Kinetics of the Formation of *N,N*-Dialkylcarbamate from Diethanolamine[‡] and Carbon Dioxide in Anhydrous Ethanol

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The rate of formation of *N,N*-dialkylcarbamate from diethanolamine and carbon dioxide in anhydrous ethanol has been found to depend on the square of the amine concentration. The rate and activation data are consistent with the two-step Danckwerts mechanism, in which a zwitterion intermediate is present at very low concentration and reacts with a second molecule of amine at the diffusion-controlled limit to give a final salt in the rate-determining step.

The absorption of CO_2 by aqueous solutions of amines is a process of great industrial importance, and the neutralisation reaction, in which the CO_2 is converted into *N,N*-dialkylcarbamate, has been much studied. The kinetics of the reaction have been studied indirectly, the rate constant being deduced from the rate of absorption of CO_2 into a flowing film of amine solution, and directly, by monitoring freshly mixed solutions of CO_2 and amine. There is still disagreement, however, about such a fundamental question as to whether the reaction is first-order or second-order in amine. Blauwhoff *et al.*[1] give a survey of the earlier data for the reaction with diethanolamine (DEA).[‡] In Table 4 of their paper, eleven papers, quoting data from a total of seven techniques, state the reaction to be first-order in DEA, and five papers, quoting data from four techniques, state the reaction to be second-order in DEA. Some of the techniques used were quite indirect, and not primarily designed to establish reaction order. The direct technique of stopped-flow spectrophotometry,[2,3] in which aqueous solutions are rapidly mixed and the consequent pH change is displayed by an indicator, comes out clearly in favour of first-order dependence on [DEA].

A possible explanation of the ambiguity is provided by Danckwerts.[4] The mechanism proposed involves two steps, in the first of which a zwitterion is formed:

$$CO_2 + R_2NH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2\overset{+}{N}HCO_2^-$$

$$R_2\overset{+}{N}CO_2^- + R_2NH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2NCO_2^- + R_2\overset{+}{N}H_2$$

If it is assumed that the zwitterion is present in only very low concentrations, the steady-state approximation can be made. If z is the zwitterion concentration, and x the concentration of ionic products:

$$\frac{dz}{dt} = k_1[CO_2][R_2NH] - k_{-1}z - k_2z[R_2NH] + k_{-2}x^2 = 0 \quad (1)$$

If it is further assumed that $k_{-2}x^2$ is small by comparison with the other terms:

$$\frac{dx}{dt} = k_2z[R_2NH] \quad (2)$$

so that

$$\frac{dx}{dt} = \frac{k_1[CO_2][R_2NH]}{1 + (k_{-1}/k_2[R_2NH])} \quad (3)$$

Either of two limiting approximations can be made. If $(k_{-1}/k_2[R_2NH]) \gg 1$, equation (3) reduces to:

$$\frac{dx}{dt} = k_1k_2[CO_2][R_2NH]^2/k_{-1} \quad (4)$$

i.e. second-order in amine. If, on the other hand, $(k_{-1}/k_2[R_2NH]) \ll 1$, equation (3) reduces to:

$$\frac{dx}{dt} = k_1[CO_2][R_2NH] \quad (5)$$

i.e. first-order in amine.

Studies of carbamate formation in aqueous solution are rendered more complex by the hydrolysis equilibrium of CO_2:[§]

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

The hydration is comparatively slow, having a rate constant of $3.6 \times 10^{-2}\ s^{-1}$ at 25 °C. In order to avoid this complication, we have studied the reaction in solution in anhydrous ethanol. There is already one study[5] of the reaction of CO_2 with monoethanolamine (MEA)[‡] and DEA in non-aqueous solvents, but this is by an indirect method, measuring the rate of absorption of gaseous CO_2. The reaction was found to be second-order in amine for both DEA and MEA in ethanol solution. In ethanediol, the reaction with MEA was also second-order, but the reaction with cyclohexylamine was first-order. These observations can be rationalised by the Danckwerts scheme. Since cyclohexylamine is a stronger base than MEA, k_{-1} is less for cyclohexylamine. Proton loss from the zwitterion is presumably diffusion-controlled, so that k_2 is similar for the two amines. The consequent effect on $k_{-1}/k_2[R_2NH]$ is sufficient to make equation (5) valid rather than equation (4).

