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Chemical Engineering Journal 73 (1999) 67–70

Chemical Engineering Journal

Short communication

Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1,3-propandiol and carbon dioxide

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Received 7 June 1998; accepted 11 November 1998

Abstract

The mechanism and kinetics of the reaction between aqueous solutions of CO_2 and a sterically hindered primary amine, 2-amino-2-methyl-1,3-propandiol (AMPD) was investigated at 278–303 K by using a stopped-flow technique. It was found that the reaction order according to power law kinetics was between 1.26 and 1.33 for amine concentration range of 0.025–1.600 kmol m^{-3}. This order was slightly higher than that of 2-amino-2-methyl-1-propanol (AMP), which was reported previously for similar conditions [E. Alper, Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-propanol and carbon dioxide, Ind. Eng. Chem. Res. 29 (1990) 1725.], and was therefore considered to be further evidence that the reaction takes place according to zwitterion intermediate mechanism. The kinetic rate parameters for aqueous AMPD solutions were obtained for 273–303 K and over the concentration range of 0.025–1.600 kmol m^{-3} of AMPD according to this mechanism. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2-Amino-2-methyl-1,3-propandiol; Carbon dioxide; Kinetics; Hindered amine; Stopped-flow

1. Introduction

Aqueous solutions of amines are often used to remove CO_2 and H_2S from a large number of industrial gas streams. There are several different processes, each suits a certain application. A recent advancement in gas treating technology is the application of sterically hindered amines which offer capacity advantages for CO_2 over the commercial amines such as monoethanolamine (MEA) [2]. On the other hand, all amines reacts with H_2S instantaneously while the reaction rate with CO_2 is finite. In the case of sterically hindered amines where the amino group is attached to a tertiary carbon atom, the reaction rate with CO_2 is often reduced due to steric hindrance. This may however be a desired property if certain calculated amount of selective removal is planned. On the other hand, it is well known that the sterically hindered amines cannot form stable carbamates leading to much higher carbonation ratios (moles CO_2/mole of amine). Therefore, 2-amino-2-methyl-1-propanol (AMP) is already commercially available primary amine which is the sterically hindered form of MEA. While the reaction order in amine is clearly an unity for MEA, it is slightly higher than one for AMP [1,3]. Therefore, Xu et al. [3] and Bosch et al. [4] considered that the reaction between aqueous AMP and CO_2 takes place according to a zwitterion intermediate mechanism as proposed by Danckwerts [5] and Blauwhoff et al. [6]. On the other hand, Saha and Bandyopadhyay [7] who investigated the kinetics of AMP at 294–318 K by gas absorption study using a wetted-wall column found that the reaction was first order in amine. Their results agreed closely with those of Alper [1] which were obtained from stopped-flow experiments. Other investigations of CO_2–amine system were recently reviewed by Versteeg et al. [8]. AMPD has a similar chemical structure to AMP where one of the –H is replaced by –OH. Therefore, it is also a sterically hindered amine which is expected to behave similarly with a smaller rate which might lead to applications in selective removal. However, there is no literature kinetic data for AMPD which is required to estimate the kinetic selectivity.

The aim of this paper is to report the results obtained by a direct technique (that is stopped-flow experiments) which does not involve gas absorption so that the findings correspond to the intrinsic homogeneous reaction rate between aqueous solutions of CO_2 and AMP.

2. Reaction kinetics

Following the proposed mechanism by Danckwerts [5] and subsequent considerable evidence (for instance,

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PII: S1385-8947(99)00017-0

Blauwhoff et al. [6], Versteeg and van Swaaij [9], Xu et al. [3], Crooks and Donnellan [10]), 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. For an amine with a stable carbamate (e.g., for MEA), the following reaction takes place:

$$\mathrm{RNH_2} + \mathrm{CO_2} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \mathrm{R\overset{+}{N}H_2COO^-} \tag{1a}$$

$$\mathrm{R\overset{+}{N}H_2COO^-} + \mathrm{B} \xrightarrow{k_\mathrm{B}} \mathrm{RNHCOO^-} + \mathrm{HB^+} \tag{1b}$$

resulting in the kinetic expression:

$$r = k_{\mathrm{obs}}[\mathrm{CO_2}] \tag{2}$$

$$= \frac{[\mathrm{CO_2}][\mathrm{Am}]}{1/k_2 + (k_1/k_2)/\sum k_\mathrm{B}\mathrm{B}} \tag{3}$$

where B is any base which can be an amine, water and OH^{-1} in an aqueous solution. Since the amine concentration was low in all experiments, the concentration of water can be considered as a constant, leading to a constant value for $k_\mathrm{w}[H_2O]$. The concentration of OH^- ion is low, thus its contribution to zwitterion dissociation is negligible as supported also by the works of Versteeg and Oyevaar [11], Bosch et al. [4], and Xu et al. [3]. This leads to an equation:

$$k_{\mathrm{obs}} = \frac{[\mathrm{Am}]}{\frac{1}{k_2} + \frac{k_1/k_2}{k_{\mathrm{Am}}[\mathrm{Am}] + k_\mathrm{w}[\mathrm{H_2O}]}} \tag{4}$$

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

3. Experimental

The experimental set-up consisted of a standard stopped-flow equipment (Hi-Tech Scientific, 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, between aqueous solutions of CO_2 and AMPD). All parts of the flow circuit were thermostatted and the temperature control was better than ±0.1 K. The product formation was monitored by fast conductimetry, the pertinent details of which can be found elsewhere [12].

