Studies on Monoalkyl Carbonates

XIV. The Monoalkyl Carbonates of Sorbitol, Mannitol and Glucose

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By addition of carbon dioxide to an aqueous solution of an alcohol and sodium hydroxide, monoalkyl carbonate and carbonate are formed as the carbon dioxide reacts with the alcoholate ion and the hydroxide ion. Sorbitol, mannitol and glucose also form monoalkyl carbonate with carbon dioxide and the velocity constant and the equilibrium constant for the formation of monoalkyl carbonate have been determined. The velocity of the decomposition of monoalkyl carbonate in strongly basic medium has also been investigated and may be explained by assuming that the decomposition is a two-stage reaction *viz.* (1) $\text{RCO}_3^- = \text{RO}^- + \text{CO}_2$; (2) $\text{CO}_2 + \text{OH}^- = \text{HCO}_3^-$

1. The present investigation deals with the equilibrium conditions and the reaction mechanism for the formation and decomposition of the monoalkyl carbonates of sorbitol, mannitol, and glucose.

2. The sorbitol was either D-sorbitol obtained from the Atlas Powder Co., stated to be of great purity, or crystalline D-sorbitol Merck. The melting point, given as 97.7° C for the stable form, was found to be 96—97° C. The mannitol was D-mannitol from the Pfanstiehl Chemical Co., stated to be pure, and had a melting point of 166—167° C. The melting point of mannitol is given as 166° C. The glucose used was 'Dextropur' from the Corn Products Co. Ltd., Copenhagen. Upon analysis it was found to contain 91.2 % glucose and 8.8 % water, thus corresponding very closely to the formula $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$.

3. As it was difficult to isolate the monoalkyl carbonates themselves the solutions were prepared in the following manner: About 0.03 moles carbon dioxide were dissolved in one litre of a solution, which was 0.10—0.50 molar with regard to alcohol and 0.1 molar with regard to NaOH, thus converting about 20—60 % of the carbon dioxide to monoalkyl carbonate and the rest to ordinary carbonate.

4. The method of analysis was the same as in previous investigations, *viz.* separation of the monoalkyl carbonate from the ordinary carbonate by precipitating the carbonate with barium chloride¹. The data presented are cor-

Table 1 a. 500 ml carbon dioxide solution in 500 ml ROH + NaOH. 0°C.

	Expt. No.	Initial concn. NaOH	Initial concn. ROH	Compositions of the solutions *			Absorbed CO ₂ mole/litre	% RCO ₂ ⁻	% RCO ₂ ⁻ (corr.)	log $k_{\text{CO}_2 \cdot \text{RO}^-}$
				COH ⁻	CROH	CRO ⁻				
Sorbitol	1	0.20	0.20	0.1164 0.0351	0.1164 0.0757	0.0836 0.0166	0.028	23.70	27.52	4.15
	2			0.1164 0.0352	0.1164 0.0756	0.0836 0.0166	0.028	24.15	27.86	4.16
Mannitol	3	0.20	0.20	0.1125 0.0355	0.1125 0.0735	0.0875 0.0185	0.027	25.70	29.51	4.15
	4			0.1125 0.0360	0.1125 0.0728	0.0875 0.0186	0.027	28.07	31.83	4.21
	5	0.20	0.50	0.0575 0.0242	0.3575 0.2005	0.1425 0.0345	0.028	48.30	52.35	4.10
	6			0.0575 0.0216	0.3575 0.2052	0.1425 0.0318	0.025	49.91	53.55	4.11
Glucose	7	0.20	0.20	0.0396 0.0099	0.0396 0.0479	0.1604 0.0481	0.023	12.41	17.59	3.10
	8			0.0396 0.0076	0.0396 0.0436	0.1604 0.0414	0.028	12.59	17.81	3.09
	9	0.20	0.50	0.0067 0.0041	0.3067 0.1721	0.1933 0.0729	0.014	28.82	37.13	2.77
	10			0.0067 0.0047	0.3067 0.1667	0.1933 0.0793	0.010	30.78	40.46	2.84
	11	0.20	1.00	0.0034 0.0016	0.8034 0.4176	0.1966 0.0704	0.020	51.74	60.73	2.85
	12			0.0034 0.0014	0.8034 0.4214	0.1966 0.0606	0.028	53.77	62.95	2.89

* Cf. footnote to Table 1.

rected for the blank values and for decomposition as mentioned in the next section. The experiments were carried out at 0°C. The velocity constants were calculated by means of Briggs' logarithms and with the time measured in minutes.

I. ON THE FORMATION OF MONOALKYL CARBONATE FROM CARBON DIOXIDE AND ALCOHOL IN BASIC SOLUTIONS, AND ON THE REACTION

$$\text{RO}^- + \text{CO}_2 = \text{RCO}_2^-$$

The first series of experiments was carried out by introducing 500 ml carbon dioxide gas into a 2.5 litre flask containing 1 litre of a basic solution of the alcohol and shaking vigorously for 2 minutes. As the manner in which the

Table 1. Carbon dioxide gas in ROH + NaOH. 0°C.

