Pyrolysis of Carbonates. Part I. The Gas-phase Pyrolysis of Some Symmetrical Primary Alkyl Carbonates

By **D. B. Bigley** * and **C. M. Wren**, University Chemical Laboratory, Canterbury, Kent

The effect of structure on the rate of pyrolysis is similar for acetates and carbonates. The rates for carbonates are *ca.* 24 times greater than those for acetates. This increase derives about equally from the lower activation energies and more positive entropies of activation. The reasons for this are discussed.

WHILE the pyrolysis of esters, in particular the acetates, of aliphatic alcohols has been widely investigated during the last 30 years,[1-3] the reactions of their carbonates have been neglected. Work until 1920 has been summarised by Hurd,[4] but only isolated papers have appeared since that date. Nace and O'Connor reported the pyrolysis of cholesteryl methyl carbonate,[5] and Smith *et al.*[6,7] compared the pyrolysis of 1-arylethyl methyl carbonates with those of esters. The most comprehensive investigation was by Gordon and Norris, who measured activation parameters for the decomposition of ethyl methyl and diethyl carbonates,[8] and showed dimethyl carbonate to be considerably more thermally stable. Salomaa [9] has recorded the products of the pyrolysis of menthyl and fenchyl methyl carbonates.

In view of the limited information available on carbonate pyrolysis we have undertaken a systematic investigation, and now report our results for primary carbonates.

EXPERIMENTAL

The carbonates were prepared by passing a known weight of carbonyl chloride into a solution of the appropriate alcohol in equal parts of benzene and pyridine at 0 °C.[10] After distillation the products had the following physical constants: diethyl carbonate, b.p. 125—126°, n_D^{25} 1·3837 (lit.,[11] b.p. 125·8°, n_D^{20} 1·3829); di-n-propyl carbonate, b.p. 69—70° and 23 mmHg., n_D^{17} 1·4033 (lit.,[11] b.p. 67·5—68° and 17 mmHg, n_D^{25} 1·3990); di-n-butyl carbonate, b.p. 68—69° and 1·7 mmHg, n_D^{20} 1·4124 (lit.,[11,12] b.p. 96—98° and 17 mmHg, n_D^{20} 1·4117); di-isobutyl carbonate, b.p. 93° and 34 mmHg, n_D^{25} 1·4060 (lit.,[11] b.p. 85° and 16 mmHg, n_D^{25} 1·4053); di-n-hexyl carbonate, b.p. 105—106° and 0·8 mmHg, n_D^{17} 1·4289 (lit.,[11] b.p. 152—154° and 20 mmHg, n_D^{25} 1·4262).

Stoicheiometry.—The products of pyrolysis were measured by heating the carbonate with an appropriate internal standard in sealed tubes at 320 °C for approximately 10 reaction half-lives. The alcohol and olefin were then estimated by v.p.c. and the carbon dioxide by vacuum-line measurement.[13] The following results were obtained: di-n-butyl carbonate: CO_2 (94%), n-butanol (99%), but-1-ene (99·7%); di-n-hexyl carbonate: CO_2 (98·5%), n-hexanol (97%), hex-1-ene (96%). The stoicheiometry for diethyl carbonate has been determined.[8] With the di-n-propyl and di-isobutyl carbonates, the expected alcohols and olefins were identified by v.p.c. but were not estimated. No other product was detectable in any case.

Kinetics.—Kinetic runs were performed in two ways. At low temperatures the break-seal tubes for the pyrolysis of βγ-unsaturated acids were used,[14] and the rate followed by either CO_2 production or carbonate loss. At high temperatures the simplified version of the Kooyman flow apparatus,[15] shown schematically in Figure 1, was used.

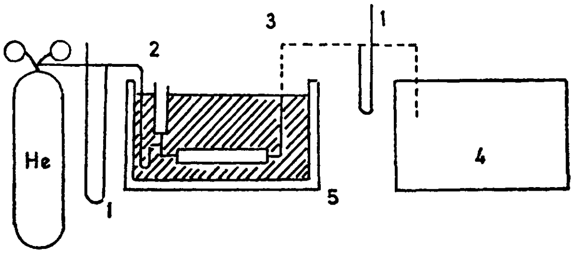


FIGURE 1 Flow apparatus: 1, Manometer; 2, 1 mm i.d. glass capillary; 3, 1 mm i.d. stainless steel tube wrapped with heating tape; 4, Pye 104 heated Katharometer v.p.c. attached to recorder and Kent Chromalog 1 integrator; 5, Stirred molten salt bath

