

Studies on Monoalkyl Carbonates

XIV. The Monoalkyl Carbonates of Tetrahydrofurfuryl Alcohol and Furfuryl Alcohol

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The velocity constants of the reaction 'alcohol + OH⁻ + CO₂ = alkyl · CO₃⁻ + H₂O' and the equilibrium constants for the equilibrium 'alkyl · CO₃⁻ + H₂O = HCO₃⁻ + alcohol' have been determined for tetrahydrofurfuryl alcohol and furfuryl alcohol. The velocity of the decomposition of the monoalkyl carbonates in strongly basic medium is investigated and may be explained by assuming that the decomposition is a two-stage reaction, *viz.* 1) monoalkyl carbonate = alkolate + CO₂; 2) CO₂ + OH⁻ = HCO₃⁻.

1. The present investigation deals with the equilibrium conditions and the reaction mechanism for the formation and decomposition of the monoalkyl carbonates of tetrahydrofurfuryl alcohol and furfuryl alcohol in aqueous medium.

2. Tetrahydrofurfuryl alcohol was purified by distillation through a wiregauze column with 49 sets of platinum plates. The obtained tetrahydrofurfuryl alcohol boiled at 178.2—178.3°C/773 mm Hg (177.6—177.7°C/760 mm Hg), $n_D^{20.0^\circ} = 1.4518$.

Furfuryl alcohol was purified first by simple distillation in vacuum and then by distillation through a wiregauze column with 49 sets of platinum plates at 100 mm Hg. The furfuryl alcohol thus obtained boiled at 171.5—172.3°C/764 mm Hg, $n_D^{20.0^\circ} = 1.4872$.

As furfuryl alcohol is unstable under ordinary conditions and discolours, it is used immediately after the distillation.

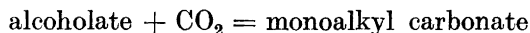
3. No solid monoalkyl carbonate was prepared. Solutions were made by dissolving carbon dioxide in basic solutions of the alcohols.

4. As to the method of analysis we refer to previous investigations¹. The data presented are corrected with regard to blank values unless otherwise stated. "Uncorr." values are not corrected at all and "corr." values are corrected not only with regard to blank values but also with regard to the decomposi-

tion mentioned in the next section. The blank values may amount to about 3 units of the percentage of monoalkyl carbonate in some of the experiments.

5. The experiments were carried out at 0°C. Velocity constants are expressed on the basis of the Briggs' logarithms and the minute.

On the formation of the monoalkyl carbonate from carbon dioxide and alcohol in basic solution and on the reaction

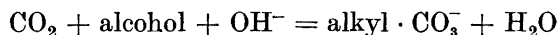


The experiments were carried out in a 2 litre flask by vigorously shaking 1 100 ml of a basic solution of the alcohols with atmospheric air of which 550 ml were substituted by carbon dioxide. The strong basic solution of furfuryl alcohol was light yellow and became slight opalescent by standing at 0°C. The solutions were immediately analysed to determine the percentage of monoalkyl carbonate. Due to the rapid decomposition of the monoalkyl carbonates, we had to correct the results by means of the velocity constant which we also have determined, see later.

By introduction of the adjusted results in the expression:

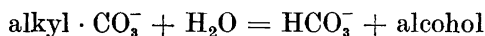
$$k' = \frac{\% \text{ monoalkyl carbonate} \cdot k_{\text{CO}_2, \text{OH}^-}}{\% \text{ carbonate} \cdot c_{\text{alcohol}}}$$

the k' values presented in Table 1 are calculated. k' is the velocity constant of the overall reaction:



For the value of $k_{\text{alkyl} \cdot \text{CO}_3^-}$ we get 0.0074 for tetrahydrofurfuryl alcohol and 0.054 for furfuryl alcohol when the values of K_{Eq} found in Table 2 are employed.

The equilibrium of the reactions



The above equilibrium was established in aqueous solutions of alcohol, potassium bicarbonate and sodium carbonate.

Table 1. Carbon dioxide in tetrahydrofurfuryl alcohol + NaOH and in furfuryl alcohol + NaOH. 0°C.

	c_{NaOH}	c_{alcohol}	Absorb. $\frac{\text{mole}}{\text{litre}}$ CO_2	% Alkyl-carbonate	% Alkyl-carbonate corr.	k'	Mean of k'
Tetrahydrofurfuryl alcohol	0.10	1.00	0.0215	51.3	57.5	$10^{4.52}$	$10^{4.51}$
	0.10	0.50	0.0198	36.5	38.3	$10^{4.49}$	
Furfuryl alcohol	0.10	1.00	0.0214	68.2	81.9	$10^{5.09}$	$10^{5.08}$
	0.10	0.50	0.0212	61.2	70.2	$10^{5.07}$	