In this study we use the direct method to measure the rate of reaction between DEA and CO_2 in anhydrous ethanol to determine the order and produce values of actual constants. Carbamate formation is monitored by conductivity, as the only ions present are the products. It was first necessary to measure the overall equilibrium constant for the reaction, since it does not go to completion. This was also measured conductimetrically.

Equilibrium Results.—Representative values for κ, the specific conductivity, for a series of solutions of CO_2 and DEA in anhydrous ethanol are given in Table 1. The measured κ was corrected, using data from runs with no CO_2 present, to allow for ionic impurities in the ethanol and the DEA. A correction was also made for the effect of changing viscosity of the solution with increasing [DEA], using values extrapolated from

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[‡] 2,2′-Iminodiethanol.

[§] 2-Aminoethanol.

Table 1. Equilibrium data[a]

$[DEA]_0$/ mol dm^{-3}	κ/µS cm^{-1}	κ_{corr}/ µS cm^{-1}	K^*/dm^3 mol^{-1}	κ_{corr}^*/ µS cm^{-1}	K/dm^3 mol^{-1}	$K_A/10^{-3}$ [b]
0.009	48	48	11.14	28	1.07	3.61
0.018	81	82	8.60	52	0.98	5.13
0.027	102	104	5.06	74	0.97	4.84
0.036	119	122	3.53	93	0.93	4.44
0.045	132	136	2.54	111	0.93	3.72
0.144	223	235	0.99	235	0.99	
0.170	235	249	0.91	249	0.91	
0.196	245	262	0.91	262	0.91	
0.222	253	272	0.97	272	0.97	
0.247	258	279	1.04	279	1.04	

[a] T 25.0 °C; $[CO_2]_0$ 0.0450 mol dm^{-3}. [b] Acid dissociation constant of the zwitterion.

Table 2. Calculation of Λ and K_3[a]

$[CO_2]_0$/mol dm^{-3}	κ/µS cm^{-1}	κ_{corr}/µS cm^{-1}	$([CO_2]_0/\kappa_{corr})$/ 10^3 mol S^{-1} cm^{-2}
0.042	266	300	141
0.036	242	272	134
0.031	223	249	126
0.027	204	227	119
0.019	168	185	106
0.014	139	151	94
0.008	101	106	79
0	11	0	

[a] T 25.0 °C; [DEA] 0.3889 mol l^{-1}. $\Lambda(R_2NH_2^+, R_2NCO_2^-) = 22.1$ S cm^2 mol^{-1}; $\Lambda(HCl) = 65.0$ S cm^2 mol^{-1}; $\Lambda(R_2NH_2^+Cl^-) = 35.6$ S cm^2 mol^{-1}; $\Lambda(R_2NCO_2^-, H^+) = 51.5$ S cm^2 mol^{-1}.

Table 3. Thermodynamic data[a]

T/°C	$\Lambda(R_2\overset{+}{N}H_2, RNOCO_2^-)$/mho cm^2 mol^{-1}	K/dm^3 mol^{-1}	K_3/dm^3 mol^{-1}
15.0	22.5	1.680	174
19.0	21.8	1.150	170
25.0	22.1	0.960	157
30.0	25.2	0.620	145
35.0	24.8	0.296	138

[a] $\Delta H^\circ = -60.0 \pm 9$ kJ mol^{-1}; $\Delta S^\circ = -203 \pm 30$ J K^{-1} mol^{-1}. $\Delta H_3^\circ = -9.0 \pm 1$ kJ mol^{-1}; $\Delta S_3^\circ = +12 \pm 4$ J K^{-1} mol^{-1}.

