

## Reactions between Carbon Dioxide and Amino Alcohols

### IV. Tris(hydroxymethyl)aminomethane \*

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It has been shown that carbon dioxide reacts with one of the hydroxyl groups in tris(hydroxymethyl)aminomethane (= tris) — not with the amino group — giving rise to the formation of monoalkyl carbonate. Thus, the reaction between tris and carbon dioxide may be treated in the same way as a reaction between an alcohol and carbon dioxide. The velocity constant for the reaction "alcohol (= tris) + OH<sup>-</sup> + CO<sub>2</sub> = alkyl-CO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O" and the equilibrium constant for the equilibrium "alkyl-CO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O ⇌ HCO<sub>3</sub><sup>-</sup> + alcohol" have been determined. The velocity of the decomposition of the monoalkyl carbonate in strongly basic medium is investigated and may be explained by assuming that the decomposition takes place through the reactions: (1) monoalkyl carbonate = alcoholate + CO<sub>2</sub>, (2) CO<sub>2</sub> + OH<sup>-</sup> = HCO<sub>3</sub><sup>-</sup>.

1. The present investigation deals with the equilibrium conditions and the reaction mechanism for the formation and decomposition of the monoalkyl carbonate formed by tris, NH<sub>2</sub>C(CH<sub>2</sub>OH)<sub>3</sub>, in aqueous medium. As this compound contains a primary amino group as well as hydroxyl groups one might expect a simultaneous formation of carbamate and alkyl carbonate when carbon dioxide is allowed to react with tris in aqueous solution. However, our experimental results are consistent with the assumption that there is a predominant formation of alkyl carbonate (for details, see next section). Therefore, tris is considered to behave like an alcohol and the experimental data have been treated in the same way as the data in earlier publications on monoalkyl carbonates. These publications (see, for instance, Ref.<sup>1</sup>) should be consulted for detailed informations concerning theory, significance of constants *etc.*

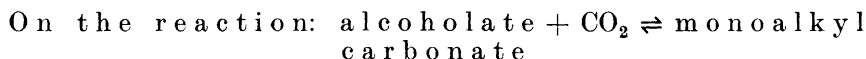
2. The tris used for the experiments was furnished by the Sigma Chemical Company as "SIGMA 121". It was used without further purification.

3. The method of analysis was essentially the same as that used in earlier investigations on carbamates and monoalkyl carbonates. The carbonate is

\* This compound will hereafter be referred to as tris.

precipitated as barium carbonate by the addition of barium chloride to solutions approx. 0.1 N in sodium hydroxide. The alkyl carbonate remains in solution. The barium carbonate is separated from the mother liquor by centrifugation and the amount of alkyl carbonate in the supernatant may be determined either by the method introduced by Tovborg-Jensen<sup>2,3</sup> or by heating the supernatant in which case the alkyl carbonate is converted to carbonate. The carbonate will precipitate as barium carbonate and may be titrated acidimetrically after washing. The total amount of carbonate and alkyl carbonate was determined in a similar way and the carbonate content was obtained as a difference. As in previous investigations it was found necessary to carry out blank determinations.

4. The experiments were carried out at 0°C. The velocity constants are calculated by means of Briggs' logarithms using the minute as the unit of time.



The experiments were carried out by shaking basic solutions of tris with a mixture of air and carbon dioxide (approx. 15 % CO<sub>2</sub>). The solutions were immediately analyzed for carbonate and non-carbonate (*i.e.* carbon dioxide combined with tris). The composition of the solutions, the total amount of carbon dioxide absorbed and the percentage of non-carbonate are listed in Table 1. It will be seen from the table (the four first experiments) that the percentage of non-carbonate is nearly independent of the concentration of hydroxyl ion for equal concentration of tris. From this it is concluded that the carbon dioxide combined with the tris has reacted with one of the alcohol groups — at least to a very great extent — and not with the amino group. The percentage of monoalkyl carbonate, formed when basic solutions of an alcohol are shaken with carbon dioxide, will depend on the concentration of the alcohol only, not on the concentration of hydroxyl ion. On the other hand, the percentage of carbamate, the reaction product between an amine and carbon dioxide, formed when basic solutions of the amine are shaken with carbon dioxide, will depend on the ratio [amine]/[OH<sup>-</sup>] (Ref<sup>4</sup>). Thus, the data in

Table 1. Carbon dioxide in tris + NaOH. 0°C.