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

	Initial solution			% Alkylcarbonate		K_{Eq}	Mean of K_{Eq}
	$c_{alcohol}$	c_{KHCO_3}	$c_{Na_2CO_3}$	uncorr.	corr.		
Tetrahydro- furfuryl alcohol	1.00	0.10	0.05	2.99	2.43 ¹	10 ^{1.61}	10 ^{1.64}
	1.00	0.20	0.10	2.39	2.16 ²	10 ^{1.65}	
	0.50	0.10	0.05	1.77	1.24 ³	10 ^{1.60}	
	0.50	0.20	0.10	1.25	1.00 ⁴	10 ^{1.69}	
Furfuryl alcohol	1.00	0.20	0.10	1.59	1.15 ⁵	10 ^{1.93}	

1 mean of 3 determinations	2.41,	2.56,	2.35
2 » » 3	»	2.30,	2.07, 2.11
3 » » 3	»	1.22,	1.22, 1.27
4 » » 3	»	0.99,	1.01, 0.99
5 » » 3	»	1.17,	1.13, 1.15

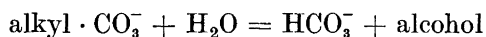
The contents of monoalkyl carbonate have been calculated as a percentage of HCO_3^- initially present; thus no attention was paid to carbonate.

In Table 2 are presented not only the '% monoalkyl carbonate' corrected for blank values and the decomposition taking place until the precipitate has been separated from the supernate, 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

$$K_{Eq} = \frac{c_{alcohol} \cdot c_{HCO_3^-} \cdot f}{c_{alkyl \cdot CO_3^-} \cdot f}$$

may be calculated, the activity constants neutralizing each other.

On the velocity of the reactions



Determinations have been made from the monoalkyl carbonate side only and in strongly basic medium, the alkyl carbonate thus being practically completely converted into carbonate.

The monoalkyl carbonate has been made by shaking the basic solutions with CO_2 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 alkyl carbonates. k_{mono} is the value of $\frac{1}{t} \log \frac{a}{a-x}$

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

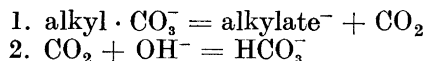


Table 3. Monoalkyl carbonate in NaOH + alcohol. 0°C.

	$C_{\text{monoalkyl-carbonate}}$	C_{NaOH}	C_{alcohol}	Min	% Monoalkyl-carbonate left	k_{mono}
Tetrahydro-furfuryl alcohol	0.012	0.10	1.00	0	100	—
				9	90.0	(0.00510)
				21	84.2	0.00356
				30	75.5	0.00407
				50	60.8	0.00432
				88	46.6	0.00376
				147	27.6	0.00381
				204	16.7	0.00381
				259	11.4	0.00364
				Mean		0.0039
	0.007	0.10	0.50	0	100	—
				7	91.5	0.00553
				16	83.9	0.00478
				35	63.8	0.00559
				53	51.5	0.00544
85				33.4	0.00560	
120				21.6	0.00554	
151				15.2	0.00542	
186	13.2	0.00474				
Mean		0.0053				
Furfuryl alcohol	0.017	0.10	1.00	0	100	—
				5	86.7	(0.0124)
				12	74.9	0.0105
				18	66.7	0.0098
				22	57.9	0.0108
				28	52.0	0.0101
				39	44.1	0.0091
				58	25.9	0.0101
				107	10.2	0.0093
				Mean		0.010
	0.013	0.10	0.50	0	100	—
				6	75.3	0.0205
				12	56.6	0.0206
				17	45.8	0.0200
				28	31.9	0.0177
37				23.5	0.0170	
51				10.1	0.0195	
80				5.25	0.0160	
Mean		0.019				

k_{mono} may be calculated at $\text{p}a_{\text{H}} > 10$ by means of the following expression

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

the values of $K_{\text{H}_2\text{O}}$ and K_{CO_2} being $10^{-14.93}$ and $10^{-6.65}$, respectively.

Upon introduction of the constants the equation for tetrahydrofurfuryl alcohol is:

$$k_{\text{mono}} = \frac{0.0074}{1 + 1.3 \cdot c_{\text{alcohol}}}$$

and k_{mono} in 1 M and 0.5 M solutions of alcohol, $\text{p}a_{\text{H}} > 10$, will then be calculated to 0.0032 and 0.0045, respectively.

For furfuryl alcohol is:

$$k_{\text{mono}} = \frac{0.054}{1 + 4.9 \cdot c_{\text{alcohol}}}$$

and k_{mono} in 1 M and 0.5 M solution of alcohol, $\text{p}a_{\text{H}} > 10$, will be calculated to 0.0092 and 0.016, respectively.

The experimental and calculated values agree rather well.

REFERENCE

1. Jensen, A., Jørgensen, E. and Faurholt, C. *Acta Chem. Scand.* 6 (1952) 1036.

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