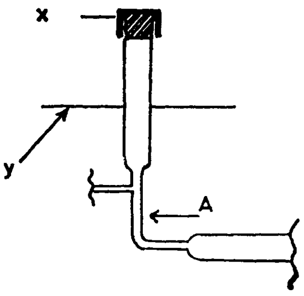


FIGURE 2 Detail of injection port in flow tube, X, Suba seal; Y, level of thermostat liquid

Carrier gas helium was led *via* a manometer into a flow tube heated by a well stirred molten salt bath. The gas was preheated by passing through a loop of capillary tube before entering the injection port. A mixture of internal standard and carbonate was introduced with a 30 μl gas-tight syringe having a 4½ in needle. The tip of the needle projected to point A in Figure 2, so that the volatilizing

---

[1] C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

[2] A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, 1967, **4**, 119.

[3] K. K. Lum and G. G. Smith, *Internat. J. Chem. Kinetics*, 1969, **1**, 401.

[4] C. D. Hurd, 'The Pyrolysis of Carbon Compounds,' The Chemical Catalog Co., New York, 1929.

[5] G. L. O'Connor and H. R. Nace, *J. Amer. Chem. Soc.*, 1953, **75**, 2118.

[6] G. G. Smith and B. L. Yates, *J. Org. Chem.*, 1965, **30**, 434.

[7] G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, 1969, **34**, 2090.

[8] A. S. Gordon and W. P. Norris, *J. Phys. Chem.*, 1965, **69**, 3013.

[9] E. Salomaa, *Ann. Acad. Sci. Fennicae*, 1959, **94**, 1.

[10] A. R. Choppin and J. W. Rogers, *J. Amer. Chem. Soc.*, 1948, **70**, 2967.

[11] S. T. Bowden and E. T. Butler, *J. Chem. Soc.*, 1939, 78.

[12] A. I. Vogel, *J. Chem. Soc.*, 1948, 1854.

[13] D. B. Bigley and J. C. Thurman, *J. Chem. Soc.* (*B*), 1966, 1076.

[14] D. B. Bigley, *J. Chem. Soc.*, 1964, 3897.

materials were swept by the carrier gas stream into the flow tube, and could not diffuse back into the cold space below the Suba seal. The products from the flow tube (*ca.* 20 cm × 1·7 cm) were swept *via* a heated capillary into the v.p.c. apparatus, and the flow rate (*ca.* 45 ml $\min^{-1}$) measured by a bubble meter at the exit port of the detector. There was no measurable pressure drop between the He source and the entrance to the v.p.c. apparatus. In a given experiment the salt-bath was heated to a temperature where *ca.* 90% reaction occurred and then allowed to cool at *ca.* 0·3 °C $\min^{-1}$ during the run; immediately after each injection the temperature of the bath was measured by a 4-lead Pt resistance thermometer and a vernier potentiometer (±0·05 °C). The results were then treated as by Kooyman *et al.*[15]

By use of the break-seal tube method, an Arrhenius plot took about 2 months; with the flow tube, the same plot took about half a day. For this reason, only three of the carbonates were investigated over the full range, and the flow tube was preferred for the majority of the work.

RESULTS

(i) *Sealed-tube Kinetics.*—The reaction was of the first order and runs were taken to *ca.* 75% completion. Runs performed in tubes packed with helices, with carbonate pressures from 150 to 500 mmHg and in the presence of cyclohexene showed no significant differences in rate, proving the reaction to be homogeneous. At least duplicate runs were performed at each temperature, with 150—400 mmHg of reactant. The rate constants were derived from the first-order plots by the method of least squares. The results are in Table 1. Arrhenius plots gave good straight lines, and the equation was again derived by the method of least squares; the activation parameters obtained from expression[16] (1) are also given in Table 1.

TABLE 1

Sealed-tube pyrolysis of carbonates

Carbonate	T/K	$10^5k/\mathrm{s}^{-1}$ (mean)	Arrhenius equation
Diethyl	553·8$_5$	0·798	E_a = 46·4 kcal mol^{-1}
	554·7	0·807	A = 1·43 × 10^{13} s^{-1}
	563·1	1·33	$\Delta S^{\ddagger}_{573^\circ}$ = −2 cal mol^{-1} K^{-1}
	575·2$_5$	3·50	$\log_e k$ = 2·33 × $10^4/T$ + 30·3
	593·9	12·8	S.D.: slope, 7·1 × 10^2; intercept, 1·3
Di-n-butyl	551·9	0·799	E_a = 43·5 kcal mol^{-1}
	568·4	2·41	A = 1·32 × 10^{12} s^{-1}
		2·33 *	$\Delta S^{\ddagger}_{573^\circ}$ = −6 cal mol^{-1} K^{-1}
	587·0	8·32	$\log_e k$ = 2·19 × $10^4/T$ +27·9
	588·0	9·30	S.D.: slope, 4·2 × 10^2; intercept, 0·7
Di-n-hexyl	552·5	0·85	E_a = 44·7 kcal mol^{-1}
	572·8	3·60	A = 4·2 × 10^{12} s^{-1}
	583·0	7·43	$\Delta S^{\ddagger}_{573^\circ}$ = −4 cal mol^{-1} K^{-1}
	596·4	18·0 *	$\log_e k$ = 2·25 × $10^4/T$ +29·1
	597·4	19·0	S.D.: slope, 3·5 × 10^2; intercept, 0·6
	600·0	20·3	

