

## Kinetics and Mechanism of the Reaction between Carbon Dioxide and Amines in Aqueous Solution

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Rate constants,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  have been measured by the conductimetric stopped-flow technique for the reaction of carbon dioxide in aqueous solution with the primary amines 2-methoxyethylamine, 2-aminoethanol, 3-aminopropan-1-ol, 2-aminopropan-2-ol, DL-aminopropan-2-ol and the secondary amines 1,1'-iminodipropan-2-ol, 2-amino-2-(hydroxymethyl)propane-1,3-diol, 2,2'-iminodiethanol, 2,2,6,6-tetramethylpiperidin-4-ol, and morpholine. The observed first-order rate constants fit the equation  $k_{\text{obs}} = k_{\text{AM}}[\text{R}_2\text{NH}]^2 + k_{\text{w}}[\text{R}_2\text{NH}][\text{H}_2\text{O}]$ . The much-quoted Danckwerts mechanism is shown to be unlikely.

The reaction of carbon dioxide with aqueous amines is of great technical importance as providing the best way of stripping carbon dioxide from gas streams. It has therefore been much studied, but with confusing and conflicting results. Blauwhoff *et al.*<sup>1</sup> give a review of the earlier literature. Fourteen studies of the reaction with 2-aminoethanol all found the rate to be proportional to the first power of the amine concentration. Eleven studies of the reaction with 2,2'-iminodiethanol, quoting data from seven techniques, found the rate to be proportional to the first power, whereas five studies, quoting data from four techniques, found the rate to be proportional to the second power of the amine concentration. Two more studies,<sup>2,3</sup> using the stopped-flow technique which should give the clearest data, subsequent to this review are clearly in favour of a first-order dependence on amine concentration. A study<sup>4</sup> in which the rate of the reaction was measured indirectly from the rate of absorption from the gas phase gave fractional orders of reaction, between unity and two, for the reaction of carbon dioxide with 3-aminopropan-1-ol in ethanol solution. In an attempt to obtain a clearer picture, we have studied the reaction in anhydrous ethanol using the novel technique of conductimetric stopped-flow, and found an unambiguous dependence of the rate on the second power of the 2,2'-iminodiethanol concentration.<sup>5</sup> In this paper we report on the kinetics of the reaction with ten amines in aqueous solution studied using the same apparatus.

### Results

All reactions were studied with large excess of amine (0.1–1 mol dm<sup>-3</sup> for secondary amines, 0.02–0.06 mol dm<sup>-3</sup> for primary amines) over CO<sub>2</sub> (10<sup>-3</sup>–10<sup>-2</sup> mol dm<sup>-3</sup>) and gave good first-order plots. The observed first-order constants,  $k_{\text{obs}}$ ,

$$k_{\text{obs}} = k_{\text{AM}}[\text{R}_2\text{NH}]^2 + k_{\text{w}}[\text{R}_2\text{NH}][\text{H}_2\text{O}] \quad (1)$$

fitted equation (1). An equation of this type has already been proposed.<sup>1</sup> The value of  $[\text{H}_2\text{O}]$  is taken as 55 mol dm<sup>-3</sup> for ready comparison of  $k_{\text{AM}}$  and  $k_{\text{w}}$ . Plots of  $k_{\text{obs}}/[\text{R}_2\text{NH}]$  gave good straight lines, from which  $k_{\text{AM}}$  and  $k_{\text{w}}$  were calculated. Typical data are shown in the Figure. Values of  $k_{\text{AM}}$  and  $k_{\text{w}}$ , together with  $\text{p}K_{\text{a}}$  literature values for the protonated amines, are tabulated in Table 1. Three of the amines were studied at 5°C intervals over the temperature range 15–35°C, and the calculated activation parameters are given in Table 2.

Detailed data for 2-aminoethanol at 25°C are given in Table 3, together with values calculated from equation (1) using values

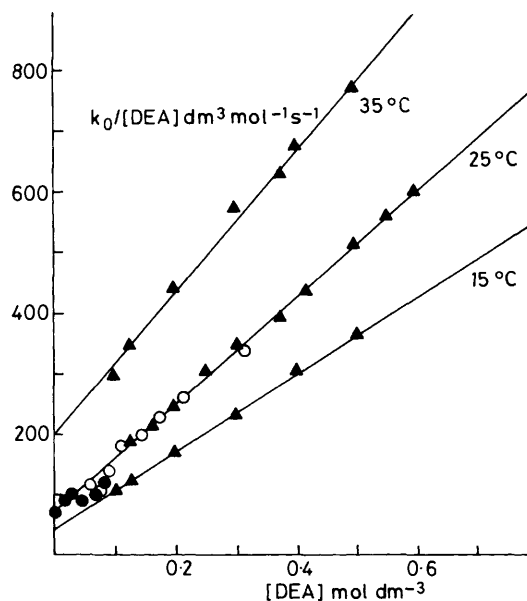


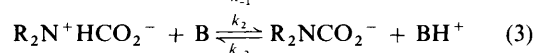
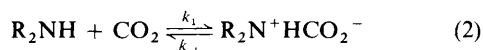
Figure. Variation of  $k_0/[\text{DEA}]$  with  $[\text{DEA}]$ . Triangles, this work, natural pH; open circles, this work, pH ca. 9; filled circles, data from ref. 2. DEA = 2,2'-iminodiethanol (diethanolamine)