	Expt. No.	Initial concn. NaOH	Initial concn. ROH	Composition of the solutions *			Absorbed CO ₂ mole/litre	% RCO ₃ ⁻	% RCO ₃ ⁻ (corr.)	log $k_{\text{CO}_2 \cdot \text{RO}^-}$
Sorbitol	1	0.1	0.1	0.0700	0.0700	0.0300	0.023	33.62	39.50	4.57
	2			0.0435	0.0713	0.0196				
	3			0.0700	0.0700	0.0300	0.026	33.72	39.62	4.57
	3			0.0402	0.0716	0.0181				
Mannitol	4	0.1	0.1	0.0670	0.0670	0.0330	0.031	32.80	39.00	4.50
	5			0.0340	0.0710	0.0165				
	6	0.1	0.25	0.0420	0.1920	0.0580	0.025	59.00	64.50	4.51
	6			0.0280	0.1960	0.0378				
	7			0.0420	0.1920	0.0580	0.008	56.80	66.00	4.54
	7			0.0380	0.1940	0.0508				
	8	0.2	0.25	0.0420	0.1920	0.0580	0.022	59.30	64.00	4.50
	8			0.0300	0.1960	0.0403				
Glucose	9	0.1	0.1	0.099	0.1490	0.1010	0.021	54.20	59.20	4.54
	10			0.083	0.1550	0.0868				
	11			0.0270	0.0270	0.0730	0.041	12.86	21.09	3.32
	11			0.0037	0.0685	0.0229				
	12	0.1	0.25	0.0270	0.0270	0.0730	0.031	14.59	22.34	3.33
	13			0.0065	0.0547	0.0384				
	14			0.0270	0.0270	0.0730	0.014	15.70	21.42	3.33
	14			0.0151	0.0371	0.0599				
	15	0.2	0.25	0.0060	0.1560	0.0940	0.035	27.09	37.83	2.96
	16			0.0021	0.1957	0.0411				
	17			0.0060	0.1560	0.0940	0.034	30.58	42.22	3.03
	18			0.0023	0.1915	0.0441				
	19	0.1	0.50	0.0060	0.1560	0.0940	0.017	32.33	43.61	3.06
	20			0.0039	0.1731	0.0695				
	21			0.0240	0.0740	0.1760	0.036	32.00	43.67	3.36
	22			0.0129	0.0989	0.1308				
	23	0.2	0.50	0.0240	0.0740	0.1760	0.035	29.44	39.72	3.39
	24			0.0130	0.0989	0.1309				
	25			0.0020	0.4020	0.0980	0.038	50.13	60.97	2.90
	26			0.0010	0.4390	0.0462				
	27	0.1	0.50	0.0020	0.4020	0.0980	0.043	47.15	58.01	2.85
	28			0.0008	0.4438	0.0381				
	29			0.0020	0.4020	0.0980	0.031	49.84	59.91	2.88
	30			0.0012	0.4322	0.0554				
	31	0.2	0.50	0.0060	0.3060	0.1940	0.049	48.91	60.87	3.06
	32			0.0035	0.3525	0.1283				

* In the column 'composition of the solutions' are two sets of values. The upper one states the concentrations of hydroxyl ion OH⁻, undissociated alcohol ROH, and alcoholate ion RO⁻ before the addition of carbon dioxide gas, and the lower set states these concentrations immediately after the addition. The lower set of values are corrected for the change in the concentration of alcohol and sodium hydroxide due to the reaction with the carbon dioxide. In further calculations the mean values of the upper and lower figures are used.

carbon dioxide was added to the solution could possibly influence the ratio between monoalkyl carbonate and carbonate (*cf.* the analogous experiments with carbamate and carbonate²) a second series of experiments was carried out. In these experiments 500 ml of a 0.06 M solution of carbon dioxide in water was added to 500 ml of the basic solution of alcohol with vigorous stirring. The two series of experiments disagree especially for sorbitol and mannitol. The difference could possibly be ascribed to the different concentrations of the reactants during the addition of the carbon dioxide.

Immediately after the addition of carbon dioxide the reaction solution was analysed for monoalkyl carbonate. The results are listed in the Tables 1 and 1a.

Because of the very rapid decomposition of the monoalkyl carbonate the results are corrected not only with respect to the blanks but also with respect to the decomposition taking place during the time which elapses between the start of the experiment and the separation of the precipitate and the supernatant by centrifugation. The blank values amounted to about 2–5 % of the total concentration of carbon dioxide. The other corrections appear from the tables.