[NaOH]	[H <sub>2</sub> NC(CH <sub>2</sub> OH) <sub>3</sub> ]	Absorb. CO <sub>2</sub> mole/litre	% non-carbonate (= % alkyl carbonate)	log <i>k'</i>
0.05	0.20	0.0258	43.1	5.60
0.10	0.20	0.0232	42.8	5.60
0.10	0.20	0.0215	44.8	5.64
0.20	0.20	0.0182	41.6	5.58
0.10	0.10	0.0196	28.9	5.64
0.10	0.30	0.0240	55.6	5.64
				mean: 5.62

Table 1 are best interpreted in such a way that there is a predominant formation of monoalkyl carbonate. The velocity constant,  $k'$ , for the gross reaction

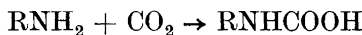


has been calculated from the expression

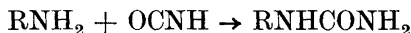
$$k' = \frac{\% \text{ monoalkyl carbonate} \times k(\text{CO}_2\cdot\text{OH}^-)}{\% \text{ carbonate} \times [\text{alcohol}]}$$

on the assumption that all of the non-carbonate is monoalkyl carbonate or, in other words, percent monoalkyl carbonate has been put equal to percent non-carbonate. A fairly constant value for  $k'$  is obtained in this way (see Table 1). The mean value for  $k'$  is  $10^{5.62}$ . For the value of  $k(\text{alkyl}\cdot\text{CO}_3^-)$  we get 0.013 when the value of  $K_{\text{Eq}}$  found in Table 3 is used.

It should be added that there is further evidence justifying the assumption that carbon dioxide reacts with one of the alcohol groups rather than with the amino group. Thus, it has been shown<sup>5</sup> that a linear free-energy relationship exists between the velocity constant,  $k(\text{CO}_2\cdot\text{Am})$ , for the reaction between an amine and carbon dioxide



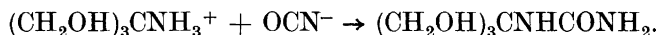
and the velocity constant,  $k(\text{OCNH}\cdot\text{Am})$ , for the reaction between the same amine and cyanic acid yielding alkylsubstituted urea



The relationship is

$$\log k(\text{OCNH}\cdot\text{Am}) = \log k(\text{CO}_2\cdot\text{Am}) - 1.08 \quad (18^\circ\text{C})$$

$k(\text{OCNH}\cdot\text{Am})$  may be obtained from the velocity constant,  $k_u$ , for the reaction



An experiment for the determination of  $k_u$  is given in Table 2. The solution contained a small amount of the free amine to ensure a basic solution, since the cyanate will partially decompose to carbonate in a more acid solution. The decrease in the concentration of the cyanate ion with time was followed by argentometric titration. The reaction will be approximately first order with respect to cyanate since there is a great excess of the aminium ion. The values of  $k$  listed in Table 2 are calculated from the expression for a unimolecular reaction.  $k_u$  (0.00067) was obtained by dividing the mean value of  $k$  by that of the aminium ion concentration (0.17). The value of  $k(\text{OCNH}\cdot\text{Am})$  may now be calculated from  $k_u$  by means of  $k(\text{OCNH}\cdot\text{Am}) = k_u \times K_{\text{Am}} \times 10^{11.03}$  (Ref.<sup>5</sup>), where  $K_{\text{Am}} = 10^{-5.95}$  (Ref.<sup>6</sup>) is the basic dissociation constant for tris. Thus, we get  $k(\text{OCNH}\cdot\text{Am}) = 10^{1.91}$ . The relationship between  $k(\text{OCNH}\cdot\text{Am})$  and  $k(\text{CO}_2\cdot\text{Am})$  gives  $k(\text{CO}_2\cdot\text{Am}) = \text{approx. } 10^3$  at  $18^\circ\text{C}$  corresponding to  $k(\text{CO}_2\cdot\text{Am})$  about  $10^{2.4}$  at  $0^\circ\text{C}$ . However, this value of  $k(\text{CO}_2\cdot\text{Am})$  is exceptionally small compared with those normally found for aliphatic amines. Further, using  $k(\text{CO}_2\cdot\text{Am}) = 10^{2.4}$  it may be calculated that only approx. 1 % of the carbon dioxide will react with the amino group under the formation

Table 2. The velocity constant for the reaction  
 $(\text{CH}_2\text{OH})_3\text{CNH}_3^+ + \text{OCN}^- \rightarrow (\text{CH}_2\text{OH})_3\text{CNHCONH}_2$ . 18°C.\*

