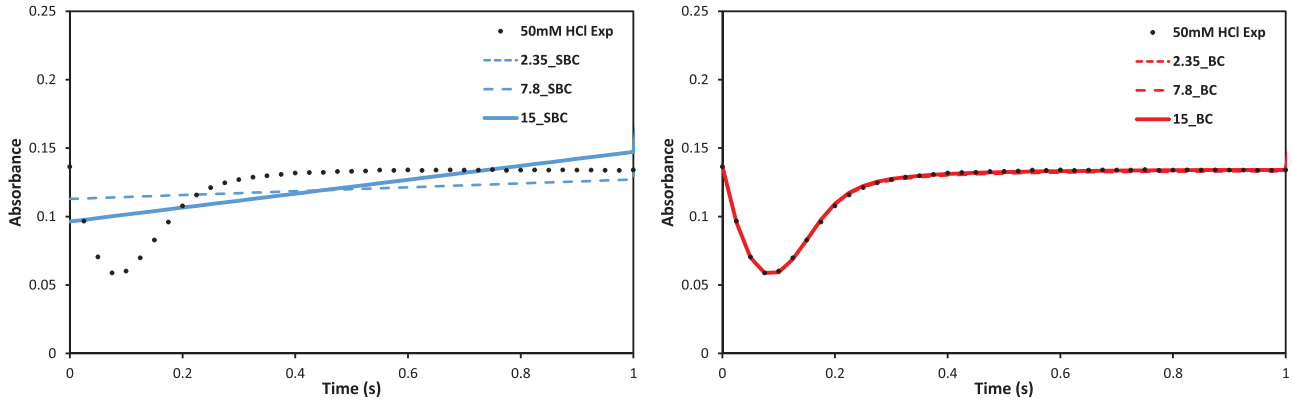

Figure 3. Effect of varying k_3 values for Eqn (3) on the predicted kinetic traces for reverse CO_2 hydration reaction at low pH with MDEA concentration of 25 mM, $KHCO_3$ concentration of 50 mM and HCl concentration of 50 mM at 590 nm using the simplified (A) and complete (B) base catalysis mechanisms. Solid points (●) represent measured absorbance data; solid (–) and dashed lines (- - -, - -) represent calculated absorbance traces.

mechanism upon using a range of k values from 2.35 to 15 $M^{-1}\cdot s^{-1}$, with the exception of the lowest value, 2.35 $M^{-1}\cdot s^{-1}$, for the simplified base catalysis mechanism. It should be noted that the trend in the initial rapid kinetic region shifts slightly from underpredicting to overpredicting using the simplified base catalysis mechanism with k values vary from 7.8 to 15.0 $M^{-1}\cdot s^{-1}$. Increasing the k value beyond the upper range (>15.0) would likely result in a continuation of the trend further toward overprediction of the kinetics in this region. Similarly, the lowest value 2.35 $M^{-1}\cdot s^{-1}$ resulted in the highest agreement overall using the complete base catalysis mechanism while the larger values resulted in a slight, but distinct, overprediction of the kinetics.

Series 3: Reversibility of the hydration reactions at low pH

The model predicted and experimental kinetic traces illustrating a typical kinetics measurements of reverse CO_2 hydration reaction at low pH with MDEA concentration of 25 mM, $KHCO_3$ concentration of 50 mM and HCl concentration of 50 mM are shown in Fig. 3(A) and (B).

From the data in Fig. 3(A), the simplified base catalysis mechanism was unable to predict the measured kinetic traces due to the absence of the reversible hydration pathways for CO_2, k_{-1} and k_{-2} in Eqns (1) and (2), from the mechanism. However, the complete base catalysis mechanism resulted in superior agreement with the measured data with the calculated traces overlapping the measured data perfectly.

By taking into account both simplified and complete base catalysis mechanisms in Figs. 1–3, a k value of 7.8 $M^{-1}\cdot s^{-1}$ for Eqn (3) gives an overall highest agreement with the measured datasets. Therefore, an overall k value of 7.80 $M^{-1}\cdot s^{-1}$ from Benitez-Garcia *et al.*,[14] representing an approximately median value from the range of published values for MDEA, was selected and applied during the analysis of the kinetic data herein for detailed comparison of the mechanisms across all measured data sets.

