

Studies on Monoalkyl Carbonates

XII. The Monoalkyl Carbonates of Ethylene Glycol and Ethylene Chlorohydrin

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1. In previous investigations¹ were studied the equilibrium conditions and the reaction mechanism in aqueous medium of different monoalkyl carbonates, *e.g.* CH_3CO_3^- and $\text{C}_2\text{H}_5\text{CO}_3^-$. The present investigation deals with the monoalkyl carbonates of ethylene glycol and ethylene chlorohydrin.

2. The ethylene glycol used was purified by distillation through a wire-gauze column² with 51 sets of platinum plates; the distillation took place *in vacuo*. One fraction was taken at 113° C and 32 mm Hg pressure, another at 103° C and 20 mm Hg pressure. At 760 mm Hg pressure the boiling point of both fractions was 197.3° C; $n_D^{24.9^\circ}$ was 1.4306 and 1.4305, respectively.

An attempt was made to purify the ethylene chlorohydrin used by the same method as that applied to the ethylene glycol. The attempt failed, however, due to a splitting off of HCl during distillation, whereas an ordinary distillation at a Hg pressure of a few mm proved succesful. The fractions used had a $n_D^{20.1^\circ} = 1.4421$, and at 760 mm Hg a boiling point of 128.6–128.9° C; a determination of halogenide content after Stepanow-Bacon gave the equivalent number 80.71 (theoretically 80.52).

3. No attempt was made to isolate the monoalkyl carbonates as substances. We were content to prepare the solutions in the following way: About 0.02 moles carbon dioxide was dissolved in one liter of a solution, which was 0.5 molar with regard to alcohol and 0.15 molar with regard to NaOH, thus converting about 50 per cent of the carbon dioxide to monoalkyl carbonate, and 50 per cent to ordinary carbonate.

4. The method of analysis was as in previous investigations precipitation with bariumchloride *i.e.* 100 ml sample solution is — provided the hydroxyl ion

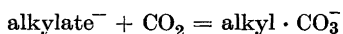
concentration of the solution is less than about 0.1 molar — made 0.1 molar with regard to hydroxyl ion by means of sodium hydroxide. By the addition of barium chloride the carbonate is precipitated, whilst the monoalkyl carbonate remains dissolved. By centrifugation the precipitate and the supernate are separated as quickly as possible. By the heating of the supernate the monoalkyl carbonate is decomposed, forming a precipitate of barium carbonate, which is titrated with 0.1 *N* HCl.

It should be noted that in the case of ethylene chlorohydrin large amounts of NaOH are consumed by ethylene chlorohydrin during the heating of the supernate, and hence sufficient sodium hydroxide was added so that the supernate after the heating was about 0.1 *N* with regard to hydroxyl ion.

Since solutions containing only carbonate, and no monoalkylcarbonate, after precipitation with barium chloride will yield a slight precipitate of barium carbonate upon heating, it was necessary to carry out blank determinations along with the determinations proper. A blank determination was carried out with 100 ml of sample solution of approximately the same composition as that of the corresponding determination proper, and was precipitated, centrifuged, heated, and so on, in identical ways. The blank values amount to about 1 to 2 units of the percentage of monoalkyl carbonate. All of the data presented are corrected with regard to blank values, unless otherwise stated.

5. All of the experiments were carried out at 0° C, the centrifugations, however, in the cold room at 1° C. The velocity constants were calculated by means of Brigg's logarithms, the unit of time being the minute.

On the formation of monoalkyl carbonate from carbon dioxide and alcohol in basic solution, and on the reactions:



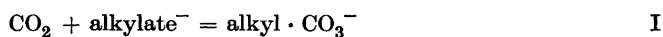
The experiments were carried out in the following way: 500 ml of an aqueous solution containing alcohol as well as sodium hydroxide were placed in a 2 liter flask. Approximately 250 ml of carbon dioxide were substituted for approximately 250 ml of atmospheric air in the gas phase above the solution, and the flask was shaken vigorously for half a minute. It should be explicitly noted that the ethylene chlorohydrin-solution was prepared immediately before adding the carbon dioxide, since ethylene chlorohydrin and NaOH will otherwise react with each other. The solution was immediately analyzed to determine how many per cent of the carbon dioxide absorbed had been converted to monoalkyl carbonate and carbonate, respectively. The results are presented in Table 1.

Since the monoalkyl carbonates are very rapidly decomposed, it was, especially in the case of ethylene chlorohydrin, necessary — by means of the velocity constants determined in section IV — to correct the analytically determined percentage of monoalkyl carbonate for the decomposition taking place during the 5 to 7 minutes passing between the start of the shaking with carbon dioxide, and the separation of precipitate and supernate by centrifugation. In the case of ethylene glycol the correction amounts to 2.5 units of the percentage of monoalkyl carbonate, whereas in the case of ethylene chlorohydrin it amounts to as much as about 10 units. The values listed in the table are corrected to zero time.

