Reactions between Carbon Dioxide and Amino Alcohols

III. Diethanolamine

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When carbon dioxide reacts with diethanolamine in aqueous solutions the product formed is a mixture of carbamate and monoalkyl carbonate. The previous conclusion of carbamate being the main product was verified for not too alkaline solutions. In strongly alkaline solution, however, the amount of monoalkyl carbonate formed was big enough for evaluating velocity constants for the formation and decomposition.

For the determination of carbonate a complexometric method was used, which was based on the reaction between barium ion and versenate ion.

1. Carbon dioxide reacts with amino alcohols containing primary and secondary amino groups to yield carbamate and monoalkyl carbonate. Previous experiments [1] show that carbamate is the main product in the case of ethanolamine and diethanolamine.

The present paper reports additional experiments with diethanolamine in order to disclose the formation of monoalkyl carbonate.

2. The method of analysis was in principle as in previous investigations. Added barium chloride precipitates carbonate, but not carbamate or monoalkyl carbonate. The barium carbonate is separated by centrifugation. In the previous method the supernatant was heated until the carbamate and monoalkyl carbonate had been decomposed and been precipitated as barium carbonate, which was titrated acidimetrically. In the numbered experiments of this publication a slightly modified method was used.

To make the separation faster, the electric centrifuge was replaced by a hand-driven one and the sample size was diminished from 100 to 8 ml. The possibility of titrating barium ion [2] with reasonable accuracy suggested the determination of excess barium ion in the supernatant. The details are as follows:

8.00 ml of the specimen is run into a centrifuge tube (15 ml) containing 1.000 ml 0.25 M barium chloride. To mix the contents the tube is inverted twice before centrifugation. 5.00 ml of the supernatant are run into 15.00 ml 0.01 M sodium versenate + 10

drops of phthaleinpurpur-I. To neutralize the sodium hydroxide a slight excess of am-
monium chloride is added. After an addition of 10 ml concentrated ammonia and 50 ml
96 % ethanol the excess of versenate is titrated with 0.005 M barium chloride.

The method is tested by titration of carbonate in solutions of potassium bicarbonate
in 0.2 N sodium hydroxide. To make sure that diethanolamine does not enhance super-
saturation this substance was added to some of the solutions. The results are in Table 1.

The precision of the method is comparable to the precision of the previous method,
maybe slightly less, which, however, is amply compensated by the increased speed. 30
seconds suffice to separate the barium carbonate from the liquid.

Table 1. Complexometric determination of carbonate.

mM CO_3^{--}/litre	found				mean	deviation
	without diethanolamine					
6.54	6.59	6.79	6.47	6.41	6.57	+0.03
8.06	8.26	7.90	8.24	8.10	8.13	+0.07
9.86	9.87	10.00	10.03	9.94	9.96	+0.10
14.95	14.87	14.82	15.00	15.09	14.95	0.00
20.34	20.28	20.30	20.37	20.48	20.36	+0.02
27.52	27.52	27.34	27.34	27.43	27.41	−0.11
	with diethanolamine					
10.43	10.26	10.49	10.40	10.58	10.43	˙ 0.00
15.17	15.17	15.28	15.15	15.26	15.22	+0.05
24.29	24.38	24.32	24.20	24.11	24.25	−0.04

3. The problem of simultaneous formation of carbamate and monoalkyl
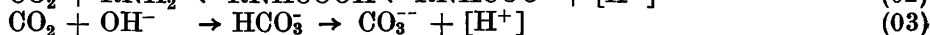carbonate is attacked in two ways.

One is to determine, how the carbon dioxide is shared instantaneously
between carbonate and non-carbonate, when it is dissolved in aqueous solu-
tions of varying concentration of sodium hydroxide and diethanolamine. The
term, non-carbonate, stands for the sum of monoalkyl carbonate and carba-
mate.