from Table 1. The percentage deviations between calculated and observed values are also given to give an idea of the quality of the data.

As a test of OH<sup>-</sup> catalysis, some runs for 2,2'-iminodiethanol at 25°C were performed at  $[\text{OH}^-]$  of ca. 10<sup>-5</sup> mol dm<sup>-3</sup> instead of the usual 10<sup>-3</sup> mol dm<sup>-3</sup>. These data points fall on the general line in the Figure, showing that reaction with OH<sup>-</sup> is not significant for the reaction conditions generally used.

### Discussion

At present, the generally accepted mechanism for these reactions is that proposed by Danckwerts,<sup>7</sup> in which a zwitterion intermediate is formed [equations (2) and (3)]. If the



zwitterion is at a steady-state low concentration, and  $k_{-2}$  is

**Table 1.** Kinetic data at 25 °C

Amine	$10^{-3} k_{AM}/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$k_w/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$pK_a$
2,2,6,6-Tetramethylpiperidin-4-ol	74.2	43	10.05
3-Aminopropan-1-ol	66.3	26	9.96
2-Aminoethanol	52.6	24	9.50
2-Aminopropan-2-ol	51.0	25	9.47
DL-Aminopropan-2-ol	35.2	54	9.42
2-Methoxyethylamine	19.7	37	9.40
Morpholine	14.2	48	8.33
2,2'-Iminodiethanol	0.87	1.4	8.88
1,1'-Iminodipropan-2-ol	0.238	0.73	8.86
2-Amino-2-(hydroxymethyl)propane-1,3-diol	0.264	0.263	8.07

Errors in  $k_{AM} \pm 3\%$ . Errors in  $k_w \pm 10\%$ .  $pK_a$  values from ref. 6.

**Table 2.** Activation parameters

Amine	$\Delta H_{AM}^\ddagger/\text{kJ mol}^{-1}$	$-\Delta S_{AM}^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta H_w^\ddagger/\text{kJ mol}^{-1}$	$-\Delta S_w^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$
2-Aminoethanol	17.5	96	49	56
2,2'-Iminodiethanol	19.5	123	53	66
1,1'-Iminodipropan-2-ol	26.5	110	47	92

Estimated errors  $\pm 10\%$ .

**Table 3.** Observed and calculated rate constants for 2-aminoethanol at 25 °C

[Amine]/ $\text{mol dm}^{-3}$	$(k_{\text{obs}}/[\text{Amine}])/$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\{k/[\text{Amine}](\text{calc})\}/$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Deviation (%)
0.020	2 450	2 384	+3.7
0.030	2 900	2 910	-0.3
0.035	3 029	3 173	-4.7
0.040	3 500	3 436	+1.8
0.045	3 689	3 699	-2.7
0.050	3 880	3 962	+2.1
0.055	4 291	4 225	+1.5
0.060	4 500	4 488	+0.3

small, then the reaction gives first-order kinetics of the observed rate constant  $k_{\text{obs}}$ , where  $k_{\text{obs}}$  is shown in equation (4) for

$$k_{\text{obs}} = \frac{k_1[\text{R}_2\text{NH}]}{1 + k_{-1}/(k_2[\text{B}])} \quad (4)$$

$$\theta = k_{\text{obs}}[\text{CO}_2]$$

$[\text{R}_2\text{NH}]$  and  $[\text{B}]$  much greater than  $[\text{CO}_2]$ . This mechanism neatly explains why some previous workers observed a rate varying with  $[\text{R}_2\text{NH}]^2$  for B as  $\text{R}_2\text{NH}$ , and some observed a rate varying with  $[\text{R}_2\text{NH}]$ . If  $k_{-1} \gg k_2[\text{B}]$ , and B is  $\text{R}_2\text{NH}$ , then equation (4) reduces to equation (5).