The values in column 5 are computed by means of the following expression

$$\frac{c_{\text{ROH}}c_{\text{OH}^-}}{c_{\text{RO}^-}} = \frac{(a - c_{\text{RO}^-})(b - c_{\text{RO}^-})}{c_{\text{RO}^-}} = \frac{K_{\text{H}_2\text{O}}}{K_{\text{A}}}$$

where a and b are the total concentrations of alcohol and sodium hydroxide, respectively, thus

$$c_{\text{ROH}} + c_{\text{RO}^-} = a$$

$$c_{\text{OH}^-} + c_{\text{RO}^-} = b$$

The acid dissociation constants for sorbitol, mannitol and glucose are: $10^{-14.14}$, $10^{-14.09}$ and $10^{-12.92}$, respectively³, and $K_{\text{H}_2\text{O}} = 10^{-14.93}$ at 0° C.

For most of the previously investigated alcohols the dissociation constants were either not known or not known with sufficient accuracy, and it was therefore convenient to compute the velocity constant k' of the gross reaction

but in this case it is possible to compute the velocity constant $k_{\text{CO}_2\text{RO}^-}$ of the reaction

by means of the expression

$$\frac{\% \text{ monoalkyl carbonate}}{\% \text{ carbonate}} = \frac{k_{\text{CO}_2\text{RO}^-} \cdot c_{\text{RO}^-}}{k_{\text{CO}_2\text{OH}^-} \cdot c_{\text{OH}^-}}$$

where $k_{\text{CO}_2\text{OH}^-} = 10^{+4.39}$

The mean values of $k_{\text{CO}_2\text{RO}^-}$ corresponding to Table 1 are $10^{4.56}$, $10^{4.52}$ and $10^{3.12}$ for sorbitol, mannitol and glucose, respectively. The mean values of $k_{\text{CO}_2\text{RO}^-}$ corresponding to Table 1a are $10^{4.16}$, $10^{4.14}$ and $10^{2.92}$ for sorbitol, mannitol and glucose, respectively.

For comparison it is convenient to state the values of the velocity constant k' computed from the expression $k' = k_{\text{CO}_2 \cdot \text{RO}} \cdot K_A / K_{\text{H}_2\text{O}}$, viz. $10^{5.35}$, $10^{5.36}$ and $10^{5.13}$, corresponding to Table 1, and $10^{4.95}$, $10^{4.98}$ and $10^{4.93}$ corresponding to Table 1a for sorbitol, mannitol and glucose, respectively.

II. THE EQUILIBRIUM OF THE REACTION $\text{RCO}_2^- + \text{HOH} = \text{HCO}_2^- + \text{ROH}$

The above equilibrium was established in aqueous solutions of alcohol, potassium hydrogen carbonate and sodium carbonate. With the alcohols studied in the present investigation the equilibrium is shifted strongly to the right, and thus the determinations of per cent monoalkyl carbonate may be attended with rather large errors as the blank values are almost of the same order of magnitude as the experimental values, and the computed K_{Eq} -values give only the order of magnitude.

a) *Sorbitol*. The equilibrium was established at 0°C in a solution 0.25 M with regard to sorbitol, 0.1 M with regard to KHCO_3 and 0.1 M with regard to Na_2CO_3 .

The monoalkyl carbonate was determined in 100 ml samples and found to be equivalent to 2.35, 2.60, 2.46, 2.50 and 2.44 ml 0.1 N HCl, respectively, with a mean value of 2.47 ml. The blank values corresponded to 1.41, 1.33, 1.38, 1.30 and 1.41 ml 0.1 N HCl, with a mean value of 1.37 ml. The true quantity of monoalkyl carbonate thus corresponds to 1.10 ml 0.1 N HCl, i. e. $\frac{1.10 \times 100}{200} = 0.55\%$ of the KHCO_3 is transformed to monoalkyl carbonate.

b) *Mannitol*. The equilibrium was established at 0°C in a solution 0.25 M with regard to mannitol, 0.1 M with regard to KHCO_3 and 0.1 M with regard to Na_2CO_3 . In the equilibrium 0.98 % of the KHCO_3 is converted to monoalkyl carbonate.

The monoalkyl carbonate in the samples corresponded to 3.09, 3.30, 3.36, 3.19, 3.41, 3.19, 3.12 and 3.29 ml 0.1 N HCl, with a mean value of 3.24 ml. The blank values corresponded to 1.49, 1.40, 1.58, 1.41, 1.40, 0.98, 1.02 and 0.92 ml 0.1 N HCl, with a mean value of 1.28 ml.

