

Reaction Mechanism and Kinetics of Aqueous Solutions of 2-Amino-2-Methyl-1,3-Propanediol and Carbonyl Sulphide

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The mechanism and kinetics of the reaction between aqueous solutions of COS and a sterically hindered primary amine, 2-amino-2-methyl-1,3-propanediol (AMPD), were investigated at 288-303 K using a stopped-flow technique. It was found that the reaction order according to power law kinetics was between 1.12 and 1.16 for an amine concentration range of 0.5 to 1.5 kmol m⁻³. This overall order indicated that the thiocarbamate formation was complex and possibly involved a zwitterion intermediate. However, the experimental results can also be explained in terms of a single-step termolecular reaction mechanism. The kinetic rate parameters for aqueous AMPD solutions were obtained for 288 to 303 K and over the concentration range of 0.5 - 1.5 kmol m⁻³ of AMPD.

Introduction

Aqueous solutions of amines are often used to remove CO₂, H₂S and COS from a large number of industrial gas streams. There are several different processes, each suiting a certain application. A recent advance in gas treating technology is the application of sterically hindered amines, which offer capacity advantages for CO₂ over commercial amines such as monoethanolamine (MEA) (Sartori and Savage¹). All amines react with H₂S instantaneously, while the reaction rates with CO₂ and COS are both finite. In the case of sterically hindered amines, where the amino group is attached to a tertiary carbon atom, the reaction rates with CO₂ and COS are often reduced significantly due to steric hindrance. This may, however, be a desired property for CO₂ if a certain calculated amount of selective removal is planned. 2-amino-2-methyl-1-propanol (AMP) is a commercially available primary amine, the sterically hindered form of MEA. Another sterically hindered amine which might be of interest in industry is 2-amino-2-methyl-1,3-propanediol (AMPD). AMPD has a similar chemical structure to AMP where one of the -H is replaced by -OH. Recently, Bouhamra et al.² studied the kinetics of reaction between aqueous AMPD and CO₂ and found that it follows, zwitterion intermediate mechanism. In selective removal, the reaction rate of the AMPD-COS system is also of interest, but such data are not available in the literature. The kinetics of other amines have been studied by Alper et

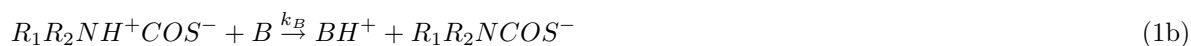
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al.³⁻⁶ and by Littel et al.⁷ in aqueous and alcoholic solutions and were found to be similar to those of CO₂, involving a zwitterion intermediate before finally forming thiocarbamates.

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

Reaction Kinetics

Following the mechanism proposed by Alper³, the general consensus for the reaction of COS with primary and secondary alkanolamines is the formation of a zwitterion intermediate, rather than one-step bimolecular thiocarbamate formation³⁻⁷. For an amine with a stable thiocarbamate (e.g., for MEA), the following reaction takes place:



resulting in the kinetic expression:

$$r = k_{obs}[CO_2] \quad (2)$$

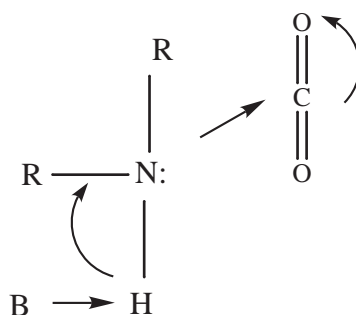
$$= \frac{[CO_2][Am]}{1/k_2 + (k_1/k_2)/\Sigma k_B B} \quad (3)$$

where B is any base, which could be amine, water or OH⁻ in an aqueous solution. The concentration of OH⁻ ion is low, thus its contribution to zwitterion dissociation is negligible as supported also by the works of, amongst others, Versteeg and Oyevaar⁸ and Xu et al.⁹ This leads to the equation:

$$k_{obs} = \frac{[Am]}{k_2 + \frac{1}{\frac{1}{k_{Am}[Am] + k_w[H_2O]}}} \quad (4)$$

Here, k_{Am} and k_w are the combination of rate constants obtained by multiplying (k_2/k_1) by the respective k_B . Thus depending on the values of the rate constants and the concentration range of the amine, the order in the amine can range between 1 and 2.

