

Reaction Mechanism and Kinetics of Aqueous Solutions of Primary and Secondary Alkanolamines and Carbon Dioxide

Olgac BAVBEK, Erdoğan ALPER

*Chemical Engineering Department, Hacettepe University,
06532, Beytepe, Ankara-TURKEY*

Received 29.01.1999

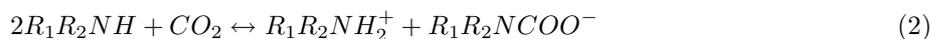
The mechanism and kinetics of the reaction between aqueous solutions of CO₂ and the alkanolamines 1-amino-2-propanol, 3-amino-1-propanol, 2-methyl aminoethanol and 2-ethyl aminoethanol were investigated using a stopped flow technique. It was found that the reaction orders according to power law kinetics were between 1.1 and 2.0, depending on the alkanolamine and the concentration ranges investigated. This fractional order was therefore considered to be further evidence that carbamate formation takes place according to a zwitterion mechanism rather than a one-step reaction. The kinetic rate parameters for these alkanolamines were evaluated from experimental data at 303 K according to this mechanism.

Introduction

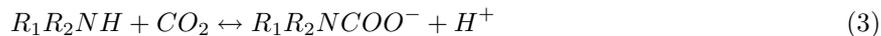
Aqueous solutions of amines are often used to remove CO₂ and H₂S from a large number of industrial gas streams. There are several different processes, each suiting a certain application¹. Aqueous solutions of alkanolamines, such as monoethanolamine and diglycolamine (primary amines) and diethanolamine and diisopropanolamine (secondary amines) are often used in industrial operations^{1,2}. It is an established fact that the basicity is provided by the amino site while the -OH group results in increased solubility in water for these alkanolamines. All of these amines - as well as the tertiary amines - react with H₂S instantaneously since it is a proton donor Bronsted acid:



On the other hand, only primary and secondary amines can form carbamate by reacting with CO₂, which is an electron acceptor Lewis acid. Here, CO₂ replaces a proton from the amino site:



This reaction has a finite rate and it is universally accepted that it is first order in carbon dioxide. In the past it was assumed that the reaction was also first order in amine as it was considered a one-step carbamate formation:



H^+ reacts with another amine instantaneously to correspond stoichiometrically to the overall reaction of Eqn.(2). The gas absorption with chemical reaction data with industrial primary amines, such as monoethanolamine and diglycolamine, fitted this reaction mechanism satisfactorily³. Although the data for diethanolamine was ambiguous (some of which could be attributed to the uncertainties of gas absorption experiments requiring solubility and diffusivity data in the reacting systems which cannot be measured directly), indicating that it may be first or second order, this mechanism was still used until recently for all the amines⁴. Recent studies which have been reviewed by Versteeg et al.⁵ clearly indicate that, depending on the concentration range, the reaction order may change from one to two. This behaviour can be modeled with a zwitterion intermediate or a two-step carbamate formation reaction. The aim of this paper is to study the reaction kinetics of certain primary (namely, 1-amino-2-propanol and 3-amino-1-propanol) and secondary (namely, 2-methyl aminoethanol and 2-ethyl aminoethanol) alkanolamines using a stopped flow technique, suitable for rapid reactions. This direct technique (that is, stopped flow experiments) does not involve gas absorption, so the findings correspond to the intrinsic homogeneous reaction rate between aqueous solutions of CO_2 and aqueous amines.

Reaction Kinetics

Following the mechanism proposed by Danckwerts⁴ and as a result of considerable further evidence (for instance, Blauwhoff et al⁶, Versteeg and van Swaaij⁷, Xu et al⁸., Crooks and Donnelean⁹, Bouhamra et al¹⁰, the general consensus for the reaction of CO_2 with primary and secondary alkanolamines is the formation of zwitterion intermediate, rather than one-step carbamate formation.



where B is any base, which can be amine, water or OH^{-1} in an aqueous solution. The reaction rate is then given by:

$$r = k_2[R_1R_2NH][CO_2] - k_1[R_1R_2NH^+COO^-] \quad (6)$$

The concentration of zwitterion is given by:

$$\frac{d[R_1R_2NH^+COO^-]}{dt} = k_2[R_1R_2NH][CO_2] - (k_1 + \sum k_B[B])[R_1R_2NH^+COO^-] \quad (7)$$