A second is to determine the rate of the decomposition of the non-carbo-
nate. Monoalkyl carbonates usually decompose with a higher rate and devia-
tion from a first order reaction should be expected.

4. The experiments were carried out at 0° and 18° C. Velocity constants
are calculated by means of Briggs' logarithms, which shall be thus under-
stood: In the integrated expressions the base e is substituted by 10 without
any compensation. As in previous publications the velocity constants are to be
multiplied by $\log_e 10$ for correction. As the reactions take place between
neutral molecules or neutral molecules and monovalent ions disregard of
activity coefficients is used as a working approximation.

5. To simplify the necessary calculations the velocity constants previously
used are substituted by symbols introduced by Christiansen [3].

When carbon dioxide reacts with alkaline solutions of amine and alcohol
and during the decomposition of the non-carbonate formed the following
processes compete:

$$CO_2 + RO^- \quad \rightleftharpoons ROCOO^- \tag{01}$$

$$CO_2 + RNH_2 \rightleftharpoons RNHCOOH \rightleftharpoons RNHCOO^- + [H^+] \tag{02}$$

$$CO_2 + OH^- \quad \rightarrow HCO_3^- \rightarrow CO_3^- + [H^+] \tag{03}$$

RO^- and RNH_2 meaning alcoholate ion and amine, respectively. The hydrogen ions are removed by hydroxyl ions.

The reactions may diagrammatically be represented by:
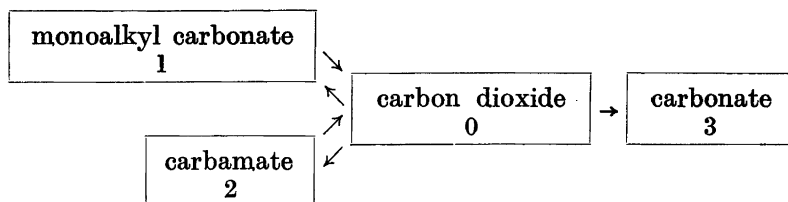
x_0, x_1, x_2, x_3 and x will be used for the concentrations of carbon dioxide, monoalkyl carbonate, carbamate, carbonate and non-carbonate, respectively.

The velocities are:

$$s_{10} = x_1 \cdot w_{10} - x_0 \cdot w_{01}$$
$$s_{20} = x_2 \cdot w_{20} - x_0 \cdot w_{02}$$
$$s_{03} = \qquad\quad x_0 \cdot w_{03}$$

where, introducing the previously used symbols

$$w_{01} = k_{CO_2 \cdot RO^-} \cdot c_{RO^-} = k' \cdot c_{ROH} \cdot c_{OH^-}$$
$$w_{02} = k_{CO_2 \cdot Am} \cdot c_{RNH_2}$$
$$w_{03} = k_{CO_2 \cdot OH^-} \cdot c_{OH^-}$$
$$w_{10} = k_{ROCOO^-}$$
$$w_{20} = k_{RNHCOO^- \cdot H^+} \cdot c_{H^+}$$

ADDITION OF CARBON DIOXIDE TO SOLUTIONS OF DIETHANOLAMINE

1. The carbon dioxide introduced is shared between non-carbonate and carbonate within a small fraction of a second. The reactions (10) and (20) may be disregarded and thus the quotient non-carbonate: carbonate is equal to $(w_{01} + w_{02})$: w_{03}.

w_{01} and w_{03} are proportional to the concentration of hydroxyl ion while w_{02} is independent.

$$\frac{w_{01} + w_{02}}{w_{03}} \text{ multiplied by } \frac{c_{OH^-}}{c_{amino\ alcohol}}$$

gives us

$$\frac{k'}{k_{CO_2 \cdot OH^-}} \cdot c_{OH^-} + \frac{k_{CO_2 \cdot Am}}{k_{CO_2 \cdot OH^-}}$$

This expression being linearly dependent on the concentration of hydroxyl ion, we can calculate k' and $k_{CO_2 \cdot Am}$ from two experiments with different concentration of hydroxyl ion (log $k_{CO_2 \cdot OH^-}$ being fixed at 4.39 and 5.02 at 0° and 18° C, respectively).