Table 1. Carbon dioxide in alcohol + NaOH, 0°.

	Initial solution		Absorbed CO ₂ mol/liter	% alkyl- carbonate	log <i>k'</i>	Mean of log <i>k'</i>
	<i>c</i> _{NaOH}	<i>c</i> _{alcohol}				
CH ₂ OH CH ₂ OH	0.15	0.50	0.0225	46.6 47.1	4.64 4.64	4.64
CH ₂ Cl CH ₂ OH			0.0194	53.6 53.1	4.76 4.75	
	0.15	0.50	0.0230	51.1	4.72	4.74

Corresponding experiments on the alcohols previously investigated might be explained by assuming that carbon dioxide reacts partly with the alkylate ion, partly with the hydroxyl ion, but not with the non-ionized alcohol:

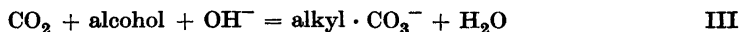


As shown previously this leads to the following expression:

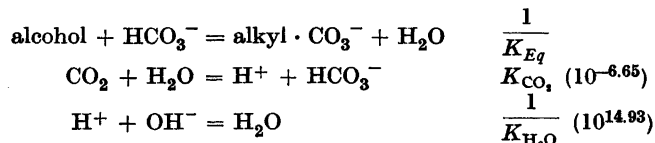
$$k' = \frac{k_{\text{CO}_2 \cdot \text{alkylate}^-}}{K_{\text{alkylate}^-}} = \frac{\text{per cent monoalkyl carbonate}}{\text{per cent carbonate}} \cdot \frac{k_{\text{CO}_2 \cdot \text{OH}^-}}{c_{\text{alcohol}}}; \text{ upon}$$

introduction in this expression of the experimental results with ethylene chlorohydrin and ethylene glycol, the *k'* values presented in Table 1 are obtained. Here $k_{\text{CO}_2 \cdot \text{alkylate}^-}$ and $k_{\text{CO}_2 \cdot \text{OH}^-}$ ($= 10^{4.39}$ at 0° C) signify the velocity con-

stants of reactions I and II, respectively, whilst $K_{\text{alkylate-}}$ is the equilibrium constant for the reaction "alcoholate ion + water = alcohol + hydroxyl ion"; k' is the velocity constant (from left to right) of the gross reaction:



From:

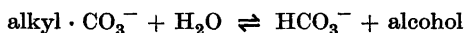


the equilibrium constant, K' , for reaction III may be calculated, and hence may also be calculated the velocity constant, $k_{\text{alkyl} \cdot \text{CO}_3^-}$, for reaction III from right to left:

$$K' = \frac{k'}{k_{\text{alkyl} \cdot \text{CO}_3^-}} = \frac{K_{\text{CO}_2}}{K_{\text{H}_2\text{O}} \cdot K_{Eq}} = \frac{10^{-6.65}}{10^{-14.93} \cdot K_{Eq}}$$

where K_{Eq} is the equilibrium constant found in section III. In this way is found for ethylene glycol $k_{\text{alkyl} \cdot \text{CO}_3^-} = 0.0063$, and for ethylene chlorohydrin $k_{\text{alkyl} \cdot \text{CO}_3^-} = 0.032$.

The equilibrium of the reactions:



The above equilibrium was established in aqueous solutions of the alcohol, hydrogen carbonate, and carbonate. By the alcohols studied in the present investigation the equilibrium is shifted strongly to the right, and thus the determinations of per cent alkyl carbonate may be encumbered with rather large errors.

Equilibrium was established at 0° C in solutions which were 1.0 *M* with regard to alcohol, 0.1 *M* with regard to KHCO_3 , and 0.05 *M* with regard to Na_2CO_3 . The content of monoalkyl carbonate was determined and was calculated as per cent of HCO_3^- initially present; thus no attention was paid to carbonate. For ethylene glycol 7 determinations in 2 series (4 + 3) were carried out, and for ethylene chlorohydrin 8 determinations in 2 series (4 + 4) were carried out; the results are presented in Table 2; to illustrate, how much importance may be attached to the accuracy of the values found, are presented in the table not only the "% alkyl carbonate" corrected for blank

values, but the uncorrected ones as well. From the experimental results the equilibrium constant of the reaction,

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

may be calculated, the activity coefficients neutralizing each other. It should be noted that the above weakly basic solutions were left for about 30 hours before being analyzed. During this time some ethylene chlorohydrin must have been decomposed. An analysis showed, however, that the amount decomposed was so slight as to be insignificant. After 30 hours the molarity of ionogen chlorine in the 1 *M* ethylene chlorohydrin was no more than 0.0008.