If we assume a quasi-steady state concentration of zwitterion, this can be obtained from Eqn.(7). Then, using this zwitterion concentration, eqn.(6) becomes:

$$r = \frac{[CO_2][Am]}{1/k_2 + (k_1/k_2)/\sum k_B B} \quad (8)$$

Since the amine concentration was low in all experiments, the concentration of water can be considered constant, leading to a constant value for $k_w [H_2O]$. The concentration of OH^- ion was also very low. Thus,

its contribution to zwitterion dissociation was negligible, as supported also by the work of Versteeg and Oyevaar¹¹, Bosch et al.¹², and Xu et al.⁸. This leads to the equation:

$$k_{obs} = \frac{[Am]}{\frac{1}{k_2} + \frac{k_1/k_2}{k_{Am} + k_w[H_2O]}} \quad (9)$$

Thus, depending on the values of rate constants and the concentration range of amine, the order in amine can vary between 1 and 2.

Experimental

The experimental set-up consisted of a standard stopped flow instrument (Hi-Tech Scientific Ltd., UK, Model SF-51) with a conductivity-detection system which could be used to measure directly the intrinsic rate of a rapid homogeneous reaction (in this case, that between aqueous solutions of CO₂ and an alkanolamine). All parts of the flow circuit were thermostatted and the temperature control was within ± 0.1 K. The product formation was monitored by fast conductimetry, details of which can be found in the literature (Alper^{3,13-15}).

Reagent grade alkanolamines were used without further purification. The concentration of amine was always much in excess of that of CO₂ (usually the molar ratio was about 20 to 1) and ranged from 0.02 to 0.05 kmol m⁻³. Therefore, the reaction followed pseudo-first order kinetics in CO₂.

Experimental results

Carbamate concentration as a function of time gave very satisfactory pseudo-first order plots according to Eqn. (8). Since the reaction between OH⁻ and CO₂ was not detected by the conductivity measurements, the fitted rate constant corresponded directly to k_{obs} in Eqn. (9). Table 1 shows the observed pseudo-first order rate constant for the primary amines 1-amino-2-propanol and 3-amino-1-propanol at 303 K. In Figure 1, the observed rate constant k_{obs} is shown as a function of concentration at 303 K for 1-amino-2-propanol and 3-amino-1-propanol. The data in Figure 1 yielded exponents of 1.11 and 1.49 for 1-amino-2-propanol and 3-amino-1-propanol respectively, according to empirical power law kinetics.

Table 1. Observed pseudo-first order rate constant for primary amines 1-amino-2-propanol and 3-amino-1-propanol at 303 K

Amine concn. kmol/m ³	k_{obs} , s ⁻¹ (1-amino-2-propanol)	k_{obs} , s ⁻¹ (3-amino-1-propanol)
0.0250	81.2	94.2
0.0275	-	113.3
0.0300	99.5	-
0.0350	121.7	178.1
0.0400	146.7	202.3
0.0425	-	234.0
0.0450	151.1	-
0.0500	175.7	254.6