    2. A preliminary experiment (4) is performed on a solution, which besides sodium hydroxide contains an amine (diethylamine) without alcohol groups and an alcohol (triethanolamine) without primary or secondary amino groups.

    In Table 2 this experiment (4) is compared with experiments (1—3) where only one of the compounds is present in the alkaline solution. From the velocity constant calculated from the experiments 1—3, it was calculated that 21.9 % monoalkyl carbonate and 39.8 % carbamate should be formed. The sum agrees reasonably with the found percentage of non-carbonate.

Table 2. Carbon dioxide in amine + alcohol + NaOH. 18°.

No.	Initial solution			Absorbed CO_2/litre	% non-carbonate		log k'	log k_{CO_2} . Am
	c_{NaOH}	$c_{Triethanol-amine}$	$c_{Diethyl-amine}$		% monoalkyl carbonate	% carbamate		
1	0.2	0.4		0.0250	54.0		5.49	
2	0.2	0.2		0.0269	35.6		5.47	
3	0.2		0.06	0.0205		50.8		5.56*
4	0.2	0.2	0.06	0.0230	experimental 65.2 calculated 21.9 + 39.8			

    * Vibeke Lund and Carl Faurholt [4] find 5.46 applying 10 % CO_2.

    3. In Table 3 are listed experimental values for addition of carbon dioxide to solutions of diethanolamine and sodium hydroxide at 0° C. The velocity constants have been calculated and the division of non-carbonate into monoalkyl carbonate and carbamate is estimated.

Table 3. Carbon dioxide in diethanolamine + NaOH. 0°.

Initial solution		Absorbed CO_2/litre	% non-carbonate experimental	$\dfrac{w_{01} + w_{02}}{w_{03}} \cdot \dfrac{c_{OH^-}}{c_{Diethanolamine}}$	log k' [1]	log k_{CO_2}. Am [2]	% non-carbonate calculated	
c_{NaOH}	$c_{Dietha-nolamine}$						% monoalkyl carbonate	% carbamate
0.1	0.1	0.0192	52.9	1.02		4.25	15.4	38.8
	0.2	0.0196	71.0	1.11		4.29	20.2	50.2
	0.3	0.0198	78.9	1.13		4.30	22.6	55.6
0.2	0.1	0.0205	41.2	1.34	4.80	4.23	19.5	23.0
	0.2	0.0200	61.5	1.53	5.04	4.33	27.7	32.2
	0.3	0.0210	71.6	1.61	5.11	4.37	32.0	37.1
0.3	0.1	0.0210	34.9	1.57	4.78	4.15	21.3	16.3
	0.2	0.0215	52.7	1.63	4.83	4.18	31.2	23.7
	0.3	0.0203	65.9	1.89	4.99	4.33	36.8	27.8
				Mean:	4.94	4.28		

    [1] Calculated from the mean of the first three determinations.
    [2] Calculated from the mean of k'.

Evidently a fairly high proportion of monoalkyl carbonate is found.

In judging the velocity constants found one must, however, as previous work [5] on the subject has shown, bear in mind that the experimental results are to no small extent dependent on the way in which carbon dioxide has been added. In all the experiments present, atmospheric air, of which 30 % was substituted by carbon dioxide, has been applied. In a 1-litre flask, containing 250 ml of the reaction mixture, 250 ml of the gas phase were substituted by carbon dioxide from a gasometer. The flask was immediately shaken vigorously for about one minute.

It should be noticed that the fifth column of Table 3 shows for constant concentration of hydroxyl ion a slight increase with an increasing concentration of diethanolamine, which might be due to a perceptible amount of hydroxyl ions being consumed by the alcohol groups of diethanolamine. Glass electrode measurements on 0.04 N NaOH and various amounts of diethanolamine, ranging from 0.0 to 0.3 M, showed no difference in potential, however.

