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Studies on Monoalkyl Carbonates

XV. The Monoalkyl Carbonates of Sucrose and Lactose

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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. Sucrose and lactose 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) $RCO_3^- = RO^- + CO_2$; (2) $CO_2 + OH^- = HCO_3^-$.

1. The present investigation deals with the equilibrium conditions and the reaction mechanism for the formation and decomposition of the monoalkyl carbonates of sucrose and lactose.

2. The sucrose used was nitrogen-free sucrose from 'De danske Sukkerfabriker'. An aqueous solution of 9.995 g sucrose per 100 ml showed an optical rotation of 13.3° at 20° C in a 20 cm tube giving a value for $[\alpha]_D^{20°}$ of 66.53 which agrees with the value given in the literature. The sucrose was thus regarded as fit for use. The lactose was 'Baker's Analyzed' lactose stated to be pure. An aqueous solution of 9.994 g lactose per 100 ml showed an optical rotation of 10.5° at 20° C in a 20 cm tube. Thus $[\alpha]_D^{20°} = 52.53$ which agrees with the value given in the literature. The lactose was thus considered to be usable and corresponded very closely to the formula $C_{12}H_{22}O_{11} \cdot H_2O$.

3. The present investigation is analogous to the investigation concerning sorbitol, mannitol and glucose [1] and the experimental method being similar, it is on the whole sufficient here to state the experimental data and the calculated constants, referring for further information to the investigation of sorbitol, mannitol and glucose.

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

	Expt. No.	Initial concn. NaOH	Initial concn. ROH	Compositions of the solutions * c_{OH^-} c_{ROH} c_{RO^-}	Absorbed CO_2 mole/litre	% RCO_3^-	% RCO_3^- (corr.)	log $k_{CO_2 \cdot RO^-}$
Sucrose	1	0.1	0.2	0.0185 0.1185 0.0815 0.0127 0.1255 0.0589	0.022	64.70	70.78	4.11
	2			0.0185 0.1185 0.0815 0.0133 0.1235 0.0605	0.021	69.50	76.03	4.24
	3	0.2	0.2	0.0612 0.0612 0.1388 0.0507 0.0633 0.1190	0.024	67.30	73.62	4.47
	4			0.0612 0.0612 0.1388 0.0515 0.0637 0.1214	0.021	64.70	70.80	4.41
	5	0.2	0.1	0.1185 0.0185 0.0815 0.1023 0.0169 0.0639	0.022	41.30	46.13	4.50
	6			0.1185 0.0185 0.0815 0.0960 0.0200 0.0710	0.021	38.40	42.88	4.41
Lactose	1	0.1	0.2	0.0059 0.1059 0.0941 0.0039 0.1165 0.0688	0.021	61.80	69.98	3.49
	2			0.0059 0.1059 0.0941 0.0049 0.1169 0.0681	0.021	62.90	71.23	3.61
	3	0.2	0.2	0.0332 0.0332 0.1668 0.0251 0.0385 0.1472	0.021	62.10	67.93	3.98
	4			0.0332 0.0332 0.1668 0.0251 0.0387 0.1471	0.021	61.60	67.39	3.97
	5	0.2	0.1	0.1059 0.0059 0.0941 0.0723 0.0179 0.0935	0.022	37.60	44.69	4.28
	6			0.1059 0.0059 0.0941 0.0840 0.0066 0.0837	0.021	39.00	46.36	4.35

* Preceding paper [1]: Footnote, Table 1.

ON THE FORMATION OF MONOALKYL CARBONATE FROM CARBON DIOXIDE AND ALCOHOL IN BASIC SOLUTION, AND ON THE REACTION $RO^- + CO_2 = RCO_3^-$

The experimental results concerning the addition of carbon dioxide to sucrose and lactose are in the Tables 1 and 1a.

The acidic dissociation constants of sucrose and lactose are [2]: $10^{-13.36}$ and $10^{-12.75}$, respectively, at 0° C.

The mean values of $k_{CO_2 \cdot RO^-}$ corresponding to Table 1 are $10^{4.36}$ and $10^{3.95}$ for sucrose and lactose, respectively. The mean values of $k_{CO_2 \cdot RO^-}$ corresponding with Table 1a are $10^{3.74}$ and $10^{3.46}$ for sucrose and lactose, respectively. The mean values of k' are $10^{5.93}$ and $10^{6.13}$ corresponding with Table 1, and $10^{5.31}$ and $10^{5.64}$ corresponding with Table 1a for sucrose and lactose, respectively.

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

	Expt. No.	Initial concn. NaOH	Initial concn. ROH	Compositions of the solutions * c_{OH^-} c_{ROH} c_{RO^-}	Absorbed CO_2 mole/litre	% RCO_3^-	% RCO_3^- (corr.)	log $k_{CO_2 \cdot RO^-}$
Sucrose	1	0.2	0.4	0.0217 0.2217 0.1783 0.0099 0.1359 0.0501	0.027	44.79	52.03	3.55
	2			0.0217 0.2217 0.1783 0.0100 0.1352 0.0504	0.027	46.09	53.53	3.60
	3	0.2	0.2	0.0612 0.0612 0.1388 0.0171 0.0551 0.0349	0.029	27.49	34.61	3.77
	4			0.0612 0.0612 0.1388 0.0176 0.0556 0.0364	0.027	23.96	29.48	3.66
	5	0.4	0.2	0.2217 0.0217 0.1783 0.0814 0.0234 0.0706	0.027	18.50	22.25	3.93
	6			0.2217 0.0217 0.1783 0.0790 0.0238 0.0696	0.029	18.92	22.74	3.94
Lactose	1	0.2	0.4	0.0062 0.2062 0.1938 0.0026 0.1304 0.0515	0.032	47.54	56.51	3.06
	2			0.0062 0.2062 0.1938 0.0026 0.1306 0.0504	0.033	48.36	57.48	3.08
	3	0.2	0.2	0.0332 0.0332 0.1668 0.0069 0.0445 0.0463	0.028	25.48	32.83	3.35
	4			0.0332 0.0332 0.1668 0.0068 0.0438 0.0457	0.029	27.76	36.18	3.42
	5	0.4	0.2	0.2062 0.0062 0.1938 0.0660 0.0084 0.0838	0.029	21.07	26.83	3.95
	6			0.2062 0.0062 0.1938 0.0645 0.0089 0.0833	0.030	20.30	25.85	3.92