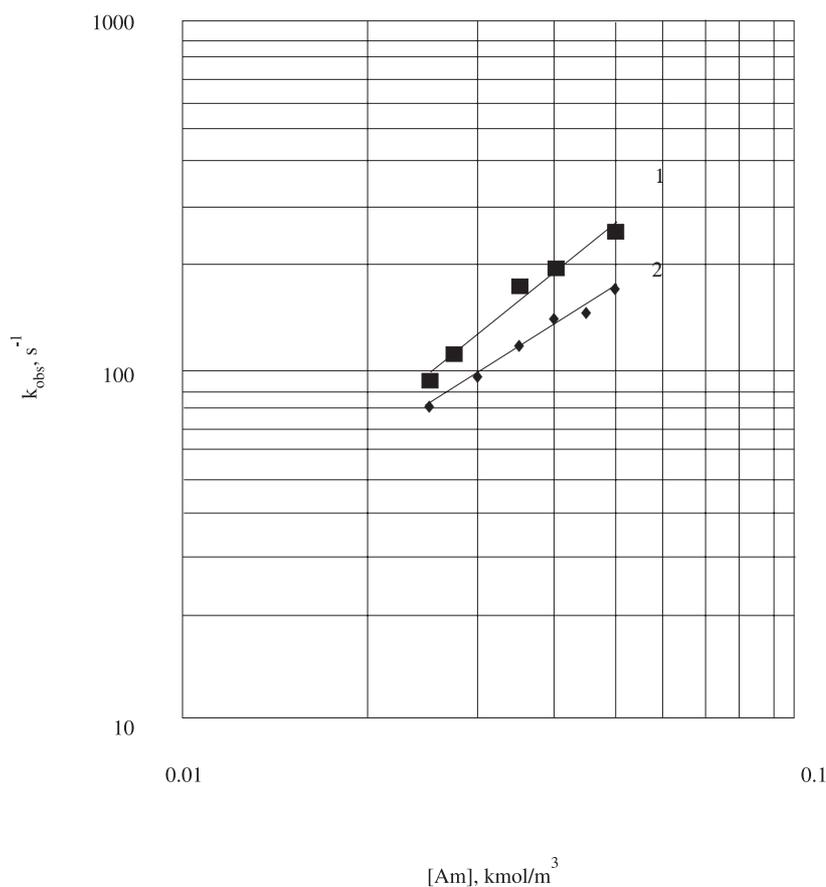


Figure 1. Observed pseudo-first order rate constants as function of primary amine concentration at 303 K. (Line 1:3-amino-1-propanol; Line 2: 1-amino-2-propanol).

Table 2 shows the observed pseudo-first order rate constant for the secondary amines 2-methyl aminoethanol and 2-ethyl aminoethanol at 303 K. Figure 2 shows the observed rate constant k_{obs} as a function of concentration at 303 K for the secondary alkanolamines 2-methylaminoethanol and 2-ethyl aminoethanol. By fitting empirical power law kinetics to data in Figure 2, the orders in amine were found to be 1.56 and 2.00 for 2-methylaminoethanol and 2-ethyl aminoethanol respectively. Clearly these results indicate that the reaction does not follow single-step carbamate formation. However, the results are in line with expectations based on the zwitterion mechanism. Therefore, these experimental data for all the amines were fitted to Eqn.(9) using the Nelder-Mead simplex algorithm of the unconstrained minimization technique¹⁶. Table 3 shows a summary of the results. The values of $k_2 k_w / k_1$ were estimated by taking an average value for $[H_2O]$ as 51 kmol m^{-3} . These values for $k_2 k_w / k_1$ are also shown in Table 3. A parity plot for Eqn. (4) for data for the primary amine 1-amino-2-propanol and the secondary amine 2-methylaminoethanol is shown in figure 3. This gives an indication of data quality and the appropriateness of Eqn. (9).

Table 2. Observed pseudo-first order rate constant for secondary amines 2-methyl aminoethanol and 2-ethyl aminoethanol at 303 K

Amine concn. kmol/m ³	k_{obs}, s^{-1} (2-methyl aminoethanol)	k_{obs}, s^{-1} (2-ethyl aminoethanol)
0.020	29.066	-
0.025	42.170	15.49
0.030	-	26.12
0.035	72.940	30.48
0.040	83.400	42.08
0.045	105.580	-