THE CONVERSION: NON-CARBONATE → CARBONATE

1. Before mentioning the experiments on the velocity of decomposition the mathematical and calculatory aspects should be examined.

The following differential equations:

$$s_{10} = -\mathrm{d}x_1/\mathrm{d}t = x_1 \cdot w_{10} - x_0 \cdot w_{01}$$
$$s_{20} = -\mathrm{d}x_2/\mathrm{d}t = x_2 \cdot w_{20} - x_0 \cdot w_{02}$$

combined with the stationarity condition for the free carbon dioxide

$$s_{10} + s_{20} = s_{03} = x_0 \cdot w_{03}$$

yield solutions of the form

$$x_1 = a_1 \cdot \exp(-k_1 \cdot t) + b_1 \cdot \exp(-k_2 \cdot t)$$
$$x_2 = a_2 \cdot \exp(-k_1 \cdot t) + b_2 \cdot \exp(-k_2 \cdot t)$$
$$x = x_1 + x_2 = A \cdot \exp(-k_1 \cdot t) + B \cdot \exp(-k_2 \cdot t)$$

$-k_1$ and $-k_2$ being roots in the auxiliary equation

$$R^2 + \frac{w_{10} \cdot (w_{02} + w_{03}) + w_{20} \cdot (w_{01} + w_{03})}{w_{01} + w_{02} + w_{03}} \cdot R + \frac{w_{10} \cdot w_{20} \cdot w_{03}}{w_{01} + w_{02} + w_{03}} = 0$$

The solution is

$$k_1 = \frac{w_{10} \cdot (w_{02} + w_{03}) + \varepsilon}{w_{01} + w_{02} + w_{03}} \qquad k_2 = \frac{w_{10} \cdot w_{20} \cdot w_{03}}{w_{10} \cdot (w_{02} + w_{03}) + \varepsilon}$$

where ε is a root in

$$\varepsilon^2 + [w_{10} \cdot (w_{02} + w_{03}) - w_{20} \cdot (w_{01} + w_{03})]\, \varepsilon - w_{10} \cdot w_{20} \cdot w_{01} \cdot w_{02} = 0$$

Now the assumption is made:

$$w_{10} \cdot w_{0i} \gg w_{20} \cdot w_{0j} \quad (i \text{ and } j = 1, 2 \text{ or } 3)$$

i. e. the monoalkyl carbonate is decomposed very fast compared with the carbamate, and w_{01}, w_{02} and w_{03} are of the same order of magnitude. This assumption is supported by the fact that the experiments clearly reveal the presence of two processes, k_1 and k_2 thus differing in order of magnitude.

Choosing ε as the positive root of the above equation, the following inequalities hold:

$$0 < \varepsilon < w_{20} \cdot (w_{01} + w_{03}) \lll w_{10} \cdot (w_{02} + w_{03})$$

When the total carbon dioxide concentration is C the initial

$$x_1 = \frac{w_{01}}{w_{01} + w_{02} + w_{03}} \cdot C \text{ and } x_2 = \frac{w_{02}}{w_{01} + w_{02} + w_{03}} \cdot C$$

Inserting these concentrations as boundary conditions we get for A and B:

$$A = \frac{w_{10} \cdot w_{01} \cdot w_{03} - w_{20} \cdot w_{01} \cdot (w_{01} + w_{02} + w_{03}) + \varepsilon \cdot (w_{01} + w_{02})}{(w_{01} + w_{02} + w_{03}) \cdot [w_{10} \cdot (w_{02} + w_{03}) - w_{20} \cdot (w_{01} + w_{03}) + 2\,\varepsilon]} \cdot C$$

$$B = \frac{w_{10} \cdot w_{02} \cdot (w_{01} + w_{02} + w_{03}) - w_{20} \cdot w_{02} \cdot w_{03} + \varepsilon \cdot (w_{01} + w_{02})}{(w_{01} + w_{02} + w_{03}) \cdot [w_{10} \cdot (w_{02} + w_{03}) - w_{20} (w_{01} + w_{03}) + 2\,\varepsilon]} \cdot C$$