Table 4. Kinetic data[a]

$[DED]_0$/mol dm^{-3}	k_{obs}/s^{-1}	k_{calc}/s^{-1}
0.40	16	16
0.50	27	24
0.75	54	55
0.79	65	61
0.90	85	79
0.95	89	88
1.00	96	97
1.05	106	107
1.19	143	137
1.25	145	152
1.50	206	218
1.58	245	242

[a] T 25.0 °C; $[CO_2]_0$ 0.040 mol dm^{-3}. From gradient $k_1k_2/k_{-1} = 97 \pm 2$ dm^3 mol^{-1} s^{-1}.

solutions of high [DEA] in which all the CO_2 had reacted. The corrected values are tabulated as κ_{corr}. Because the solvent is of comparatively low permittivity, ion-pairing must be allowed for; κ_{corr} cannot be used as a direct measurement of carbamate concentration. The ion-pairing equilibrium:

$$R_2\overset{+}{N}H_2 + R_2NCO_2^- \rightleftharpoons R_2\overset{+}{N}H_2{\cdot}R_2NCO_2^-$$

has equilibrium constant K_3, given by:

$$K_3 = [R_2\overset{+}{N}H_2{\cdot}R_2NCO_2^-]/[R_2\overset{+}{N}H_2][R_2NCO_2^-] \quad (6)$$

At high [DEA] all the CO_2 is present as either $R_2NCO_2^-$ or as $R_2\overset{+}{N}_2{\cdot}R_2NCO_2^-$.

$$\kappa = (\Lambda^2/10^6K_3)([CO_2]_0/\kappa) - \Lambda/10^3K_3 \quad (7)$$

where Λ is the molar conductivity of the ionised carbamate. Table 2 gives the data from which Λ and K_3 are calculated from the gradient and intercept of the straight-line plot. The values of $[R_2\overset{+}{N}H_2]$ and $[R_2NCO_2^-]$ were then calculated from κ_{corr} at low [DEA], and $[CO_2]$ and $[R_2NH]$ were calculated from mass balance considerations. This gave a series of values for K, represented in Table 1 as K^*, where

$$K = [R_2\overset{+}{N}H_2][R_2NCO_2^-]/[R_2NH]^2[CO_2] \quad (8)$$

Inspection of Table 1 shows that there is a serious error at the lowest [DEA] values. This is attributed to protonation of the solvent ethanol by the zwitterion at amine concentrations at less than the 2:1 molar ratio needed to produce *N,N*-dialkyl carbamate from CO_2. In other words, the solutions contain ionised carbamic acid. The molar conductivity of the ionised acid was calculated, using Kohlrausch's law, to be 51.5 S cm^2 mol^{-1}, from the molar conductivities of HCl (65.0 S cm^2 mol^{-1}), $(HOC_2H_5)_2\overset{+}{N}H_2$, Cl^- (35.6 S cm^2 mol^{-1}), and $(HOC_2H_5)_2\overset{+}{N}H_2$, $(HOC_2H_5)_2NCO_2^-$ (22.1 S cm^2 mol^{-1}).

An iterative method was used to calculate the values of κ_{corr} at low [DEA] so as to give the same values of K^* as at high [DEA]. These values are tabulated as κ_{corr}^* in Table 1. The corrected values of κ^* are listed as K.

As can be seen in Table 1, the values of K_A are reasonable constant, considering the number of steps from the raw data. This confirms the hypothesis that the high values of κ^* at low [DEA] are due to free carbamic acid formation.

The experiments were repeated over a range of temperatures from 15—35 °C to give the data shown in Table 3, from which enthalpies and entropies of reaction were calculated. ΔH° and ΔS° are the values for the formation of ionic products from the reagents, and ΔH_3° and ΔS_3° are the values for ion-pair formation from the ionic products.

Kinetics Results.—Kinetics were studied under pseudo-first-order conditions, with DEA in large excess. Good first-order plots were invariably obtained. Representative observed first-order rate constants, k_{obs}, are listed in Table 4. A plot of k_{obs} against $[DEA]^2$ gave a good straight line, showing the reaction to be second-order in amine. The values of k_{calc} in Table 4 are those calculated for k_{obs} for a gradient of 97 dm^6 mol^{-2} s^{-1}.