An alternative reaction mechanism which can explain fractional orders was proposed by Crooks and Donnellan¹⁰ for CO₂-aqueous amine systems. According to their theory, the reaction is single-step and termolecular and assumes that the reaction proceeds via a loosely bound encounter complex as initial product. This mechanism can be adopted to thiocarbamate formation, as shown below:



Here, B could be another amine or water molecule. This leads to the following equation for the observed rate constant:

$$k_{\text{obs}} = k_{Am}[Am]^2 + k_w[\text{H}_2\text{O}][Am] \quad (5)$$

Eq.(4) and Eq.(5) become indistinguishable if k_2 is very large, so that $1/k_2$ is effectively zero.

Experimental

The experimental set-up consisted of a standard stopped flow equipment (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 COS 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 (Alper¹¹).

Reagent-grade AMPD was used without further purification. The concentration of amine was always much in excess of that of COS (usually the molar ratio was about 20 to 1) and ranged from 0.5 to 1.5 kmol m^{-3} .

Experimental results

Figure 1 shows a typical result of stopped-flow experiments at 303 K and at an AMPD concentration of 0.925 kmol/ m^3 . Stopped flow data gave very satisfactory pseudo-first order plots according to Eq. (2). Since the reaction between OH^- and COS was not detected by the conductivity measurements, the fitted rate constant corresponded directly to k_{obs} in Eq.(2). Table 1 shows the experimental data, that is, k_{obs} as a function of AMPD concentration, at two different temperatures. In Figure 2, the observed rate constant k_{obs} is shown as a function of AMPD concentration at 288 K and 303 K. Using the least-square-method, an empirical power law kinetics was fitted to these data and the fractional orders of 1.12 and 1.16 were obtained for 288 K and 303 K respectively. The order suggests that both the zwitterion intermediate and termolecular reaction mechanisms may be appropriate for this chemical reaction. A Nelder-Mead simplex algorithm of the constrained minimization technique was used to analyze these data. However, it was not possible to obtain convergence with positive rate constants for Eq. (4). On the other hand, the data can be regressed satisfactorily for Eq. (5), yielding the two rate constants of k_{Am} and k_w . It should be noted that Eq.(4) and Eq.(5) are identical if k_2 is very large. Table 2 shows a summary of the results. A parity plot for Eq.(4) for data at 288 K and 303 K is shown in Figure 3.

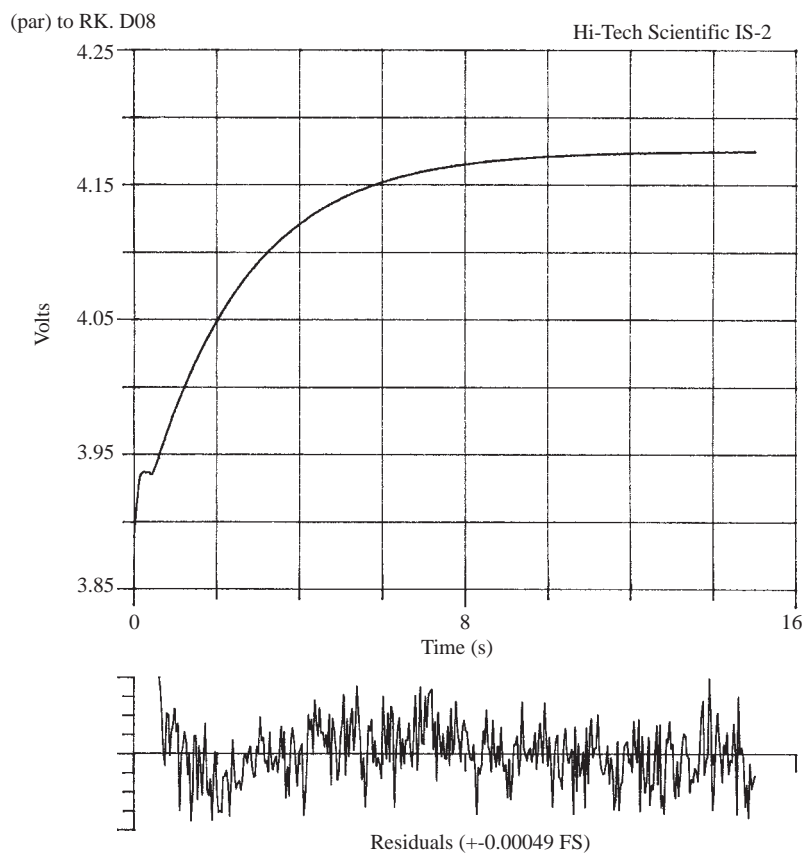


Figure 1. A typical experimental run at 303 K with 0.925 kmol/m³ of 2-amino-2-methyl-1,3-propanediol (AMPD).