Reagent grade AMPD were used without further purification. The concentration of amine was always much in excess of that of CO_2 (usually the molar ratio was about 20–1) and ranged between 0.025 and 1.6 kmol m^{-3}.

4. Experimental results

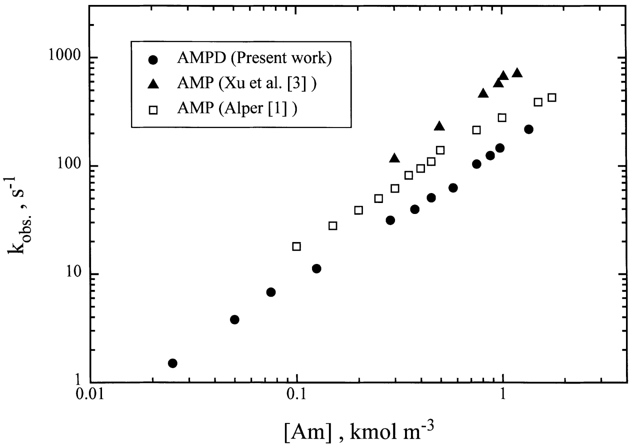

Fig. 1. Observed pseudo-first order rate constants as function of 2-amino-2-methyl-1,3-propandiol (AMPD) concentration at 298 K (figure also shows the literature data for 2-amino-2-methyl-1-propanol (AMP) for comparison).

Stopped-flow data gave very satisfactory pseudo-first order plots according to Eq. (2). Since the reaction between OH^- and CO_2 was not detected by the conductivity measurements, the fitted rate constant corresponded directly to k_{obs} in Eq. (4). In Fig. 1, the observed rate constant k_{obs} is shown as function of AMPD concentration at 298 K. The same figure shows also the literature data of observed rate constant for AMP for comparison [1,3]. The data of Saha and Bandyopadhyay [7] agree closely with those of Alper [1]. As expected the observed reaction rate for AMPD is much more smaller than that of AMP which is caused by added hindrance and charge effect of –OH group which replaces –H in AMP.

In Fig. 2, the observed rate constant k_{obs} is shown as function of AMPD concentration at three different temperatures of 278, 288 and 303 K. Using the least square method, an empirical power law kinetics was fitted to these data and the fractional orders obtained are given in Table 1. The order which ranges between 1.26 and 1.33 for the concen-

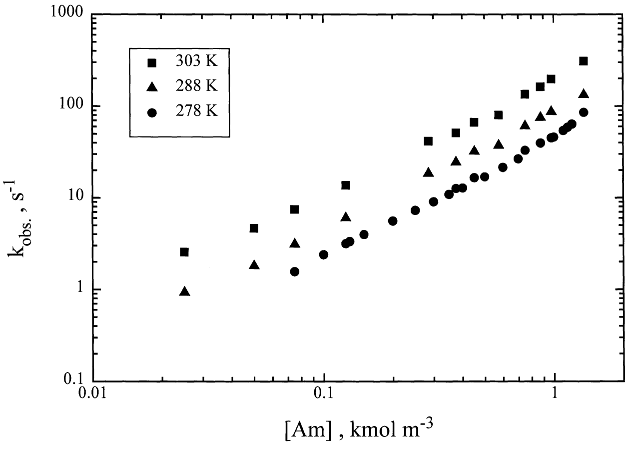

Fig. 2. Observed pseudo-first order rate constants as function of 2-amino-2-methyl-1,3-propandiol (AMPD) concentration at three different temperatures.

Table 1
Kinetic data of aqueous AMPD–CO_2 and AMP–CO_2 systems

Amine	Temperature (K)	Order	k_2 ($m^3\ kmol^{-1}\ s^{-1}$)	k_2k_{Am}/k_1 ($m^6\ kmol^{-2}\ s^{-1}$)	k_2k_w/k_1 ($m^6\ kmol^{-2}\ s^{-1}$)
AMPD	278	1.33	71.4	330.0	0.33
AMPD	288	1.28	120.7	647.0	0.74
AMP	288	–	524.7[a]	1501.4[a]	1.14[a]
AMPD	303	1.25	242.1	1630.0	2.65

[a] Kinetic data of Xu et al. [3].

tration range of this study clearly indicates that the zwitterion is appropriate for this chemical reaction. These experimental data were fitted to Eq. (4) by using the Nelder-Meade simplex algorithm of the unconstrained minimization technique. Table 1 shows the summary of results. The values of k_2k_w/k_1 were estimated by taking an average value for [H_2O] as 51 kmol m^{-3}. These values of k_2k_w/k_1 are also shown in Table 1. Table 1 shows also the literature data for AMP for comparison. Parity plot for Eq. (4) for data at 288 and 303 K are shown in Figs. 3 and 4, respectively, which give an indication of data quality.