$$k_{\text{obs}} = k_1 k_2 [\text{R}_2\text{NH}]^2 / k_{-1} \quad (5)$$

A mechanism with four adjustable rate constants can be stretched to cover a wide range of experimental data, but the data presented in this paper stretch the mechanism beyond the point of credibility. Let us consider 2,2'-iminodiethanol, as an example of a well-studied amine, at 25 °C and make some intelligent guesses. We denote  $k_2$  for amine as B by  $k_{2AM}$  and  $k_2$  for water as B by  $k_{2w}$ , and likewise for  $k_{-2}$  and for  $K_2$ , the equilibrium constant for the second step, where  $K_2 = k_2/k_{-2}$ , and equation (6) holds. We also define the overall equilibrium

$$K_{2w} = [\text{H}_3\text{O}^+]/[\text{R}_2\text{N}^+\text{HCO}_2^-][\text{H}_2\text{O}] \quad (6)$$

constants  $K_{AM}$  and  $K_w$  in equations (7) and (8).

$$K_{AM} = [\text{R}_2\text{NCO}_2^-][\text{R}_2\text{NH}_2^+]/[\text{R}_2\text{NH}][\text{CO}_2] \quad (7)$$

$$K_w = [\text{R}_2\text{NCO}_2^-][\text{H}_3\text{O}^+]/[\text{R}_2\text{NH}][\text{CO}_2][\text{H}_2\text{O}] \quad (8)$$

Values of  $K_{AM}$  for some amines have been experimentally determined, and published values are listed in Table 4. Values of  $K_w$  may be readily calculated from published values of  $K_a$ , the dissociation constant of the conjugated acid of the amine, since  $K_w = K_{AM}K_a/[\text{H}_2\text{O}]$ . If equation (5) is valid, as implied by the observed dependence of the rate of the reaction on  $[\text{R}_2\text{NH}]^2$ , then  $k_{-2AM} = k_{AM}/K_{AM} = 0.31 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This gives  $K_{2AM}$ , from  $k_{2AM}/k_{-2AM}$ , to be  $3 \times 10^{10}$  (dimensionless). Since  $K_{AM} = 3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $K_1$  may be estimated from  $k_{2AM}/k_{-2M}$  to be  $10^{-7} \text{ dm}^3 \text{ mol}^{-1}$ . This value is independent of the nature of B. If we now consider the route with water as B, we find  $k_{2w}$ , from  $k_w/K_w$  to be  $2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Our earlier value of  $K_1$  gives  $K_{2w}$ , from  $K_w/K_1$ , to be 0.7 (dimensionless). Thus  $k_{2w}$  is calculated from  $K_{2w}/k_{-2w}$  to be  $1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Hence we estimate both  $k_{2w}$  and  $k_{-2w}$  to be *ca.*  $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , which is typical for  $\Delta pK$  around zero for proton transfer from nitrogen centres.<sup>9</sup> These conclusions are thus so far in accord with the Danckwerts mechanism. However, this implies that the acid dissociation constant, given by  $K_{2w}$ , is *ca.*  $40 \text{ mol dm}^{-3}$ , and its  $pK_a$  is  $-1.6$ . It hardly seems possible that the carbamic acid is so strong. We may have overestimated  $k_{2AM}$ . If we take the value to be the lowest reasonably possible, namely  $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $K_{2w}$  becomes  $7 \times 10^{-3}$  (dimensionless). This does not require the carbamic acid to be so strong, but does give  $k_{2w}$  to be  $1.4 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

It could be that 2,2'-iminodiethanol and water give the two limiting cases of the Danckwerts mechanism; *i.e.*  $k_{-1} \gg k_{2AM}[\text{R}_2\text{NH}]$  but  $k_{-1} \ll k_{2w}[\text{H}_2\text{O}]$ . However this implies that  $k_{2w} \gg k_{2AM}$ , which is impossible.

The most telling argument against the Danckwerts mechanism is that it was proposed to account for data which are now seen to be misleading. The rate is proportional to  $[\text{R}_2\text{NH}]^2$  at high  $[\text{R}_2\text{NH}]$ , and to  $[\text{R}_2\text{NH}]$  at low  $[\text{R}_2\text{NH}]$  where the major contribution is from the water-catalysed rate. Intermediate amine concentrations give the effect of a fractional order. A good example is given by the results of Barth *et al.*,<sup>2</sup> whose data are included in the Figure. Their technique precluded the study of a wide range of amine concentrations,