Comparison of simplified and complete base catalysis with parallel hydration mechanisms

Absorbance data at 590 nm together with corresponding predicted traces for MDEA are shown in Fig. 4. The Figs. 4(A)–(C) represent measured and predicted kinetic traces from series 1 using the parallel hydration mechanism, simplified base catalysis mechanism, and complete base catalysis mechanisms, respectively. Similarly Figs. 4(D)–(F) and (G)–(I) represent the absorbance data and predicted traces for measurement series 2 and 3, respectively.

We see from Figs. 4(A)–(C), that agreement between the measured and predicted kinetic traces using the simple parallel hydration and complete base catalysis mechanism are excellent and comparable. Similar to the data in Fig. 1(A), agreement between the measured and predicted kinetic traces is noticeably poor across all measurements in series 1 using the simplified base catalysis mechanism in the absence of direct pathways for CO_2 hydration with water and hydroxide. The

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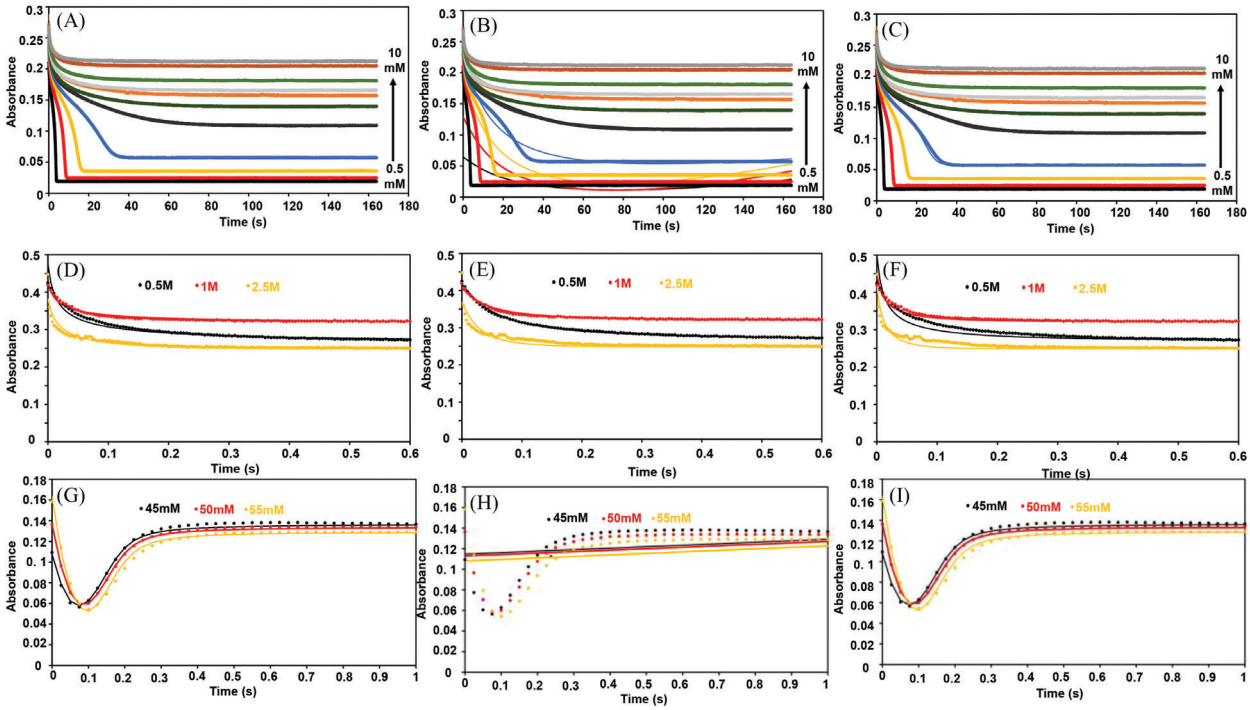

Figure 4. Absorbance traces at 590 nm together with predicted traces using the parallel hydration mechanism, simplified base catalysis mechanism, and complete base catalysis mechanism. All data corresponds to 25.0°C.