Disregarding ε and $w_{20} \cdot w_{0i}$ in sums and differences of $w_{10} \cdot w_{0j}$ reduces k_1, k_2, A and B to

$$k_1 \sim w_{10} \cdot \frac{w_{02} + w_{03}}{w_{01} + w_{02} + w_{03}}$$

$$k_2 \sim w_{20} \cdot \frac{w_{03}}{w_{02} + w_{03}}$$

$$A \sim \frac{w_{03}}{w_{02} + w_{03}} \cdot \frac{w_{01}}{w_{01} + w_{02} + w_{03}} \cdot C$$

$$B \sim \frac{w_{02}}{w_{02} + w_{03}} \cdot C$$

The significance of the approximated expressions is directly seen from the diagram, imagining the monoalkyl carbonate being quickly decomposed partly to carbamate and partly to carbonate while the carbamate slowly decomposes to carbonate. k_1 is a fraction of w_{10} corresponding to the carbon dioxide from 10 not reverting along 01. k_2 is a fraction of w_{20} corresponding to the carbon dioxide from 20 not reverting along 02 and neglecting the reaction 01. A is the fraction of the initial monoalkyl carbonate, which is temporarily not converted to carbamate. B is the amount of carbamate that was formed initially when no alcohol groups were present.

w_{03} ($= k_{CO_2 \cdot OH^-} \cdot c_{OH^-}$) is known, hence B, A, k_2 and k_1 give us w_{02}, w_{01}, w_{20} and w_{10}, successively.

To get the parameters A, B, k_1 and k_2 of each experiment, the results are subjected to a linear regression analysis in two steps. From the experimental values where the contribution of $A \cdot \exp(-k_1 \cdot t)$ is vanishing, $\log x$ is taken as
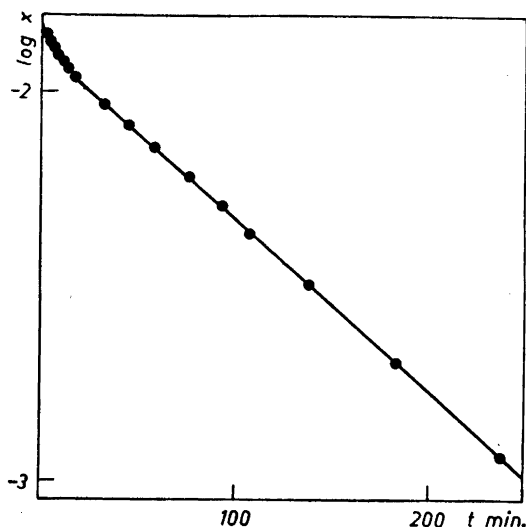
Fig. 1. The decomposition of the non-carbonate from solution 4.

the dependent variable and t as the independent variable. We then have an estimate of B and k_2. The contribution from the term $B \cdot \exp(-k_2 \cdot t)$ is extrapolated back to the first values and the differences are formed. The differences are subjected to a similar analysis and we have an estimate of A and k_1.

We proceeded on the lines laid down by A. Hald [6]. x is assumed to have a normal distribution with constant variance. Hence the variance on log x is inversely proportional to the square of x. Therefore, to each value of x a weight has been ascribed proportional to the square of the value.

2. The decomposition of the non-carbonate in the solutions from Table 2 is investigated. The three first solutions which either contain alcohol groups or amino groups give a first order rate as expected. The last, however, containing both alcohol groups and amino groups, deviates distinctly in the beginning of the experiment, *cf.* Fig. 1.

Table 4. Decomposition of non-carbonate from Table 2. Experimental part.