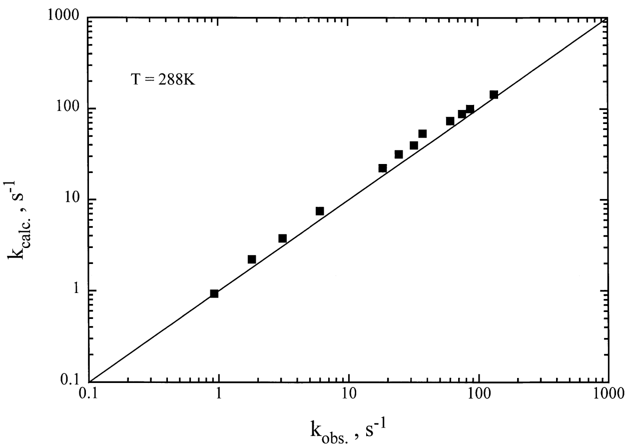

Fig. 3. Parity plot for Eq. (4) for data at 288 K (k_2=120.7 $m^3\ kmol^{-1}\ s^{-1}$; k_2k_{Am}/k_1=647.0 $m^6\ kmol^{-2}\ s^{-1}$; k_2k_w/k_1=0.74 $m^6\ kmol^{-2}\ s^{-1}$).

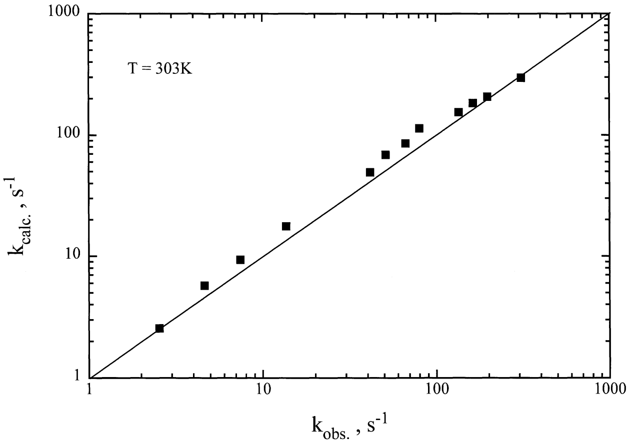

Fig. 4. Parity plot for Eq. (4) for data at 303 K (k_2=242.1 $m^3\ kmol^{-1}\ s^{-1}$; k_2k_{Am}/k_1=1630.0 $m^6\ kmol^{-2}\ s^{-1}$; k_2k_w/k_1=2.65 $m^6\ kmol^{-2}\ s^{-1}$).

Arrhenius plots were also obtained for the rate constant k_2 and the combined rate constants of k_2k_{Am}/k_1 and k_2k_w/k_1. Fig. 5 shows the Arrhenius plots for the rate constant k_2. Similar plots were also obtained for the combined rate constants. The respective activation energies for k_2, k_2k_{Am}/k_1 and k_2k_w/k_1 were found to be 33.7, 44.7 and 62.05 kJ mol^{-1}, respectively.

5. Conclusions

CO_2 reacts with the sterically hindered amine 2-amino-2-methyl-1,3-propandiol (AMPD) 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 for the amine concentration range of 0.025–1.600 kmol m^{-3}. When compared with the rate constant of sterically hindered amine 2-amino-2-methyl-1-propanol (AMP), the rate constants for AMPD are smaller than that of AMP as expected from the chemical structures of these primary amines. On the other

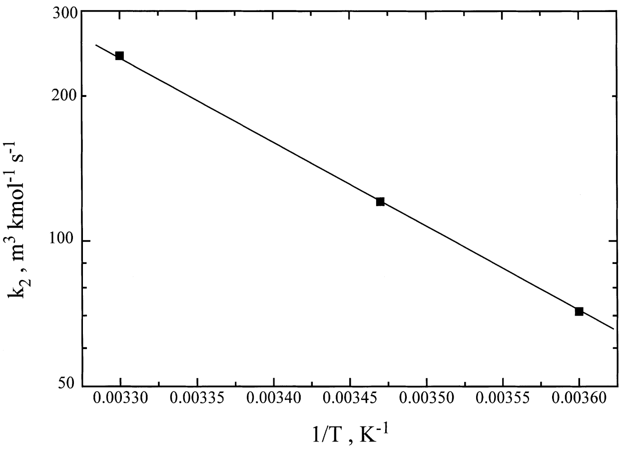

Fig. 5. Arrhenius plot for the rate constant k_2.

hand, like all amines, AMPD reacts with H_2S instantaneously so that the slower rate of AMPD with CO_2 can lead to the employment of this amine industrially where controlled selectivity is desired.

6. Nomenclature

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

Acknowledgements

The authors gratefully acknowledge the support of Kuwait University, under research grant EC-43 for realising the experimental part of this work.

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