<i>t</i> min	% cyanate left	<i>k</i>
343	91.1	0.000119
1309	69.3	0.000122
1959	58.8	0.000117
3054	43.7	0.000118
4241	33.4	0.000113
5645	23.7	0.000111
7402	15.6	0.000109
		mean: 0.000115

$$k_d = 0.000115/0.17 = 0.000670$$

\* Initial solution: 0.180 M  $(\text{CH}_2\text{OH})_3\text{CNH}_3\text{NO}_3$  0.04 M  $(\text{CH}_2\text{OH})_3\text{CNH}_2$  0.0203 M KOCN.

of carbamate when solutions of tris and sodium hydroxide in approx. equal concentrations are shaken with carbon dioxide.

The equilibrium of the reaction:  
 $\text{alkyl} \cdot \text{CO}_3^- + \text{H}_2\text{O} = \text{HCO}_3^- + \text{alcohol}$

The above equilibrium was established in aqueous solutions of tris, potassium bicarbonate and sodium carbonate. The experiments are given in Table 3. " % alkyl carbonate " is that percentage of the bicarbonate initial present which is converted to alkyl carbonate.  $K_{\text{Eq}}$ , the equilibrium constant for the reaction, was calculated from the experimental data by means of

$$K_{\text{Eq}} = \frac{[\text{alcohol}] \times [\text{HCO}_3^-] \times f}{[\text{alkyl} \cdot \text{CO}_3^-] \times f}$$

where the activity coefficients cancel. The total concentration of tris minus the concentration of alkyl carbonate has been set equal to [alcohol] since practically all of the tris will be present as  $(\text{CH}_2\text{OH})_3\text{CNH}_2$ , not as  $(\text{CH}_2\text{OH})_3\text{CNH}_3^+$ . ( $K_{\text{Am}} = \text{approx. } 10^{-6}$  (Ref.<sup>6</sup>)).

Table 3. The solutions of carbonate-monoalkyl carbonate in equilibrium. 0°C.

Initial solution			% alkyl carbonate	log $K_{\text{Eq}}$
[alcohol]	[KHCO <sub>3</sub> ]	[Na <sub>2</sub> CO <sub>3</sub> ]		
0.50	0.10	0.20	7.50 <sup>a</sup>	0.78
0.20	0.20	0.10	3.18 <sup>b</sup>	0.77
				mean: 0.78

<sup>a</sup> mean of 2 determinations: 7.44 7.56

<sup>b</sup> » » 4 » 3.17 3.18 3.19 3.20

Table 4. Monoalkyl carbonate in NaOH + alcohol.\* 0°C.

<i>t</i> min.	% alkyl carbonate left	<i>k</i>
9	67.1	0.00101
14	63.6	0.00234
24	61.1	0.00209
55	53.1	0.00201
94	42.3	0.00222
146	38.1	0.00175
210	27.6	0.00181
270	24.1	0.00168
		mean: 0.0019

\* Initial solution: 0.1 M NaOH 0.5 M alcohol 0.0066 M alkyl·CO<sub>3</sub><sup>-</sup>.

The velocity of the reaction:  
 alkyl·CO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O = HCO<sub>3</sub><sup>-</sup> + alcohol

Experiments were carried out from the monoalkyl carbonate side only and in strongly basic solution where the alkyl carbonate is converted practically completely into carbonate.

The monoalkyl carbonate has been made by shaking the basic solution with carbon dioxide. The solution, therefore, contained ordinary carbonate, which is of no importance in the present investigation.

A typical experiment is listed in Table 4.  $k_{\text{mono}}$  is  $(1/t)\log a/(a-x)$ .

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

1. alkyl·CO<sub>3</sub><sup>-</sup> = alcoholate + CO<sub>2</sub>
2. CO<sub>2</sub> + OH<sup>-</sup> = HCO<sub>3</sub><sup>-</sup>.

Thus,  $k_{\text{mono}}$  may be calculated (at pH > 10) from the following expression

$$k_{\text{mono}} = \frac{k' \times K_{\text{Eq}} \times K(\text{H}_2\text{O})/K(\text{CO}_2)}{1 + k' \times [\text{alcohol}]/k(\text{CO}_2 \cdot \text{OH})}$$

One gets  $k_{\text{mono}} = 0.013/(1 + 17.0 \times [\text{alcohol}]) = 0.0014$  in the present case. The agreement between this value and the experimental value found in Table 4 (0.0019) is considered to be satisfactory.

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