According to the kinetic analysis, the gradient of the plot of k_{obs} against $[DEA]^2$ is k_1k_2/k_{-1}. Since

$$K = k_1k_2/k_{-1}k_{-2} \quad (9)$$

k_{-2} may be calculated. Values of k_{-2} for temperatures in the range 15—35 °C are listed in Table 5, together with the calculated values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

Table 5. Activation data[a]

T/°C	k_{-2}/dm^3 mol^{-1} s^{-1}
15.0	41
19.0	74
25.0	97
30.0	166
35.0	392

[a] $\Delta H^‡ = 78 \pm 9$ kJ mol^{-1}; $\Delta S^‡ = +50 \pm 5$ J K^{-1} mol^{-1}.

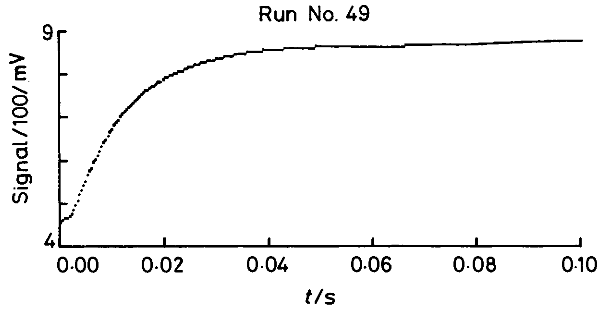

Figure. A typical run. $T = 25$ °C; [DEA] 0.9 mn dm^{-3}; [CO$_2$] 0.05 mol dm^{-3}

Experimental

Materials.—Commercial samples were used. Carbon dioxide, from cylinders (Distillers), was dried over 4Å Microsieve. Diethanolamine (BDH, AR grade) was used without further purification. Ethanol (James Burroughs, AR grade) was dried over 4Å Microsieve.

Equilibrium Measurements.—A stock solution of CO$_2$ was prepared by bubbling CO$_2$ gas from a cylinder through anhydrous ethanol until saturation. A sample was transferred to a closed three-neck Quickfit 250 cm^3 flask, under positive nitrogen pressure, and titrated with 1.000 mol dm^{-3} NaOH from an Agla micrometer syringe, using phenolphthalein as indicator. The rest of the CO$_2$ solution was transferred under positive nitrogen pressure to a similar flask in a water thermostat, fitted with a pair of conductivity electrodes. Small aliquots of concentrated (6.27 mol dm^{-3}) DEA solution in ethanol were added from an Agla micrometer syringe, and the conductivity after each addition was measured, using a digital meter (PTI 58). In order to investigate ion-pairing, the DEA concentration had to be high and constant, with various concentrations of CO$_2$. This was achieved by withdrawing aliquots of the solution at the end of the titration, and making up the lost volume with DEA solutions of the appropriate concentration.

Kinetic Measurements.—Solutions of DEA and CO$_2$ in ethanol were mixed in a stopped-flow apparatus (Hi-Tech Scientific Ltd). The observation cell is a cylindrical cavity (3 mm diameter, 3 mm length) in a Teflon block, the ends being sealed by platinum foil electrodes. The electrodes were coated with platinum black using the standard procedure. The conductivity was measured by a circuit due to Knipe *et al.*,[6] which gives an output voltage directly proportional to solution conductivity. The voltage was digitised by a 12-bit A/D converter (AI 13, Interactive Structures Ltd) and displayed on and processed by an Apple IIe microcomputer. A typical trace is shown in the Figure. All traces were analysed according to simple first-order kinetics, and gave good first-order plots.

Discussion

The thermodynamic data are readily interpreted. The small $-\Delta H^{\ominus}$ for ion-pairing is reasonable for a weak interaction. The small $\Delta S^{\ominus}$ is at first sight surprising for an aggregation process, but the large decrease in entropy due to association is presumably offset by the loss in order as solvating ethanol molecules are released from the ions. Carbamate formation has a fairly large $-\Delta H^{\ominus}$, and the low equilibrium constant is due to the counter-acting effect of a large $-\Delta S^{\ominus}$. Three species aggregate to two, and there is a large increase in solvent order due to solvation of the ions formed.