c) *Glucose*. Equilibrium was established at 0°C in a solution 0.5 M with regard to glucose, 0.1 M with regard to KHCO_3 and 0.1 M with regard to Na_2CO_3 . In different determinations the monoalkyl carbonate was equivalent to 1.84, 1.94, 2.31, 3.07, 1.56 and 1.52 ml 0.1 N HCl, respectively, with a mean value of 1.87 ml. The blank values were equivalent to 1.03, 0.81, 0.95, 1.05, 1.24, 1.27 and 1.32 ml 0.1 N HCl, respectively, with a mean value of 1.10 ml. In the equilibrium 0.38 % of the KHCO_3 is transformed to monoalkyl carbonate.

d) From the above values and

$$K_{\text{Eq}} = \frac{c_{\text{ROH}} c_{\text{HCO}_2^-} f}{c_{\text{RCO}_2^-} f}$$

K_{Eq} has the values 45, 25, and 128 for sorbitol, mannitol and glucose, respectively, but as suggested above these values only state the order of magnitude of K_{Eq} .

III. ON THE VELOCITY OF THE REACTIONS $\text{RCO}_3^- + \text{HOH} = \text{HCO}_3^- + \text{ROH}$

The solutions mentioned in the Tables 1 and 1a were all directly used for the kinetic determinations. The results corresponding to the experiments represented in the Tables 1 and 1a coincide, and therefore to save space only a limited number of the experiments corresponding to Table 1a are represented in Table 2.

Table 2. Monoalkyl carbonate in $\text{NaOH} + \text{alcohol}$. 0°C .

	1	2	3			4	5	6
	Expt. No.	Initial concn. RCO_3^-	Composition of the solutions COH^- CROH CRO^-			t min	% RCO_3^- left	k_{mono}
Sorbitol	1	0.0077	0.0351 0.0287	0.0757 0.0847	0.0166 0.0153	10	73	0.014
						20	53	0.014
						30	41	0.013
						40	31	0.013
						50	24	0.013
						60	18	0.012
						Mean		0.013
Mannitol	3	0.0080	0.0355 0.0287	0.0735 0.0827	0.0185 0.0173	10	76	0.012
						20	56	0.013
						30	43	0.012
						40	32	0.012
						50	25	0.012
						60	21	0.011
						Mean		0.012
	5	0.0147	0.0242 0.0170	0.2005 0.2230	0.0345 0.0270	10	85	0.0069
						25	66	0.0072
						42	50	0.0071
						55	41	0.0070
						70	33	0.0069
						85	27	0.0068
						Mean		0.0070
Glucose	7	0.0040	0.0099 0.0082	0.0479 0.0542	0.0481 0.0458	6	62	0.035
						12	43	0.031
						18	30	0.029
						24	23	0.027
						Mean		0.030
	10	0.0040	0.0047 0.0039	0.1667 0.1739	0.0793 0.0761	6	71	0.025
						12	59	0.019
						18	44	0.020
						24	36	0.018
						30	32	0.017
						Mean		0.020
	11	0.0121	0.0016 0.0010	0.4176 0.4410	0.0704 0.0590	6	81	0.015
						16	60	0.014
						26	44	0.014
						36	34	0.013
						Mean		0.014

k_{mono} is the value of $\frac{1}{t} \log \frac{a}{a-x}$

In Table 2, column 2, the initial concentration of monoalkyl carbonate are computed from % RCO_3^- (corr.) in Table 1a. The initial compositions of the solutions and the compositions after the reaction is completed are given in column 3. In the kinetic experiments represented in columns 4–6, $t = 0$ corresponds to the fifth minute after the addition of the carbon dioxide.

The mechanism of these reactions is assumed to be similar to that of previously investigated decompositions of monoalkyl carbonates, *i. e.*

k_{mono} may be calculated at $\text{pH} > 10$ by means of the expression

$$k_{\text{mono}} = \frac{k_{\text{CO}_2 \cdot \text{RO}^-} \cdot \frac{K_{\text{Eq}} \cdot K_{\text{A}}}{K_{\text{CO}_2}}}{1 + \frac{k_{\text{CO}_2 \cdot \text{RO}^-}}{k_{\text{CO}_2 \cdot \text{OH}^-}} \cdot \frac{K_{\text{A}}}{K_{\text{H}_2\text{O}}} \cdot c_{\text{ROH}}}$$

the values of K_{CO_2} being $10^{-6.65}$, but in this case the experimental values of K_{Eq} are very uncertain, so it may be better to calculate K_{Eq} from the experimental values of k_{mono} .

By calculation of K_{Eq} by means of the mean values of $k_{\text{CO}_2 \cdot \text{RO}^-}$ from Table 1a, which may be considered as the most correct values², and the mean values of c_{ROH} during the experiments, the following values are obtained (Table 3).

Table 3.

	Expt. No.	K_{Eq}	
		calc.	found
Sorbitol	1	35	45
Mannitol	3	31	25
	5	29	
Glucose	7	79	128
	10	71	
	11	78	

In view of the uncertainty (*cf.* section II) in the experimental values of K_{Eq} they agree quite well with the above calculated values.

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