discrepancies likely extend from the pH of the solutions and small amounts of hydroxide present in the solutions from the protonation of water by MDEA. The latter hydroxide pathway has a significantly faster rate constant (1.1×10^4 $M^{-1}{\cdot}s^{-1}$ at 25.0°C) compared to the base catalysis pathway (7.8 $M^{-1}{\cdot}s^{-1}$). It is interesting to note the strange kinetic behavior predicted by the simplified base catalysis mechanism at low MDEA concentrations and long reactions times. This effect extends from the large changes in pH during the reactions due to excess CO_2(aq) and the inability of the simplified base catalysis chemical model to adequately accommodate such changes.

Conversely, from the data in Figs. 4(D)–(F), agreement between the measured and predicted kinetic traces is noticeably improved for measurement series 2 using the simplified base catalysis mechanism and is similar to the excellent agreement observed for the parallel hydration and complete base catalysis mechanisms. This is due to the relative contribution of the hydroxide and hydration reaction pathways for CO_2 at the high MDEA concentrations here which are some 250 times higher than in measurement series 1. In this case, the kinetics are influenced by the base catalysts hydration pathway driven by the concentration of MDEA, despite the 1000 times slower rate constant for the base catalysis pathway (compared to the direct hydroxide pathway). On the other hand, similar agreement is still observed between the measured and predicted kinetic traces using both the parallel hydration and complete base catalysis pathways.

Finally, the reversibility of the hydration reactions at low pH is accurately predicted using the parallel hydration and complete base catalysis. The simplified base catalysis mechanism is the clear exception again due to the absence of direct reversible pathways for CO_2 via the water pathway at low pH. The superior and similar agreement between the measured and predicted kinetic traces using the parallel hydration and complete base catalysis can be attributed to the direct dehydration pathway as opposed to any contribution from the inclusion of the base catalysis reaction in the latter mechanism variant.

Validity of the base catalysis pathway and implications for analysis of amine solutions

While the simplified base catalysis pathway can satisfactorily predict the kinetic behavior of CO_2 in high concentration tertiary amine solutions >0.5 M,

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this mechanism cannot be applied directly to low concentration measurement conditions without OH^-/H_2O pathways for absorption of CO_2. It is also clear from the data here that the base catalysis pathway, when expressed as an irreversible reaction, is not capable of predicting the reverse of the hydration reactions at low pH conditions without reversible kinetic pathways for CO_2 via water and hydroxide. While the complete base catalysis mechanism is capable of predicting all kinetic data here across all measurement series, this is largely due to the foundation of the mechanism which is made up of the parallel hydration reactions. No clear improvement in the agreement between the measured and predicted kinetic traces was observed over the parallel hydration mechanism alone which is a strong indication that the base catalysis effect observed and quantified in previous reports is in fact a pH effect induced by the amine as opposed to a catalytic activation of water as often stated. From the data here, the same kinetic insight can be obtained using the parallel hydration mechanism which does not require independent determination of rate constants for the base catalysis pathway, only requiring known values for the CO_2 hydration reactions and protonation constant of the amine.

Conclusions

The kinetic reactivity of CO_2 in two tertiary amine solutions of MDEA has been investigated in this work via stopped-flow spectrophotometric kinetic measurements at 25.0°C. Three different mechanism variants have been evaluated including the base catalysis pathway for CO_2 in the absence and presence of parallel reactions via water and hydroxide. From the data here the simplified base catalysis mechanism is inadequate for prediction of CO_2 reactivity at low tertiary amine concentrations and during the reverse of the hydration reactions at low pH. The complete base catalysis mechanism and parallel hydration mechanisms are able to accurately predict the kinetic behavior of CO_2 absorption into MDEA solutions under all conditions. However, the results here indicate the parallel hydration mechanism is the simplest and most robust mechanism. With the application of the parallel hydration mechanism, the reaction mechanism of tertiary amine systems and mixed tertiary and primary/secondary systems can be easily simulated and therefore accelerate the further application of the mixed amine solvents for CO_2 capture.

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