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Studies on Monoalkyl Carbonates

XVII. The Monoalkyl Carbonate of the Glycolate Ion

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The velocity constant of the reaction '$^-OOC \cdot CH_2OH + OH^- + CO_2 = {}^-OOC \cdot CH_2CO_3^- + H_2O$' and the equilibrium constant of the reaction '$^-OOC \cdot CH_2 \cdot CO_3^- + H_2O = {}^-OOC \cdot CH_2OH + HCO_3^-$' have been determined. The velocity of the decomposition of the monoalkyl carbonate, $^-OOC \cdot CH_2CO_3^-$, in strongly basic medium is investigated and may be explained by assuming that the decomposition is a twostage reaction *viz.* 1) $^-OOC \cdot CH_2CO_3^- = {}^-OOC \cdot CH_2O^- + CO_2$; 2) $CO_2 + OH^- = HCO_3^-$.

1. The present investigation deals with the equilibrium conditions and the reaction mechanisms for the formation and decomposition of the monoalkyl carbonate of glycolate ion in aqueous medium.

The glycolate ion solution was prepared from glycolic acid and the equivalent amount of sodium hydroxide by gentle boiling, so that anhydrides that might be present were converted into sodium glycolate.

2. The glycolic acid employed was obtained partly from the Riedel-de Haen A. G. as an aqueous solution, and partly from The Fischer Scientific Company as crystals stated to be pure. Upon analysis the solution was found to contain 53.5 % of acid by direct titration with 1 N sodium hydroxide, and 57.3 % of glycolic acid and its anhydrides, determined by boiling with extra sodium hydroxide and titration the excess of sodium hydroxide with hydrochlorid acid. The crystals of glycolic acid — having a rather moist appearance — were dried over phosphorus pentoxide losing about 1.9 % in weight. Thereafter they contained 99.5—100.3 % of glycolic acid. Both samples were free of heavy metals and of halides and gave identical results during the investigations.

3. No attempt was made to prepare the solid monoalkyl carbonate. Solutions were made by dissolving carbon dioxide in solutions which were 0.5—2 M with regard to sodium glycolate and 0.1—0.75 M with regard to sodium hydroxide, thus converting 25—60 % of the carbon dioxide into monoalkyl carbonate and the rest of it into ordinary carbonate.

4. The method of analysis was in principle as in previous investigations [1], *viz.* separation of the monoalkyl carbonate from the ordinary carbonate by precipitating the carbonate with barium chloride and separating the barium carbonate by centrifugation. The supernate was then analysed by means of an apparatus for determination of carbon dioxide introduced by Tovborg Jensen [2]. To the supernate is added a large excess of 2 M hydrochloric acid causing an immediate decomposition of the monoalkyl carbonate. The carbon dioxide evolved is then absorbed in 0.1 N barium hydroxide after which the excess of barium hydroxide is titrated electrometrically with 0.1 N hydrochloric acid to pH = 8.5.

By analogy with the investigations on the monoalkyl carbonate of the lactate ion [3] there has, however, been certain difficulties in separating the barium carbonate from the monoalkyl carbonate. Barium chloride added to the solution containing monoalkyl carbonate and carbonate causes no immediate precipitation of barium carbonate. Only after 2—3 min. a fine-grained precipitate consisting of barium carbonate began to settle, the precipitation of which lasted about 15 min.

In order to accelerate the precipitation a good deal of sodium carbonate solution was set to the solution of barium chloride before the reaction mixture was added. Furthermore the 2 M solutions — due to their rather high viscosity — were diluted with equal parts of water before the centrifugation. After shaking for 2 min. and centrifugating for 3 the precipitation of the barium carbonate succeeded. Due to these difficulties it may be taken in consideration that the data presented may be encumbered with larger errors than usual on analogous investigations.

The data presented are, unless otherwise stated, corrected not only with regard to blank values but also with regard to the decomposition of monoalkyl carbonate taking place during the analysis, see later.

5. The experiments were carried out at 0°C. Velocity constants are expressed on the basis of the Brigg's logarithms, the unit of time being the minute.

On the formation of the monoalkyl carbonate from carbon dioxide and glycolate ion and on the reaction

$$^{-}OOC \cdot CH_2O^{-} + CO_2 \rightleftharpoons {}^{-}OOC \cdot CH_2CO_3^{-}$$

The experiments were carried out in a 0.5 litre flask by vigorously shaking 200 ml of a basic solution of sodium glycolate with atmospheric air of which about 100 ml was substituted by carbon dioxide. The solutions were immediately analysed to determine the percentage of monoalkyl carbonate.

By introduction of the adjusted results in the expression:

$$k' = \frac{\% \text{ monoalkyl carbonate} \cdot k_{CO_2OH^-}}{\% \text{ carbonate} \cdot c_{\text{alcohol}}},$$

the k' values presented in Table 1 are calculated, k' being the velocity constant of the overall reaction: $CO_2 + {}^{-}OOC \cdot CH_2OH + OH^{-} = {}^{-}OOC \cdot CH_2CO_3^{-} + H_2O$.

Table 1. Carbon dioxide in sodium glycolate + sodium hydroxide. 0°C.

c_{NaOH}	$c_{glycolate}$	Absorbed CO_2 mole/litre	% Alkyl-carbonate	log k'	Mean of log k'
0.25	0.50	0.0233	25.2	4.22	
0.10	0.50	0.0167	25.2	4.22	
0.20	1.00	0.0208	40.5	4.22	4.23
0.50	1.00	0.0208	38.5	4.19	
0.75	2.00	0.0312	59.5	4.26	
0.50	2.00	0.0184	60.8	4.28	

For the value of the velocity constant of the reverse process $k_{^-OOC\cdot CH_2CO_3^-}$ we get 0.0079 employing the value of K_{eq} mentioned in Table 2.

