

## Studies on Monoalkyl Carbonates

## XIII. The Monoalkyl Carbonate of Allyl Alcohol

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The equilibrium conditions and the reaction mechanism for the formation and decomposition of various monoalkyl carbonates in aqueous medium, the most recent being  $\text{CH}_2\text{OH}\cdot\text{CH}_2\cdot\text{CO}_3^-$  and  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_3^-$ <sup>1</sup>, have been studied previously. The present investigation deals with the monoalkyl carbonate of allyl alcohol.

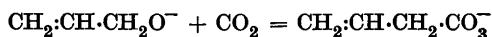
The allyl alcohol used was distilled with carbon tetrachloride<sup>2</sup> through a platinum wiregauze column<sup>3</sup>. The allyl alcohol thus obtained boiled at 96.7° C (751mmHg),  $n_D^{20.0^\circ} = 1.4132$ . By a bromometric titration an equivalent weight of 58.28 was obtained: theoretically for  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{OH}$  58.08. The above mentioned boiling point is corrected for calibration errors; stem corrections have been done.

No attempt was made to isolate the allyl carbonate as a substance. Where it has been used it was made by adding carbon dioxide to a basic solution of the alcohol, the carbon dioxide thus being converted partially to monoallyl carbonate and partially to ordinary carbonate.

As to the method of analysis we refer to previous investigations<sup>1</sup>. 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 decomposition mentioned in the next section. The blank values amount to less than 1 unit of the percentage of monoalkyl carbonate in the equilibrium experiments where the concentration of monoalkyl carbonate + hydrocarbonate is 0.1–0.2 *M*. They amount to 5–6 units (in a single case up to 8 units) in the experiments where the concentration is about 0.02 *M*.

The experiments were carried out at 0° C. The velocity constants were calculated by means of Briggs' logarithms, the unit of time being the minute.

On the formation of allyl carbonate from carbon dioxide and allyl alcohol in basic solutions, and on the reaction



The experiments were carried out in a 2 litre flask by vigorously shaking 500 ml of a basic solution of allyl alcohol with atmospheric air of which 250 ml were substituted by carbon dioxide. The solution was immediately analysed to determine the percentage of allyl carbonate. The results are listed in Table 1. Since allyl carbonate is very rapidly decomposed, the results are corrected not only for the blank values, but also for the decomposition taking place during the 6–7 minutes which elapse between the start of the shaking with carbon dioxide and the separation of the precipitate and the supernate by centrifugation. The corrections appear from the Table.

By the introduction of the experimental results in the expression

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

the  $k'$  values presented in Table 1 are calculated.

$k'$  is the velocity constant of the gross reaction:



and  $k_{\text{CO}_2 \cdot \text{OH}^-}$  ( $10^{4.39}$ ) is the velocity constant of the reaction:



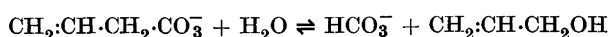
Table 1. Carbon dioxide in allyl alcohol + NaOH. 0°.

Initial solution		Absorbed CO <sub>2</sub> mol/liter	% alkyl- carbonate	% alkyl- carbonate (corr.)	$k'$	Mean of $k'$
$c_{\text{NaOH}}$	$c_{\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{OH}}$					
0.50	1.00	0.0131	51.1	53.3	10 <sup>4.45</sup>	10 <sup>4.44</sup>
0.50	1.00	0.0209	50.1	52.1	10 <sup>4.43</sup>	
0.50	1.00	0.0123	51.4 50.8	53.8 53.2	10 <sup>4.46</sup> 10 <sup>4.45</sup>	
0.50	0.50	0.0211	33.2	35.2	10 <sup>4.43</sup>	
0.50	0.50	0.0195	33.4 32.1	35.7 34.4	10 <sup>4.44</sup> 10 <sup>4.41</sup>	

For the value of  $k_{\text{allyl}\cdot\text{CO}_3^-}$ , being the velocity constant of the reaction "CH<sub>2</sub>:CH·CH<sub>2</sub>·CO<sub>3</sub><sup>-</sup> = CH<sub>2</sub>:CH·CH<sub>2</sub>O<sup>-</sup> + CO<sub>2</sub>" we get 0.0059 when the value of  $K_{Eq}$  found in Table 2 is employed.