* Tubes packed with helices.

TABLE 2

Kinetics of pyrolysis of primary carbonates by the flow-tube method (708—663 °C)

Carbonate	No. of runs	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$10^2k_{700^\circ}/\mathrm{s}^{-1}$ *
Diethyl	13	47·2	0·0	7·4
Di-n-propyl	7	47·2	0·0	7·3$_5$
Di-n-butyl	8	45·5	−1·8	9·7
Di-isobutyl	7	48·8	0·7	3·2
Di-n-hexyl	8	44·1	−3·4	13·0

* ±3%.

$$k = (kT/h) \exp (\Delta S^{\ddagger}/R) \exp (-\Delta H^{\ddagger}/RT) \qquad (1)$$

(ii) *Flow-tube Kinetics.*—Runs were performed as described in the Experimental section covering 10—90% reaction. A typical plot is shown in Figure 3. In order to ensure consistent results it was found necessary to coat the tube with silicone grease by passing a solution of the grease in $CHCl_3$ through the cold tube, and evaporation of the $CHCl_3$. The tube was re-coated every 30—40 runs. Runs in packed tubes and in the presence of cyclohexene showed no significant deviations. The results are in Table 2.

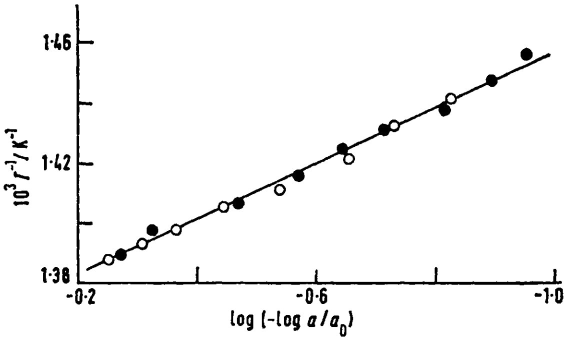
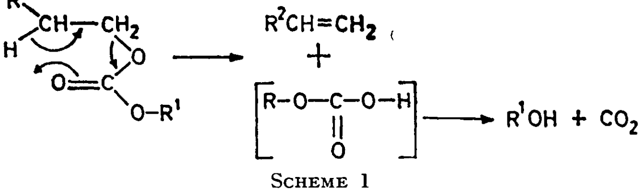


FIGURE 3 Flow-tube pyrolysis of di-isobutyl carbonate, ●, run I; ○, run II

DISCUSSION

All the compounds studied showed good first-order kinetics, three having been studied over a temperature range of 155 °C. The rates of reaction were not affected by large increases in the surface : volume ratio or by the addition of 200 mol % of cyclohexene. The reactions were therefore homogenous and unimolecular. No product was detectable except those shown in Scheme 1, which were obtained essentially quantitatively.



SCHEME 1

---

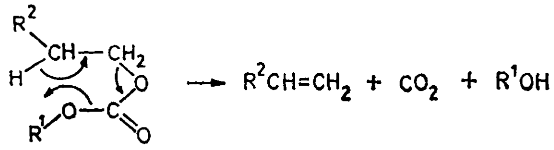
[15] J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.

[16] K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, New York, 1950, p. 75.

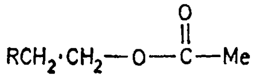
Only diethyl carbonate has been studied previously,[8] and the values obtained for the activation energy ($E_a = 46$ kcal mol^{-1}, log $A = 13{\cdot}9$ s^{-1}) is within experimental error of that reported here ($E_a = 46{\cdot}4$ kcal mol^{-1}, log $A = 13{\cdot}2$ s^{-1}). Unfortunately, the agreement between rate constants calculated from the Arrhenius equations is less good. The extrapolated rate from our lower-temperature break-seal tube method is $k_{700°} = 0{\cdot}051$ s^{-1}, compared with the flow-tube value of 0·074 s^{-1} (Table 2). The equation obtained by Gordon and Norris gives $k_{700°} = 0{\cdot}35$ s^{-1}.