* Preceding paper [1]. Footnote, Table 1.

THE EQUILIBRIUM OF THE REACTION $RCO_3^- + HOH = HCO_3^- + ROH$

The equilibrium was established in aqueous solutions of the alcohol, potassium hydrogen carbonate and sodium carbonate.

a) Sucrose. Equilibrium was established at 0° C in a solution 0.25 M with regard to sucrose, 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. In different determinations the monoalkyl carbonate was equivalent to 3.29, 3.16, 3.09, 3.06, 3.30, 3.34, 3.44 and 3.54 ml 0.1 N HCl, respectively, with a mean value of 3.28 ml. The blank values were equivalent to 1.50, 1.35, 1.37, 1.45, 1.51, 1.35, 1.50, 1.50 and 1.45 ml 0.1 N HCl, respectively, with a mean value of 1.44 ml. The true quantity of alkyl carbonate thus corresponds to 1.84 ml 0.1 N HCl, *i. e.* 0.92 % of the $KHCO_3$ is transformed to monoalkyl carbonate.

Table 2. Monoalkyl carbonate in NaOH + alcohol. 0°C.

	1	2	3	4	5	6
	Expt. No.	Initial concn. RCO_3^-	Composition of the solutions c_{OH^-} c_{ROH} c_{RO^-}	t min	% RCO_3^- left	k_{mono}
Sucrose	4	0.0080	0.0176 0.0556 0.0364 0.0132 0.0672 0.0328	6	76	0.020
				12.5	57	0.020
				18	47	0.018
				24	37	0.018
				30	30	0.017
				36	26	0.016
				Mean:		0.018
	2	0.0144	0.0100 0.1352 0.0504 0.0066 0.1606 0.0394	10	69	0.016
				20	53	0.014
				30	41	0.013
				40	33	0.012
				50	27	0.012
				60	22	0.011
				Mean:		0.013
	6	0.0066	0.0790 0.0238 0.0696 0.0699 0.0279 0.0721	10	65	0.019
				20	44	0.018
				30	36	0.015
				40	26	0.015
				50	20	0.014
				60	15	0.014
				Mean:		0.016
Lactose	3	0.0092	0.0069 0.0445 0.0463 0.0043 0.0603 0.0397	6	76	0.020
				12	50	0.025
				18	37	0.024
				24	30	0.022
				30	25	0.020
				36	19	0.020
				Mean:		0.022
	1	0.0181	0.0026 0.1304 0.0515 0.0014 0.1654 0.0346	10	68	0.017
				20	50	0.015
				30	37	0.015
				40	28	0.014
				50	21	0.014
				60	16	0.013
				Mean:		0.015
	6	0.0078	0.0645 0.0089 0.0833 0.0513 0.0113 0.0887	6	71	0.025
				12	54	0.023
				18	40	0.022
				24	34	0.020
				30	27	0.019
				36	24	0.017
				Mean:		0.021

b) Lactose. The equilibrium was established at 0° C in a solution 0.25 M with regard to lactose, 0.1 M with regard to $KHCO_3$ and 0.1 M with regard to Na_2CO_3. In the equilibrium 0.39 % of the $KHCO_3$ is transformed to mono-

Table 3.

	Expt. No.	K_{Eq}	
		calc.	found
Sucrose	4	26	27
	2	27	
	6	18	
Lactose	3	19	64
	1	24	
	6	11	

alkyl carbonate. The monoalkyl carbonate in the samples was equivalent to 2.24, 2.39, 2.29, 2.25, 2.34, 1.98, 3.00, 3.19 and 2.71 ml 0.1 N HCl with a mean value of 2.49 ml. The blank values correspond to 1.67, 1.72, 2.20, 1.66, 1.80, 1.38 and 1.62 ml 0.1 N HCl with a mean value of 1.72 ml.

Thus K_{Eq} has the values 27 and 64 for sucrose and lactose, respectively, but these values only state the order of magnitude of K_{Eq}.

ON THE VELOCITY OF THE REACTIONS $RCO_3^- + HOH = HCO_3^- + ROH$

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

The initial concentration of monoalkyl carbonate computed from $\%\,RCO_3^-$ (corr.) in Table 1a are given in Table 2, column 2.

The initial compositions of the solutions and the compositions after the reaction is completed are given in column 3.

The mean values of c_{ROH} during the experiment and the mean values of $k_{CO_2 \cdot RO^-}$ from Table 1a [1] are used to calculate K_{Eq} from the experimental values of k_{mono} and the following values are obtained (Table 3).

The agreement between the calculated and the experimental values is quite good for sucrose whereas for lactose the experimental value is 3—6 times the calculated and thus not in as good agreement as to be wished.

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