

303. *Physicochemical Studies of Some Cyclic Carbonates. Part II.\**  
*The Rates of Hydrolysis of Ethylene Carbonate and of Propylene Carbonate.*

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The kinetics of the hydrolyses of ethylene carbonate and propylene (*i.e.*, methylethylene) carbonate, in alkaline aqueous media, at 25° have been studied; rate constants,  $k_{\text{OH}}$ , are 48.8 and 17.8 l. mole<sup>-1</sup> min.<sup>-1</sup>, respectively. Conductimetry was used to study the initial rates of the water-catalysed hydrolyses of these two compounds; at 25°, the initial rate constants  $k_{\text{H}_2\text{O}}$  were  $14.2 \times 10^{-7}$  and  $7.1 \times 10^{-7}$  min.<sup>-1</sup>, respectively. At 18°,  $k_{\text{H}_2\text{O}}$  for ethylene carbonate was  $5.7 \times 10^{-7}$  min.<sup>-1</sup>, leading to an activation energy for its initial hydrolysis of 22.5 kcal./mole.

ETHYLENE CARBONATE for use in cryoscopy was reported to be non-hygroscopic, and no precautions were taken to prevent the absorption of moisture from the air.<sup>1</sup> We have found, however, that the conductivity of samples of carefully purified cyclic carbonates, left in stoppered conductivity cells in a thermostat, progressively increases. The effect appeared to be due to hydrolysis; as it is intended to carry out reactions in water, and in aqueous solutions, in order to study complex-formation of metal ions by cyclic carbonates, it seemed of interest to obtain rates of hydrolysis of ethylene carbonate and of propylene carbonate, in aqueous alkaline solution and in water.

*Alkaline Hydrolysis.*—Alkaline hydrolyses were followed by titration, as in Skrabal and Baltadschiewa's studies of open-chain esters.<sup>2</sup> The rates were so much greater than those for hydrolysis by water molecules that we may write for the rate equation in alkaline solution:

$$dx/dt = k_{\text{OH}}[\text{OH}^-][\text{C}_2\text{H}_4\text{CO}_3] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $k_{\text{OH}}$  is the rate constant,  $[\text{C}_2\text{H}_4\text{CO}_3]$  is the concentration of ethylene carbonate, and  $x$  is the amount of ethylene carbonate hydrolysed; an analogous equation applies for propylene carbonate. The reaction  $\text{C}_2\text{H}_4\text{CO}_3 + \text{OH}^- + \text{H}_2\text{O} \longrightarrow (\text{CH}_2\cdot\text{OH})_2 + \text{HCO}_3^-$  proceeds rapidly even in very dilute solutions of caustic alkalis, and it was convenient to study the rate of hydrolysis in sodium carbonate solution. From the hydrolysis:  $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HCO}_3^-$ , of hydrolysis constant  $K'$ , we can express the hydroxyl-ion concentration as

$$[\text{OH}^-] = K'[\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that eqn. (1) becomes

$$dx/dt = k[\text{C}_2\text{H}_4\text{CO}_3][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $k = k_{\text{OH}} \times K'$ . If the initial concentrations of cyclic carbonate and of alkali carbonate are equal, eqn. (3) becomes  $dx/dt = k(a - x)^2/x$ , where  $a$  is the initial concentration, and  $x$  the amount of ester hydrolysed. The extent of reaction can thus be determined from the change in carbonate ion-bicarbonate ion ratio with time, as found by titration.

Integration of this special form of the rate equation gives:

$$k = \frac{1}{t} \left[ \frac{a}{a-x} - 1 - \ln \frac{a}{a-x} \right] = \frac{Z}{t}$$

and  $k$  can be obtained from the graph of  $Z$  against time  $t$ . To obtain the rate constant  $k_{\text{OH}}$  from  $k$ , we have for the second dissociation of carbonic acid:

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = \frac{[\text{CO}_3^{2-}]K_w}{[\text{HCO}_3^-][\text{OH}^-]}$$

\* *J.*, 1958, 1936, is considered as Part I.

<sup>1</sup> Gross and Schuerch, *Analyt. Chem.*, 1956, **28**, 227.

<sup>2</sup> Skrabal and Baltadschiewa, *Monatsh.*, 1924, **45**, 95.