The activation parameters obtained by the two different methods agree within the limits of experimental error ($\pm 1{\cdot}5$ kcal mol^{-1} and ± 2 cal mol^{-1} K^{-1} respectively), although the entropies of activation calculated at higher temperature are consistently less negative than those from the lower temperature. It is difficult to assess whether this trend is real, but it might indicate a loosening of the transition state at higher temperature.

The average $\Delta S^{\ddagger}$ from Table 2 is $-0{\cdot}9$ cal mol^{-1} K^{-1} while that for the corresponding acetates is $-7{\cdot}1$ cal mol^{-1} K^{-1}.[15] There are two alkyl groups available for elimination in the carbonates and $\Delta S^{\ddagger}$ should be adjusted by a factor of $R \ln 2$. The remaining difference (4·8 cal mol^{-1} K^{-1}) is probably outside individual experimental error, and is certainly outside the error of an average for the five compounds. The loss of rotational degrees of freedom in going from an approximately linear molecule to the transition states shown in either Scheme 1 or 2 must be similar. The main difference lies in the difficulty of bringing the two bulky alkyl groups R^1 and R^2 near to each other in Scheme 2. It therefore follows from comparison with acetate pyrolysis, that the expected value for the entropy of activation should be in the region of -7 to -8 cal mol^{-1} K^{-1}, with that for Scheme 2 perhaps being the more negative. It is possible to account for the more positive values of $\Delta S^{\ddagger}$ found for carbonates in terms of a looser transition state. If the C_{α}–O bond is more broken in the transition state for carbonates than it is for acetates, the two halves of the molecule will behave as more independent particles, and the entropy of activation will become more positive. A second possible explanation can be derived from conformational arguments. For both acetates and carbonates linear conformations such as (I) are the most probable. Two of the most significant of the many bent conformations are structures (II) and (III). The latter will be far less important in the carbonates in that a methyl group is replaced by a bulky –OR group; its population will be shared by other conformations, including the reacting one (II). In other terms when the groups flanking the carbonyl are large alkoxy-groups they will tend to be as far separated as possible, as in (I) and (II). In either case the population of the reacting conformation is enhanced, and a less negative entropy of activation should result.

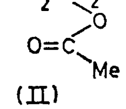


SCHEME 2

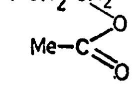


$\mathrm{RCH_2{\cdot}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}Me}$

(I)



(II)



(III)

The most striking feature of the present results is the very close parallelism between the relative rates of carbonate and acetate pyrolysis, presented in Table 3.

TABLE 3

Rates of pyrolysis of n-alkyl carbonates and acetates at 762 K

Alcohol	Carbonate k/s^{-1}	Relative rate (carbonate)	Acetate [15] 10^2k/s^{-1}	$\frac{k_{\text{carbonate}}}{k_{\text{acetate}}}$
Ethyl	1·26	1·0	5·7	22
Propyl	1·27	1·0	5·2	24
Butyl	1·50	1·2	6·8	22
Pentyl			7·2	25
Hexyl	1·80	1·4		
Isobutyl	0·60	0·48	2·6	23

The absolute rate varies by 300% in the carbonates, but the ratio $k_{\text{carbonate/acetate}}$ changes only from 22 to 25.

The reduction of β-hydrogen atoms available for elimination from three to two in passing from ethyl to propyl carbonate is almost exactly balanced by the stabilization of the incipient double bond in the transition state. Increase in length of the alkyl group stabilizing the incipient double bond gives rise to further small increases in rate consistent with their inductive effects. At the same time there is a steady drop in E_a (Table 2). However, the whole range is on the limit of experimental error, and neither it nor the entropies of activation should be examined too rigorously. In particular, with isobutyl carbonate, E_a is the highest and $\Delta S^{\ddagger}$ the most positive of the series. This is unexpected, since the β-hydrogen atoms are reduced from two to one, and $\Delta S^{\ddagger}$ should become more negative. The extra β-methyl group should not offset this change, as it was seen above that a single methyl group just offsets a reduction from three to two β-hydrogen atoms. Accordingly the rate of reaction should be the slowest in the series, as found, but E_a should also be the lowest. It is possible that the activation parameters are in error, but it is curious that isobutyl acetate shows exactly the same trend with respect to other primary acetates.[15]

We thank the S.R.C. for a studentship (to C. M. W.).

[1/2316 *Received, 6th December,* 1971]