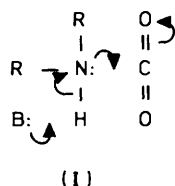
**Table 4.** Equilibrium data

Amine	$10^3 K_{AM}(25^\circ\text{C})/\text{dm}^3 \text{ mol}^{-1}$	$-\Delta H^\circ_{AM}/\text{kJ mol}^{-1}$	$-\Delta S^\circ_{AM}/\text{J K}^{-1} \text{ mol}^{-1}$
2-Aminoethanol	87	84	188
2,2'-Iminodiethanol	2.8	72	174
1,1'-Iminodipropan-2-ol	4.4	59	127
	$10^{-9} K_w(25^\circ\text{C})/\text{dm}^3 \text{ mol}^{-1}$	$-\Delta H^\circ_w/\text{kJ mol}^{-1}$	$-\Delta S^\circ_w/\text{J K}^{-1} \text{ mol}^{-1}$
2-Aminoethanol	496	34	230
2,2'-Iminodiethanol	67	29	240
1,1'-Iminodipropan-2-ol	1.1	29	230

Estimated errors:  $K \pm 5\%$ ;  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\pm 10\%$ . Calculated from data in ref. 8.

and they come to the conclusion, on the basis of the data shown, that the reaction is first order in amine. In a later paper<sup>3</sup> they give results for 2-aminoethanol obtained by computer fitting to data for  $[R_2NH]$  in the range 0.175–0.00487 mol dm<sup>-3</sup>. This is the same concentration range as for the data in Table 3. Barth *et al.* build the assumption that the reaction is first order in amine into their computer model, and obtain a rate constant of  $4\,700 \pm 630 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , which is in good numerical agreement with the data in Table 4, although the interpretation is quite different.

We conclude that the reaction is single-step and termolecular, with a mechanism of type (I). The activation data are in accord



with this mechanism. Values of  $\Delta H^\ddagger$  for  $R_2NH$  as B are very low, and the reaction is only slow enough to be monitored by the stopped-flow technique because  $\Delta S^\ddagger$  is large and negative. Values of  $\Delta H^\ddagger$  when B is  $H_2O$  are larger, as expected from the lower basicity of water, but this is offset by the lower values of  $-\Delta S^\ddagger$ , as it is easier to place  $H_2O$  in the correct place to accept a proton. The variation of reactivity with the nature of the amine is also as expected. Primary amines are more reactive than secondary amines, due to steric hindrance in the latter. Two of the secondary amines, 2,2,6,6-tetramethylpiperidin-4-ol and morpholine, are especially noteworthy, in that they react as fast as primary amines because the substituent groups are tucked back behind the nitrogen. Increased basicity of the nitrogen also causes increased reactivity. The hydroxy group, present in most of the amines studied, takes no part in the reaction. Amines in which it is missing (2-methoxyethylamine, morpholine) and in which it is tucked back away from the reaction centre (2,2,6,6-tetramethylpiperidin-4-ol) do not show anomalously low reactivity. The sole function of the hydroxy group is to facilitate solution in water.

This mechanism may be regarded as the limiting case of the Danckwerts mechanism for  $k_{-1} \gg k_2[B]$ . The initial product is not a zwitterion, but a loosely-bound encounter complex, so that a discussion of its  $pK_a$  is inappropriate. Most of these complexes break up to give reagent molecules again, a few react with a second molecule of amine, or a water molecule, to give ionic products. Bond formation and charge separation occur only in the second step.

## Experimental

**Materials.**—Amines were supplied by the Aldrich Chemical Company, and were all AnalaR grade, with the exception of 2-amino-2-(hydroxymethyl)propane-1,3-diol and 2,2,6,6-tetramethylpiperidin-4-ol which were Gold Label quality (>99.9%). The amines were used without further purification. Carbon dioxide was supplied in cylinders by Distillers p.l.c.

**Kinetic Measurements.**—Aqueous solutions of amine (0.1–1 mol dm<sup>-3</sup>) and  $CO_2$  (ca. 0.01 mol dm<sup>-3</sup>) were mixed in a stopped-flow apparatus (Hi-Tech Scientific Ltd.) and product formation monitored by fast conductimetry, as previously described.<sup>5</sup> All traces were analysed according to simple first-order kinetics, and gave good first-order plots.

The hydrolysis of the amines gave the solutions a natural  $[OH^-]$  of ca.  $1\text{--}2 \times 10^{-3} \text{ mol dm}^{-3}$ . It was not possible to test for a contribution to the total rate from  $OH^-$  as B by adding excess of  $OH^-$  because the reaction of  $CO_2$  with  $OH^-$  to form  $HCO_3^-$  became significant. The rate constant for this reaction<sup>10</sup> at 25 °C is  $8.9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The kinetic traces showed a rapid initial decrease in conductivity as  $OH^-$  was replaced by the less mobile  $HCO_3^-$ , followed by a slower increase as the carbamate salt formed. A check on the effect of  $OH^-$  was made by using solutions of 2,2'-iminodiethanol to which some HCl had been added to convert about half into the protonated form. This reduced  $[OH^-]$  to ca.  $10^{-5} \text{ mol dm}^{-3}$ .

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