When  $k'$  and  $k_{\text{alkyl}\cdot\text{CO}_3^-}$  for allyl alcohol is compared to the corresponding values for n-propyl alcohol <sup>4</sup>, it can be seen that the introduction of the double bond influences the velocity constants significantly.

### The equilibrium of the reactions



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

The contents of alkyl carbonate have been calculated as a percentage of HCO<sub>3</sub><sup>-</sup> initially present; thus no attention was paid to carbonate.

In Table 2 are presented not only the "% allyl 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,

$$K_{Eq} = \frac{c_{\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{OH}} \cdot c_{\text{HCO}_3^-} \cdot f}{c_{\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CO}_3^-} \cdot f}$$

may be calculated, the activity constants neutralizing each other.

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

Initial solution			% alkylcarbonate		$K_{Eq}$	Mean of $K_{Eq}$
$c_{\text{CH}_2:\text{CH}\cdot\text{CH}_2\text{OH}}$	$c_{\text{KHCO}_3}$	$c_{\text{Na}_2\text{CO}_3}$	uncorr.	corr.		
1.00	0.10	0.05	3.17	2.48 <sup>1</sup>	10 <sup>1.59</sup>	10 <sup>1.61</sup>
1.00	0.20	0.10	2.87	2.44 <sup>2</sup>	10 <sup>1.60</sup>	
0.50	0.10	0.05	1.78	1.16 <sup>3</sup>	10 <sup>1.63</sup>	
0.50	0.20	0.10	1.47	1.15 <sup>4</sup>	10 <sup>1.63</sup>	

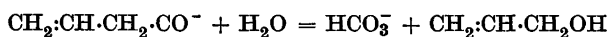
<sup>1</sup> Mean of 4 determinations: 2.48, 2.51, 2.52, 2.41

<sup>2</sup> » » 4 » 2.44, 2.42, 2.39, 2.51

<sup>3</sup> » » 4 » 1.23, 1.16, 1.12, 1.13

<sup>4</sup> » » 4 » 1.13, 1.17, 1.18, 1.13

On the velocity of the reactions:



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

The alkyl carbonate has been made by shaking the basic solution with  $\text{CO}_2$  as stated in the introduction. The solution, therefore, contains ordinary carbonate, which, however, is of no importance in the present investigation.

In Table 3 are listed the experimental results of the decomposition of allyl carbonate.  $k_{\text{Mono}}$  is the value of  $\frac{1}{t} \log \frac{a}{a-x}$ .

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

Initial solution			Min.	% alkyl-carbonate left	$k_{\text{Mono}}$
$c_{\text{alkylcarbonate}}$	$c_{\text{NaOH}}$	$c_{\text{alcohol}}$			
0.010	0.50	1.00	0	100	—
			15	91.3	0.00262
			42	74.3	0.00307
			96	48.9	0.00323
			145	35.5	0.00311
			206	22.4	0.00315
			276	12.1	0.00332
			361	6.6	0.00326
			∞	(0)	—
				Mean:	0.0031
0.007	0.50	0.50	0	100	—
			7	93.7	0.00404
			16	86.5	0.00392
			27	77.8	0.00404
			47	67.1	0.00369
			86	42.1	0.00437
			142	21.8	0.00466
			204	11.6	0.00458
			∞	(0)	—
				Mean:	0.0042

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:

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

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

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

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

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

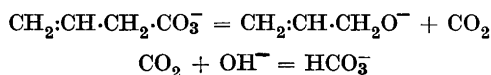
$$k_{\text{Mono}} = \frac{0.0059}{1 + 1.12 \cdot c_{\text{alcohol}}}$$

$k_{\text{Mono}}$  for allyl carbonate in 1 *M* and 0.5 *M* solutions of allyl alcohol,  $\text{p}a_{\text{H}} > 10$ , will then be calculated to 0.0028 and 0.0038, respectively.

The experimental and calculated values agree well.

#### SUMMARY

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



#### REFERENCES

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