The equilibrium of the reaction

$$^-OOC\cdot CH_2CO_3^- + H_2O = HCO_3^- + ^-OOC\cdot CH_2OH$$

The above equilibrium was established in aqueous solutions of glycolate ion, potassium bicarbonate and sodium carbonate. The content of monoalkyl carbonate has been calculated as a percentage of HCO_3^- initially present; thus no attention was paid to the carbonate.

In Table 2 are presented not only the '% monoalkyl carbonate' corrected for blank values and the decomposition taking place during the analysis but the uncorrected as well. This has been done in order to illustrate the accuracy that may be attached to the values found. From the experimental results the equilibrium constant of the reaction

$$K_{eq} = \frac{c_{^-OOC\cdot CH_2OH}\cdot f \cdot c_{HCO_3^-}\cdot f}{c_{^-OOC\cdot CH_2CO_3^-}\cdot f^2}$$

may be calculated, the activity constants neutralizing each other as a first approximation.

Table 2. The solutions of carbonate-monoalkyl carbonate in equilibrium, 0°C.

Initial solution			% Alkyl carbonate		log K_{eq}	Mean of log K_{eq}
$c_{glycolate}$	c_{KHCO_3}	$c_{Na_2CO_3}$	uncorr.	corr.		
1.00	0.10	0.05	2.64a)	1.70	1.78	
1.00	0.20	0.10	1.76b)	1.24	1.90	1.88
2.00	0.20	0.10	3.65c)	2.05	1.97	

a) mean of 4 determinations 2.65, 2.74, 2.52, 2.64
b) » » 3 » 1.58, 1.99, 1.72
c) » » 3 » 3.74, 3.53, 3.67

Table 3. Monoalkyl carbonate in sodium hydroxide + glycolate ion, 0°C.

$c_{\text{monoalkyl carbonate}}$	c_{NaOH}	$c_{\text{glycolate}}$	Min	% monoalkyl carbonate left	k_{mono}
0.0054	0.25	0.50	0	100	—
			8	75	(0.01540)
			17	76	0.00724
			25	67	0.00762
			40	50	0.00763
			54	45	0.00636
			91	22	0.00727
			126	11	0.00757
			164	6	0.00737
					Mean 0.0073
0.0038	0.10	0.50	0	100	—
			7	91	0.00617
			18	74	0.00717
			27	62	0.00775
			38	54	0.00702
			51	40	0.00781
			81	34	0.00581
			111	19	0.00658
			156	7	0.00742
					Mean 0.0070
0.006	0.20	1.00	0	100	—
			11	90	0.00425
			28	75	0.00454
			55	72	0.00263
			144	29	0.00375
			187	32	0.00268
			277	11	0.00353
			327	7	0.00355
			347	9	0.00296
					Mean 0.0035
0.011	0.50	1.00	0	100	—
			9	93	0.00329
			24	76	0.00501
			54	64	0.00356
			85	50	0.00352
			113	38	0.00373
			160	25	0.00379
			234	18	0.00321
			287	11	0.00330
					Mean 0.0037
0.008	0.20	1.00	0	100	—
			10	98	(0.00096)
			28	87	0.00216
			54	65	0.00353
			99	33	0.00492
			156	25	0.00382
			278	8	0.00396
			288	6	0.00422
					Mean 0.0038
0.016	0.50	2.00	0	100	—
			9	96	0.00172
			17	91	0.00238
			32	87	0.00183
			61	70	0.00252
			103	69	0.00162
			152	53	0.00179
			300	28	0.00183
			425	19	0.00169

On the velocity of the reactions

$$^{-}OOC \cdot CH_2CO_3^- + H_2O = {}^{-}OOC \cdot CH_2OH + HCO_3^-$$

Determinations have been made from the monoalkyl carbonate side only and in strongly basic medium, the monoalkyl carbonate thus being practically converted into carbonate. The monoalkyl carbonate has been made by shaking the basic solutions with carbon dioxide as stated in the introduction. The solutions, therefore, contain ordinary carbonate, which, however, is of no importance in the present investigations.

In Table 3 are listed the experimental results of the decomposition of the monoalkyl carbonate. k_{mono} stands for $1/t \log a/a-x$.

The experiments are interpreted in a similar way to the one applied to the monoalkyl carbonates previously investigated, the decomposition being a two-stage reaction, *viz.* 1) $^{-}OOC \cdot CH_2CO_3^- = {}^{-}OOC \cdot CH_2O^- + CO_2$; 2) $CO_2 + OH^- = HCO_3^-$

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

$$k_{mono} = \frac{k' \cdot K_{eq} \dfrac{K_{H_2O}}{K_{CO_2}}}{1 + k' \cdot \dfrac{c_{^-OOC \cdot CH_2OH}}{k_{CO_2OH^-}}}$$

the values of K_{H_2O} and K_{CO_2} being $10^{-14.93}$ and $10^{-6.65}$, respectively.

Upon introduction of the constants the equation is

$$k_{mono} = \frac{0.0065}{1 + 0.69\, c_{^-OOC \cdot CH_2OH}}$$

and k_{mono} in 0.5 M, 1 M, and 2 M solutions of glycolate ion, $pa_H > 10$, will be calculated to 0.0048, 0.0038, and 0.0027, respectively.

The experimental and calculated values agree fairly good.

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