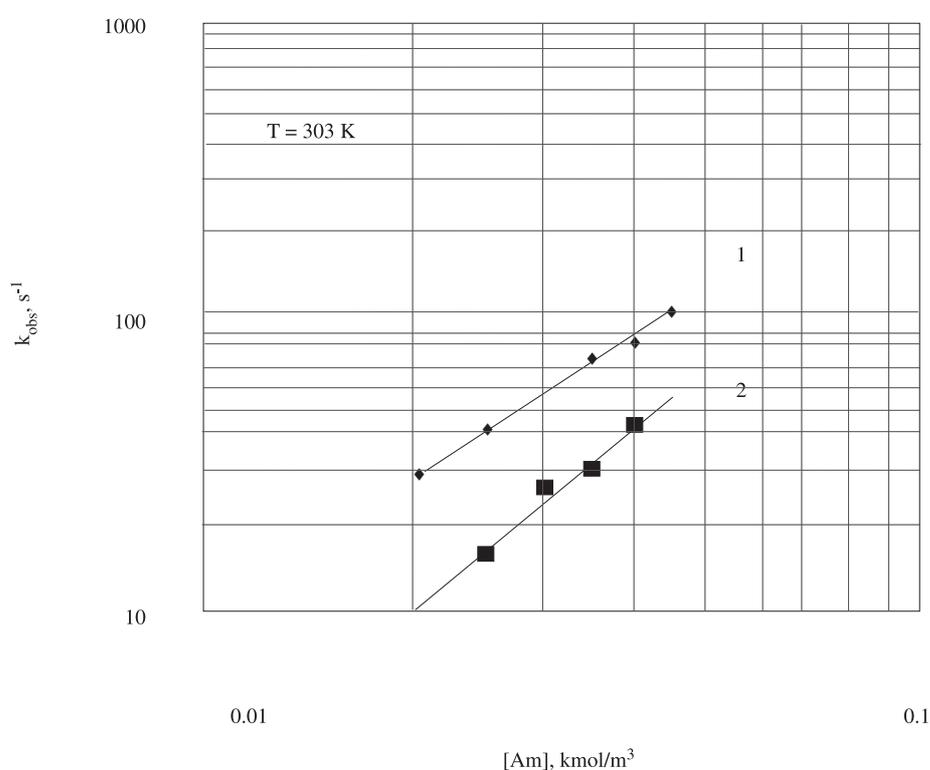

Figure 2. Observed pseudo-first order rate constants as function of secondary amine concentration at 303 K. (Line 1: 2-methyl aminoethanol; Line 2: 2-ethyl aminoethanol).

Table 3. Rate constants of primary and secondary amines according to Eqn.(4) at 303 K

Amine	Order k_2	$k_2 k_{Am} / k_1$ ($m^3 kmol^{-1} s^{-1}$)	k_2 ($m^6 kmol^{-2} s^{-1}$)	$k_2 k_w / k_1$ ($m^3 kmol^{-1} s^{-1}$)
1-amino-2-propanol	1.11	8600	39500	83.0
3-amino-1-propanol	1.49	11260	70700	76.4
2-methyl aminoethanol	1.56	6491	60900	12.8
2-ethyl aminoethanol	2.00	-	26200	-

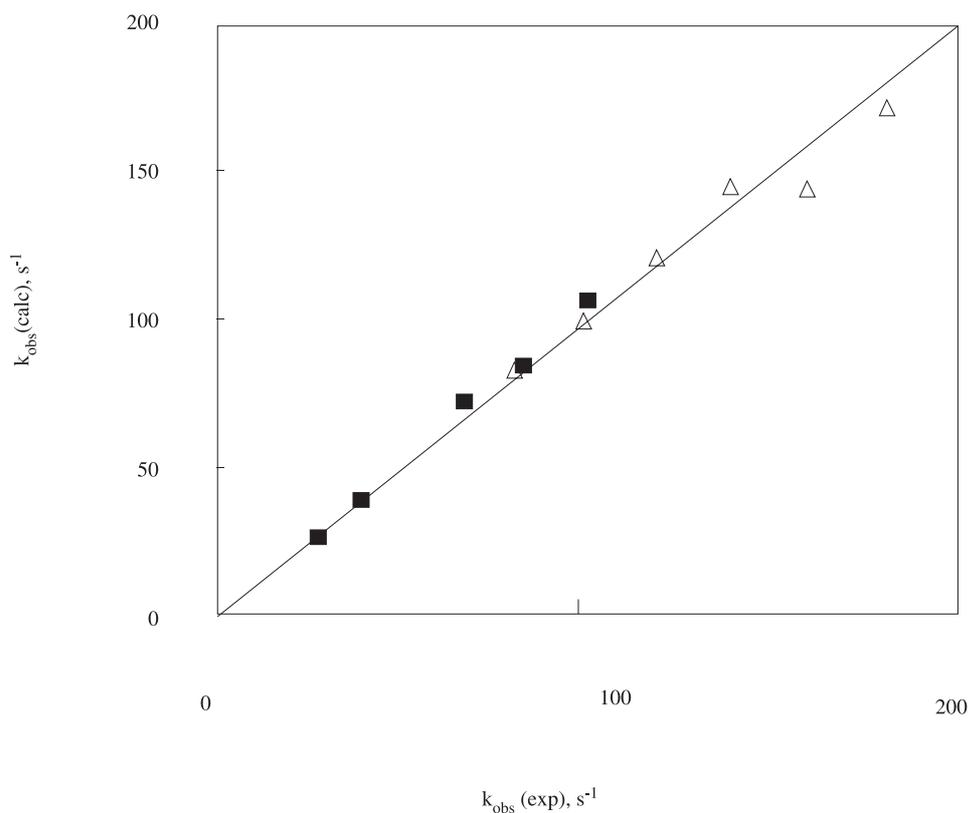


Figure 3. Parity plot for Eqn. (4) for data of 1-amino-2-propanol and 2-methyl aminoethanol at 303 K. (Calculated observed rate constant was obtained by using the rate constants of Table 3.)