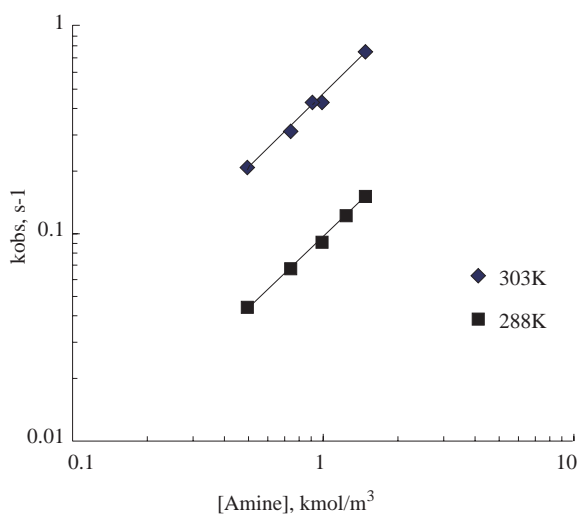


Figure 2. Observed pseudo-first-order rate constants as a function of 2-amino-2-methyl-1,3-propanediol (AMPD) concentration at two different temperatures.

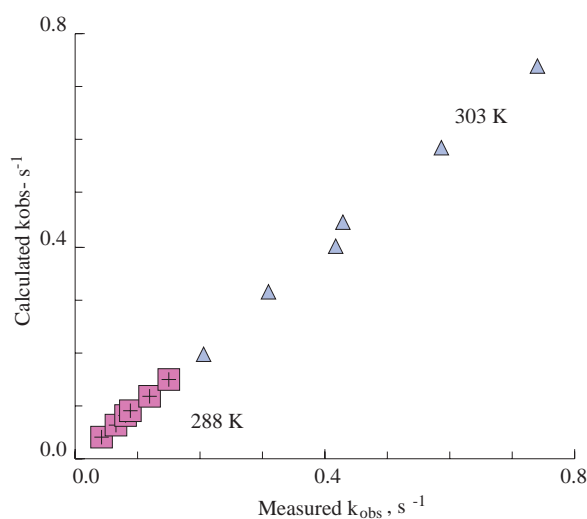


Figure 3. Parity plot for Eq.(5) for data at 288K and 303 K using the rate constants given in Table 3.

Table 1. Experimental data of stopped flow experiments

[AMPD] kmol/m ³	[H ₂ O] kmol/m ³	k_{obs} (288K) s ⁻¹	k_{obs} (303 K) s ⁻¹
0.500	5.05	0.2087	0.0439
0.750	4.80	0.3109	0.0671
0.925	4.57	0.4192	0.0800
1.000	4.56	0.4291	0.0904
1.250	4.31	0.5880	0.1196
1.500	4.05	0.7439	0.1514

Table 2. Fitted reaction rate parameters

	k_{Am} (m ³ /kmol) ² s ⁻¹	k_W (m ³ /kmol) ² s ⁻¹
288 K	0.0302	0.0134
303 K	0.1600	0.0620

Conclusions

The reaction between COS and the sterically hindered amine 2-amino-2-methyl-1,3-propanediol (AMPD) is not a simple bimolecular reaction. Results fit to both a zwitterion intermediate mechanism and a termolecular reaction mechanism. When compared with the rate constant of sterically hindered amine 2-amino-2-methyl-1-propanol (AMP), the rate constant for AMPD is smaller than that for AMP, as expected from the chemical structures of these primary amines (the rate constant for AMP was reported by Littel et al.⁷). The reaction rate of COS with AMPD is much slower than that of CO₂, which was recently reported by Bouhamra et al.² On the other hand, like all amines, AMPD reacts with H₂S instantaneously, so that the slower rate of AMPD with CO₂ could lead to the use of this amine in industry, where controlled selectivity is desired. However, because of its very slow reaction rate, COS would not be removed in such cases. Hence caution should be exercised if the gas contains a significant amount of COS.

References

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Appendix A: Nomenclature

B	any base (i.e., amine, OH^{-1} or water)
k_{Am}	combined rate constant according to Eq.(4) or Eq.(5), $(\text{m}^3/\text{kmol})^2 \text{ s}^{-1}$
k_B	rate constant according to Eq. (4), $\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$
k_{obs}	observed pseudo-first-order rate constant according to Eq. (2), s^{-1}
k_W	combined rate constant according to Eq.(4) or Eq.(5), $(\text{m}^3/\text{kmol})^2 \text{ s}^{-1}$
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, $\text{kmol m}^{-3} \text{ s}^{-1}$