Since only one rate constant is obtained, a complete description of the kinetics can only be achieved by intelligent guesswork. It is reasonable to assume that k_2 is diffusion-controlled, being an exergonic proton transfer between nitrogen centres. If we make allowance for steric factors, k_2 may be taken to be of the order of 10^8 dm^3 mol^{-1} s^{-1}. Since k_{-2} is about 10^2 dm^3 mol^{-1} s^{-1} at 25 °C, K_2, defined by

$$K_2 = \frac{[R_2NCO_2^-][R_2\overset{+}{N}H_2]}{[R_2\overset{+}{N}HCO_2^-][R_2NH]} = k_2/k_{-2} \tag{10}$$

is of the order of 10^6 (dimensionless). Since K is about 1 dm^3 mol^{-1}, K_1, defined by

$$K_1 = \frac{[R_2\overset{+}{N}HCO_2^-]}{[R_2NH][CO_2]} = k_1/k_{-1} \tag{11}$$

is of the order of 10^{-6} dm^3 mol^{-1}.

For second-order kinetics in the Danckwerts scheme, k_{-1} must be much greater than k_2[R$_2$NH]. In a typical experiment [R$_2$NH] is of the order of 1 mol dm^{-3}, so that k_{-1} must be much greater than 10^8 s^{-1}. If we take k_{-1} as 10^9 s^{-1}, then k_1 becomes 10^3 dm^3 mol^{-1} s^{-1}.

We can test the validity of the assumptions made in the Danckwerts scheme. From equation (1):

$$Z = \frac{k_1[CO_2][R_2NH] + k_{-2}x^2}{k_{-1} + k_2[R_2NH]} \tag{12}$$

Substitution of typical values of CO$_2$ (10^{-2} mol dm^{-3}), (R$_2$NH) (1 mol dm^{-3}), and x (10^{-2} mol dm^{-3}) gives a value of z of 10^{-8} mol dm^{-3}, in accordance with the idea that the zwitterion is a reaction intermediate at very low concentration. Substitution of these typical concentrations into the right-hand-side (r.h.s.) of equation (1) gives:

$$k_1\,[CO_2][R_2NH] = 10 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$k_{-1}z = 10 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$k_2z[R_2NH] = 10^{-2} \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$k_{-2}x^2 = 10^{-2} \text{ mol dm}^{-3}\text{ s}^{-1}$$

These values are compatible with the assumptions made in deriving equation (4).

It is reasonable to assume that the activation energy for the exergonic proton transfer is low, so that the $\Delta H^‡$ value calculated from the temperature variation of k_{-2} gives a good estimate of $\Delta H_2^{\ominus}$, the enthalpy change for the second step. If we make this assumption, then $\Delta H_3^{\ominus}$, the enthalpy of formation of the zwitterion, becomes +20 kJ mol^{-1}. If K_1 is 10^{-6} dm^3 mol^{-1}, then $\Delta G^{\ominus}$, is +34 kJ mol^{-1} at 298 K, which implies a value of -47 J K^{-1} mol^{-1} for $\Delta S_1^{\ominus}$. The decrease in entropy is attributable to association of reactant molecules, and to the greater solvation of the zwitterion product. Hence $\Delta S_2^{\ominus}$ is estimated to be $-157\ \mathrm{J\ K^{-1}\ mol^{-1}}$, reflecting the still greater solvation of the ionic products. Since $\Delta S^{\ddagger}$ for the reverse second step is $+50\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta S^{\ddagger}$ for the reaction of zwitterion and amine is estimated to be $-107\ \mathrm{J\ K^{-1}\ mol^{-1}}$. This is in accordance with increasing solvation as the ions are formed in the transition state.

Although the received opinion among investigators of this reaction is that it proceeds by a two-step mechanism, it is worth noting that the data presented in this paper are also consistent with a single-step termolecular reaction. The observed rate is then the rate of the forward reaction. Analysis of the variation of rate constant with temperature gives $\Delta H^{\ddagger}$ to be $19 \pm 2\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S^{\ddagger}$ to be $-144 \pm 5\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The large negative $\Delta S^{\ddagger}$ is as expected for a termolecular reaction, and the reaction is moderately fast because of the low $\Delta H^{\ddagger}$.

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