$\Lambda_x$ , the equivalent conductivity of the solution corresponding to an amount of hydrolysis  $x$ , differs from the sum of the ionic mobilities in aqueous solution of these ions, because of the cyclic carbonate which is present. If the validity of Walden's rule is assumed, the sum of the limiting mobilities can be corrected for the measured viscosity of the solution to give  $\Lambda_x$ . If  $K_1$  is the first dissociation constant for carbonic acid, eqn. (4) is:  $x = [\text{H}^+] + [\text{H}^+]^2/K_1$ , and as  $[\text{H}^+] = c$ , obtained from eqn. (5),  $x$  can be obtained. From the variation in  $c$ , and hence of  $x$ , with time, the values of  $dx/dt$  listed in Table 3, at different initial concentrations of ethylene carbonate [ $\text{C}_2\text{H}_4\text{CO}_3$ ], were obtained. The concentrations of hydrogen and bicarbonate ions originally present in the conductivity water can be obtained from its conductivity, and allowed for.

TABLE 3. *Initial rates of hydrolysis by water.*

a) Ethylene carbonate.						
Expt.	Temp.	$\Lambda_x$	$10^6 dx/dt$	$[\text{C}_2\text{H}_4\text{CO}_3]$	$10^7 k_{\text{OH}^-}[\text{OH}^-]$	$10^7 k_{\text{H}_2\text{O}}$
1	25°	391.6	19.5	0.1291	1.4	13.7
2		389.9	30.3	0.1980	1.1	14.2
3		386.7	38.5	0.2452	0.9	14.8
					Average	14.2
1	18°	354.0	26.7	0.4327	0.4	5.8
2		353.8	27.3	0.4352	0.5	5.7
3		351.9	39.7	0.6620	0.4	5.6
					Average	5.7
b) Propylene carbonate.						
				$[\text{C}_3\text{H}_6\text{CO}_3]$		
1	25°	392.5	16.55	0.2254	0.4	6.9
2		392.0	23.7	0.3102	0.4	7.2
3		390.5	31.05	0.3964	0.5	7.3
					Average	7.1

Allowance is made for the contribution of the alkaline hydrolysis to the rate, by calculating  $k_{\text{OH}^-}[\text{OH}^-]$  at each initial concentration, and subtracting this from the total rate, which is  $(dx/dt)/(1/[\text{C}_2\text{H}_4\text{CO}_3])$ .

The change in rate between 18° and 25° for ethylene carbonate corresponds to an activation energy, for the initial hydrolysis, of 22.5 kcal./mole.

*Discussion.*—The water-catalysed hydrolysis of ethylene carbonate at 25° is very slow, and the concentration of hydroxyl ions in conductivity water contributes about 7% of the observed total rate. The rate for propylene carbonate is almost exactly one-half of that for ethylene carbonate; the transition state in this hydrolysis is a neutral complex, so that it appears that the methyl group shields the adjacent oxygen atom from attack by a water molecule, introducing a steric probability factor of  $\frac{1}{2}$  into the rate equation.

The hydroxyl-ion hydrolysis of ethylene carbonate is about three times as rapid as that of propylene carbonate; the steric factor may be increased, in this case, by the polar effect of the methyl group substituent towards alkaline hydrolysis.<sup>4</sup>

## EXPERIMENTAL

*Materials.*—Ethylene carbonate and propylene carbonate were commercial samples, carefully purified as described in Part I, and having the physical properties there recorded. Conductivity water produced by ion exchange, of specific conductance *ca.*  $0.5 \times 10^{-6}$  mho (determined for each sample), was used as solvent.

*Procedure.*—In following the alkaline hydrolyses, samples of the ester-sodium carbonate solution were withdrawn after definite intervals, cooled in an ice-bath, and titrated against hydrochloric acid of equivalent concentration to that of the sodium carbonate. Phenolphthalein was used as indicator, and titration continued to pH 8.3, as shown by comparison with a prepared buffer solution containing the same indicator.

The water hydrolyses were followed by the change in conductivity, as measured in a conductivity cell of the Hartley-Barrett type, having bright platinum electrodes; the cell was

connected in a conventional Wheatstone bridge circuit, and a. c. power was supplied by an oscillator of frequency 1500 c./sec.

The titration technique can be used over a much wider concentration range than the conductimetric, since the use of the limiting ionic mobilities is permissible only at extreme dilution. Initial rates only are reported for the water hydrolyses; the kinetic relationship for the alkaline hydrolysis is seen to hold over at least 75% of the reaction.

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