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Reactions between Carbon Dioxide and Amino Alcohols

II. Triethanolamine

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1. The present investigation deals with the equilibrium conditions and the reaction mechanism for the formation and decomposition of the monoalkyl carbonate of triethanolamine in aqueous medium. It should be mentioned that tertiary amines do not react with carbon dioxide to form carbamates. The conditions are thus analogous to those of previously investigated alcohols [1].

2. The triethanolamine used was purified by converting it into the chloride according to Germann and Knight [2]. Melting point was found to be 177—79° C, when heated 3—4°/min. By argentometric titration we obtained results corresponding to a content of 100.0 % triethanolammonium chloride. In the experiments the solutions of triethanolamine were prepared not of the free amine but of the chloride to which was added an equivalent amount of sodium hydroxide.

3. No solid monoalkyl carbonate was prepared. Solutions were made by dissolving carbon dioxide in basic solutions of the triethanolamine.

4. As to the method of analysis we refer to previous investigations [1]. The data presented are corrected with regard to blank values unless otherwise stated. "Uncorr." values are not corrected at all and "corr." values are corrected not only with regard to blank values but also with regard to the decomposition mentioned in the next section. The blank values may amount to about 3 units of the percentage of monoalkyl carbonate in some of the experiments.

5. The experiments were carried out at 0° C. Velocity constants are expressed on the basis of the Briggs' logarithms and the minute.

6. Hall and Sprinkle [3] have found pK for triethanolamine at 0° C to be 8.22. As pH in all the solutions used for experiments is above 10 it means that we can ignore the triethanolammonium ions in this connection.

ON THE FORMATION OF THE MONOALKYL CARBONATE FROM CARBON DIOXIDE AND TRIETHANOLAMINE IN BASIC SOLUTION AND ON THE REACTION:

$$N(CH_2{\cdot}CH_2OH)_2{\cdot}CH_2{\cdot}CH_2O^- + CO_2 = N(CH_2{\cdot}CH_2OH)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_3^-$$

The experiments were carried out in a flask by vigorously shaking the solution of triethanolamine and sodium hydroxide with atmospheric air of which about 30 % was substituted by carbon dioxide. The solution was immediately analysed to determine the percentage of monoalkyl carbonate. Due to the rapid decomposition of the monoalkyl carbonate, we had to correct the results by means of the velocity constants which we also have determined, see later.

By introduction of the adjusted results in the expression:

$$k' = \frac{\%\text{ monoalkyl carbonate}}{\%\text{ carbonate}} \cdot \frac{k_{CO_2 \cdot OH^-}}{c_{\text{alcohol}}}$$

the k' values presented in Table 1 are calculated. k' is the velocity constant of the overall reaction:

$$CO_2 + N(CH_2 \cdot CH_2OH)_3 + OH^- = N(CH_2 \cdot CH_2OH)_2 \cdot CH_2 \cdot CH_2 \cdot CO_3^- + H_2O$$

Table 1. Carbon dioxide in triethanolamine + NaOH. 0°.

Initial solution		Absorbed CO_2 mole/liter	% monoalkyl carbonate	% monoalkyl carbonate (corr.)	k'	Mean of k'
c_{NaOH}	$c_{N(CH_2 \cdot CH_2OH)_3}$					
0.10	0.10	0.0206	31.6	34.1	$10^{5.13}$	$10^{5.14}$
0.10	0.20	0.0200	50.2	53.1	$10^{5.15}$	
0.10	0.50	0.0199	70.6	72.7	$10^{5.13}$	

For the value of $k_{\text{alkyl} \cdot CO_3^-}$ we get 0.0073 when the value of K_{Eq} found in Table 2 is employed.

THE EQUILIBRIUM OF THE REACTIONS:

$$N(CH_2 \cdot CH_2OH)_2 \cdot CH_2 \cdot CH_2 \cdot CO_3^- + H_2O \rightleftharpoons HCO_3^- + N(CH_2 \cdot CH_2OH)_3$$

The above equilibrium was established in aqueous solutions of triethanolamine, potassium bicarbonate and sodium carbonate.

In Table 2 are presented the contents of monoalkyl carbonate calculated as a percentage of HCO_3^- initially present. In order to illustrate the accuracy that may be attached to the values, the uncorrected values have also been listed. From the experimental results the equilibrium constant of the reaction

$$K_{Eq} = \frac{c_{N(CH_2 \cdot CH_2OH)_3} \cdot c_{HCO_3^-} \cdot f}{c_{N(CH_2 \cdot CH_2OH)_2 \cdot CH_2 \cdot CH_2 \cdot CO_3^-} \cdot f}$$

may be calculated, the activity constants neutralizing each other.