In the literature, data can be found for some of the amines. For instance, Hikita et al.¹⁷, Sada et al.¹⁸ and Crooks and Donnelean¹⁹ reported data for 3-amino-1-propanol. The reported pseudo-first order rate constants are in the same order of magnitude with those of the present study. However, these authors interpreted their results on the assumption that the reaction was first order in amine (i.e. one-step carbamate formation). Therefore it is not possible to compare their rate constants with the results presented here. This also applies to the data of Penny and Ritter²⁰, who reported results with 1-amino-2-propanol, and Sotelo et al.²¹, who presented gas absorption data with 2-methylaminoethanol. No data could be found in the literature for the reaction between CO_2 and 2-ethyl aminoethanol.

Conclusions

CO_2 reacts with primary and secondary alkanolamines according to a zwitterion intermediate mechanism leading eventually to carbamate ion where both steps are rate-controlling since the reaction order is fractional and between 1 and 2, the value being different for each amine and the concentration range studied. It is clear from the mechanism that the reaction is effectively first order if the deprotonation of zwitterion by a base is fast. This is to be expected if the amino site of the amine (which is the main base for concentrated solutions) is not sterically hindered, so the approach of a base to the positively charged part of the zwitterion is relatively easy.

Appendix A: Nomenclature

B	any base (i.e. amine, OH^{-1} or water)
k_{Am}	rate constant for amine according to eqn.(4), $\text{m}^3 \text{ kmol s}^{-1}$
k_B	second order rate constant for zwitterion deprotonation by base B, $\text{m}^3 \text{ kmol s}^{-1}$
k_{obs}	observed pseudo-first order rate constant according to eqn.(2), s^{-1}
k_w	rate constant for water according to eqn.(4), $\text{m}^3 \text{ kmol s}^{-1}$
k_1	reverse first order rate constant for zwitterion deprotonation, s^{-1}
k_2	zwitterion formation rate constant, $\text{m}^3 \text{ kmol s}^{-1}$
r	specific reaction rate for amine- CO_2 system, $\text{kmol m}^3 \text{ s}^{-1}$

References

1. G. Astarita, D. W. Savage and A. Bisio, "Gas Treating with Chemical Solvents", Wiley-Interscience, New York, 1983.
2. Doraiswamy, L. K. and M. M. Sharma, "Heterogeneous Reactions: Analysis, Examples and Reactor Desing", Vol.2, John Wiley & Sons, New York, 1984.
3. E. Alper, The Chemical Engng.J., **44**, 107-112 (1990).
4. P. V. Danckwerts, Chem. Engng. Sci. **34**, 443-448 (1979).
5. G. F. Versteeg, L. A. J. van Dijk and P. M. van Swaaij, Chem.Engng.Sci., **144**, 113-158 (1996).
6. P. M. M. Blauwhoff, G. F. Versteeg and W. P. M. van Swaaij, Chem.Engng.Sci. **39**, 207-225 (1984).
7. G. F. Versteeg and W. P. M. van Swaaij, Chem. Engng.Sci. **43**, 573-585, (1988).
8. S. Xu, Y.-W. Wang, F. D. Otto and A. E. Mather, Chem. Engng. Sci. **51**, 841-850 (1996).
9. J. E. Crooks and J. P. Donnellan, J. Chem. Soc., Perkin Trans. 2 191-94, (1989).
10. W. Bouhamra, O. Bavbek and E. Alper, "Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-3-propandiol and carbondioxide", Chem. Engng.J. (1999) (accepted for publication).
11. G. F. Versteeg and M. H. Oyevaar, The reaction between CO_2 and diethanolamine at 298 K, Chem. Engng. Sci. **44**, 1264-68 (1989).
12. H. Bosch, G. F. Versteeg and P. M. van Swaaij, Chem. engng. Sci. **45**, 1167-1173 (1990).
13. E. Alper, Ind. Engng. Chem. Res. **29**, 1725-31 (1990).
14. E. Alper M. M. Roweih and W. Bouhamra, Chem. Engng. J. **55**, 53-59 (1993).
15. E. Alper, Turk. J. Chem. **17**, 183-87 (1993).
16. J. E. Dennis and D. J. Woods, SIAM, 116-23 (1987).
17. H. Hikita, S. Asai, H. Ishikawa and M. Honda, Chem. Engng. J. **13**, 7-12 (1977).

18. E. Sada, H. Kumazawa, Y. Osawa, M. Matsuura and Z. Q. Han, *Chem. Engng. J.* **33**, 87-95 (1986).
19. J. E. Crooks and J. P. Donnellan, *J. Chem. Soc., Perkin Trans. 2* 331-33 (1989).
20. D. E. Penny and T. J. Ritter, *J. Chem. Soc. Faraday Soc.* **79**, 2103-2109 (1983).