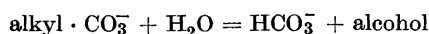
Table 2. The solution of carbonate-alkylcarbonate in equilibrium. 0°.

	Initial solution			% alkylcarbonate		K_{Eq}
	c_{alcohol}	c_{KHCO_3}	$c_{\text{Na}_2\text{CO}_3}$	incorr.	corr.	
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	1.0	0.1	0.05	4.18	3.50 ¹	10 ^{1,44}
$\begin{array}{c} \text{CH}_2\text{Cl} \\ \\ \text{CH}_2\text{OH} \end{array}$	1.0	0.1	0.05	1.70	0.88 ²	10 ^{2,05}

¹ Mean of 7 determinations: 3.43, 3.48, 3.67, 3.43, 3.48, 3.58, 3.45.

² » » 8 » » 0.96, 0.78, 0.93, 0.86, 0.91, 0.89, 0.83, 0.87.

On the velocity of the reactions:



Concerning the preparation of the solutions used we refer to the introduction. The initial concentration of monoalkyl carbonate was in the case of ethylene glycol approximately 0.010 *M*, and in the case of ethylene chlorohydrin approximately 0.006 *M*. The concentration of alcohol was in both experiments 0.49 *M*, and the molarity of sodium hydroxide was 0.12 and 0.11, respectively.

In Table 3 “% alkyl carbonate left” indicates how many per cent of the monoalkyl carbonate have not yet been decomposed. In both cases the reaction may, after a sufficiently long time, be considered as having run to completion, and as k_{mono} is found the calculated value of $\frac{1}{t} \log \frac{a}{a-x}$.

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. $\text{alkyl} \cdot \text{CO}_3^- = \text{alkylate}^- + \text{CO}_2$
2. $\text{CO}_2 + \text{OH}^- = \text{HCO}_3^-$

and, as shown in a previous investigation^{1b}, the velocity constant k_{mono} may at $\text{pH} >$ about 10 be calculated by means of the following expression:

$$k_{\text{mono}} = \frac{k_{\text{alkyl} \cdot \text{CO}_3^-}}{1 + \frac{k_{\text{CO}_2 \cdot \text{alkylate}^-}}{K_{\text{alkylate}^-}} \cdot \frac{c_{\text{alcohol}}}{k_{\text{CO}_2 \cdot \text{OH}^-}}} = \frac{k' \cdot K_{\text{Eq}} \cdot \frac{K_{\text{H}_2\text{O}}}{K_{\text{CO}_2}}}{1 + k' \cdot \frac{c_{\text{alcohol}}}{k_{\text{CO}_2 \cdot \text{OH}^-}}}$$

which, upon introduction of the constants, gives for ethylene glycol:

$$k_{\text{mono}} = \frac{0.0063}{1 + 1.78 \cdot c_{\text{alcohol}}} = 0.0034 \text{ (calc.)}$$

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

	Initial solution			Min.	% alkyl-carbonate left	k_{mono}
	$c_{\text{alkylcarbonate}}$	c_{NaOH}	c_{alcohol}			
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	0.010	0.12	0.49	0	100	—
				20	84.6	0.00363
				44	70.3	0.00348
				88	46.6	0.00376
				148	28.9	0.00365
				195	20.0	0.00358
				256	11.2	0.00371
				Mean:	0.0036	
$\begin{array}{c} \text{CH}_2\text{Cl} \\ \\ \text{CH}_2\text{OH} \end{array}$	0.006	0.11	0.49	0	100	—
				8.5	72.0	0.0168
				17	51.6	0.0172
				25	35.9	0.0180
				33	25.9	0.0180
				40	18.7	0.0181
				49	15.0	0.0170
				Mean:	0.018	

and for ethylene chlorohydrin:

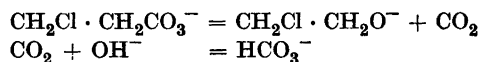
$$k_{\text{mono}} = \frac{0.032}{1 + 2.24 \cdot c_{\text{alcohol}}} = 0.015 \text{ (calc.)}$$

0.49 being introduced for c_{alcohol} .

The experimental and the calculated values agree surprisingly well; especially when the errors of determination of K_{Eg} and k' are taken into consideration.

SUMMARY

The velocity constant of the reaction " $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{O}^- + \text{CO}_2 = \text{CH}_2\text{Cl} \cdot \text{CH}_2\text{CO}_3^-$ " and the equilibrium constant for the reaction " $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{CO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{Cl} \cdot \text{CH}_2\text{OH} + \text{HCO}_3^-$ " have been determined. The velocity of the decomposition of $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{CO}_3^-$ in strongly basic medium was investigated and may be explained in assuming that the decomposition is a two-stage reaction, *viz.*



The monoalkyl carbonate of ethylene glycol was studied in a similar way.

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