No.	A *	B	C	k_1	k_2
1	0.0135		0.0250	0.0302	
2	0.0096		0.0269	0.0445	
3		0.0104	0.0205		0.00392
4	0.0021	0.0129	0.0230	0.0665	0.00436

* Regarding the significance of symbols, see text.

Table 5. Decomposition of non-carbonate from Table 2. Calculated part.

No.	$\log k'$	$\log \dfrac{k_{CO_2 \cdot Am}}{}$	k_{ROCOO^-}	$k_{RNHCOO^-} \cdot H^+ \cdot K_{H_2O}$	% monoalkyl carbonate	% carbamate
1	5.49		0.066		54.0	
2	5.47		0.069		35.6	
3		5.56		0.00135		50.8
4	5.50	5.65	0.084	0.00160	20.6	44.6

In Tables 4 and 5 the experimental values, *i. e.* the parameters calculated from the experimental values by the regression analysis, and the calculated velocity constants are listed, respectively. The results from the mixture of the amine and alcohol are seen to agree with the experiments where only one of the groups is present.

To get a comparison between parameters from the regression analysis and the concrete, experimental values, Table 6 has been constructed.

Table 6. Comparison between experimental values from solution No. 4 and the corresponding regression analysis.

Experimental		$A \cdot \exp(-k_1 \cdot t) + B \cdot \exp(-k_2 \cdot t)$ *			Deviation
t	x				
0	(0.01498)	0.00207	+	0.01291	
2.1	0.01409	0.00150	+	0.01264	+0.00005
4.0	0.01355	0.00112	+	0.01241	−0.00002
6.3	0.01296	0.00079	+	0.01212	−0.00005
8.3	0.01235	0.00058	+	0.01188	+0.00011
11.0	0.01192	0.00038	+	0.01156	+0.00002
13.7	0.01154	0.00025	+	0.01125	−0.00004
17.0	0.01095	0.00015	+	0.01089	+0.00009
31.9	0.00928	0.00002	+	0.00937	+0.00011
45.1	0.00826	0.00001	+	0.00821	−0.00004
58.3	0.00722	0.00000	+	0.00719	−0.00003
76.0	0.00606	0.00000	+	0.00602	−0.00004
93.1	0.00513	0.00000	+	0.00507	−0.00006
107.5	0.00434	0.00000	+	0.00439	+0.00005
137.6	0.00321	0.00000	+	0.00324	+0.00003
183.2	0.00203	0.00000	+	0.00205	+0.00002
236.8	0.00115	0.00000	+	0.00120	+0.00005

* Numerical values of A, B, k_1 and k_2 are found in Table 4.

3. Finally, similar experiments were made on diethanolamine at 18° C. Here also a deviation from a first order reaction was found which clearly showed the formation of monoalkyl carbonate. Experimental and calculated results are listed in Tables 7 and 8, respectively.

Table 7. Formation and decomposition of non-carbonate of diethanolamine. 18°.
Experimental part.

No.	Initial solution		A *	B	C	k_1	k_2
	c_{OH^-}	$c_{diethanolamine}$					
5	0.2	0.2	0.0009	0.0106	0.0199	0.065	0.00084
6	0.3	0.1	0.0014	0.0063	0.0245	0.070	0.00103
7	0.3	0.3	0.0019	0.0108	0.0206	0.047	0.00057

* Regarding the significance of symbols, see text.

Table 8. Formation and decomposition of non-carbonate of diethanolamine. 18°.
Calculated part.

No.	$\log k'$	$\log k_{CO_2 \cdot Am}$	k_{ROCOO^-}	$k_{RNHCOO^- \cdot H^+} \cdot K_{H_2O}$	%monoalkyl carbonate	% carbamate
5	5.06	5.05	0.072	0.00033	9.1	48.3
6	5.09	5.02	0.076	0.00035	7.8	23.8
7	5.25	4.99	0.058	0.00031	19.2	42.4
Mean	5.14	5.02	0.069	0.00033		

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