Table 2. The solution of carbonate—monoalkyl carbonate in equilibrium. 0°.

Initial solution			% monoalkyl carbonate		K_{Eq}	Mean of K_{Eq}
$c_{N(CH_2 \cdot CH_2OH)_3}$	c_{KHCO_3}	$c_{Na_2CO_3}$	uncorr.	corr.		
0.50	0.10	0.10	5.56	4.94[1]	$10^{0.98}$	$10^{1.00}$
0.20	0.20	0.10	2.09	1.87[2]	$10^{1.02}$	

[1] Mean of 4 determinations: 4.85, 4.89, 5.02, 5.00.

[2] Mean of 4 determinations: 1.88, 1.84, 1.86, 1.91.

ON THE VELOCITY OF THE REACTIONS:

$$N(CH_2 \cdot CH_2OH)_2 \cdot CH_2 \cdot CH_2 \cdot CO_3^- + H_2O = HCO_3^- + N(CH_2 \cdot CH_2OH)_3$$

Determinations have been made from the monoalkyl carbonate side only and in strongly basic medium, the monoalkyl carbonate thus being almost completely converted into carbonate.

The solutions of monoalkyl carbonate have been made by shaking a solution of NaOH + triethanolamine with CO_2 and the solution, therefore, also contains ordinary carbonate, which, however, is of no importance to the present investigation.

In Table 3 are listed the experimental results of the decomposition of the monoalkyl carbonate. k_{Mono} is the value of $\frac{1}{t} \cdot \log \frac{a}{a-x}$.

Table 3. Monoalkyl carbonate in NaOH + alcohol. 0°.

Initial solution			Min.	%monoalkyl carbonate left	k_{Mono}
$c_{monoalkyl\ carbonate}$	c NaOH	$c_{alcohol}$			
0.007	0.10	0.10	0	100	—
			5	93.0	0.00630
			11	87.1	0.00545
			19	76.4	0.00615
			33	65.1	0.00565
			62	46.4	0.00538
			102	29.9	0.00514
			164	14.7	0.00508
				Mean:	0.0056
0.011	0.10	0.20	0	100	—
			9	91.1	0.00450
			21	79.8	0.00467
			38	69.6	0.00414
			70	52.4	0.00401
			108	37.6	0.00393
			178	20.7	0.00384
			279	10.2	0.00355
				Mean:	0.0041
0.014	0.10	0.50	0	100	—
			13	93.8	0.00214
			30	86.8	0.00205
			50	78.8	0.00207
			88	65.0	0.00213
			137	52.1	0.00207
			219	36.2	0.00202
			346	18.4	0.00212
				Mean:	0.0021

The experiments are interpreted in a way similar to the one applied to the monoalkyl carbonates previously investigated. The decomposition takes place through the reactions:

$$1.\ \text{alkyl} \cdot CO_3^- = \text{alkylate}^- + CO_2$$

$$2.\ CO_2 + OH^- = HCO_3^-$$

k_{Mono} may be calculated at $pa_H > 10$ by means of the following expression:

$$k_{\text{Mono}} = \frac{k' \cdot K_{Eq} \cdot \dfrac{K_{H_2O}}{K_{CO_2}}}{1 + k' \cdot \dfrac{c_{\text{alcohol}}}{k_{CO_2 \cdot OH^-}}}$$

the values of K_{H_2O} and K_{CO_2} being $10^{-14.93}$ and $10^{-6.85}$, respectively.

Upon introduction of the constants the equation for triethanolamine is:

$$k_{\text{Mono}} = \frac{0.0073}{1 + 5.6 \cdot c_{\text{alcohol}}}$$

k_{Mono} for the monoalkyl carbonate of triethanolamine in 0.5 M, 0.2 M and 0.1 M solutions of triethanolamine, pH $>$ 10, will then be calculated to 0.0019, 0.0034 and 0.0047, respectively. The experimental and calculated values agree well.

SUMMARY

The velocity constants of the reaction "$N(CH_2{\cdot}CH_2OH)_3 + OH^- + CO_2 = N(CH_2{\cdot}CH_2OH)_2 \cdot CH_2{\cdot}CH_2{\cdot}CO_3^- + H_2O$" and the equilibrium constant for the reaction "$N(CH_2{\cdot}CH_2OH)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_3^- + H_2O = N(CH_2{\cdot}CH_2OH)_3 + HCO_3^-$" have been determined. The velocity of the decomposition of $N(CH_2{\cdot}CH_2OH)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_3^-$ in strongly basic medium was investigated and may be explained by assuming that the decomposition is a two-stage reaction, *viz.*

monoalkyl carbonate = alcohol + carbon dioxide
carbon dioxide = carbonate.

REFERENCES

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