Carbonate Pyrolysis. Part III.[1] The Gas-phase Pyrolysis of Some Unsymmetrical and t-Alkyl Carbonates

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There is evidence of steric hindrance to the pyrolysis of di-t-alkyl carbonates. This may be estimated by using data from the unsymmetrical compounds. The relative rate data then show that the extent of charge production on the α-carbon atom is similar to that in acetates.

IN previous Parts [1,2] we have examined the pyrolysis of primary and secondary dialkyl carbonates. We now present data for two tertiary and three alkyl methyl carbonates.

EXPERIMENTAL

The di-t-alkyl carbonates were prepared by passing a known weight of carbonyl chloride into a stirred suspension of the sodium salt of the alcohol in benzene. With the unsymmetrical carbonates, carbonyl chloride was replaced by methyl chloroformate, and the temperature was kept below 10 °C to minimise *trans*-esterification.[3] The identity of the products was confirmed by n.m.r. and mass spectrometry: di-t-butyl carbonate, b.p. 160—161 °C, m.p. 36·5—37·5° (lit.,[3] b.p. 158 °C, m.p. 39·5—40·5 °C); di-t-pentyl

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[1] Part II, D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 1744.

[2] D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 926.

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

carbonate, b.p. 92·5—93·5 °C at 23 mmHg, n_D^{20} 1·4189; methyl n-hexyl carbonate, b.p. 75—76 °C at 20 mmHg, n_D^{19} 1·4123; methyl 1-methylpentyl carbonate, b.p. 66—67 °C at 20 mmHg, $n_D^{19.5}$ 1·4080; methyl t-pentyl carbonate, b.p. 58 °C at 20 mmHg, n_D^{20} 1·4053.

Stoicheiometry.—Only di-t-butyl carbonate was investigated fully. It gave [1,2] t-butyl alcohol, 99·5%; isobutene, 104%; and carbon dioxide, 97%. The olefin isomer distributions [2] from the other carbonates were as follows: from methyl t-pentyl carbonate, 2-methylbut-1-ene, 71% and 2-methylbut-2-ene, 29%; from di-t-pentyl carbonate, 2-methylbut-1-ene, 70% and 2-methylbut-2-ene, 30%; from methyl 1-methylpentyl carbonate, hex-1-ene, 51% and hex-2-enes, 49%; and from bis-(1-methylpentyl) carbonate,[1] hex-1-ene, 49% and hex-2-enes, 52%. No product other than the expected alcohols and olefins could be detected.

TABLE 1

Flow-tube pyrolysis of some dialkyl carbonates *

Carbonate	E_a / kcal mol^{-1}	$\Delta S^‡$ / cal mol^{-1} K^{-1}	$k_{629\ K}$/ s^{-1}	Rate ratio †
Di-t-butyl	34·0	−6·5	2·01	1410
Di-t-pentyl	35·7	−2·4	4·05	2840
Methyl n-hexyl	45·6 (44·1)	−3·1 (−3·3)	1·13 × 10^{-3}	0·8 (2·2)
Methyl 1-methyl-pentyl	42·4 (40·3)	−1·3 (−3·4)	3·53 × 10^{-2}	25 (44)
Methyl t-pentyl	34·7 (35·7)	−4·3 (−2·4)	3·48	2440 (2840)

* Figures in parentheses are the data for the symmetrical dialkyl carbonates.[1,2] † The ratio is that of *k* for the cited carbonate at 629 K to *k* for diethyl carbonate at 629 K.

Kinetics.—Di-t-butyl carbonate showed evidence of the incursion of a radical mechanism at low temperature in the sealed-tube method.[2] At higher temperatures, the presence of cyclohexene had no effect. Thus at 454·5 K, k = 1·74 × 10^{-5} or 1·20 × 10^{-5} s^{-1} in the presence of cyclohexene; at 495·3 K, k = 3·73 × 10^{-4} or 3·88 × 10^{-4} s^{-1} in the presence of cyclohexene. As a precaution, all runs were done in the presence of cyclohexene, whereupon runs gave good first-order plots to *ca.* 70% completion. An Arrhenius plot over the range 453—498 K gave E_a = 38·0 kcal mol^{-1}, A = 2·4 × 10^{13} s^{-1}, and $\Delta S_{550\ K}$ = −0·5 cal mol^{-1} K^{-1}. The results from the flow-tube method [2] are shown in Table 1. All these carbonates survived the normal tests for a homogeneous unimolecular reaction.[2]

TABLE 2

Effect of α-methylation on the rate of pyrolysis of dialkyl carbonates at 629 K and of acetates at specified temperatures

Alkyl group	Carbonate $k_{629\ K}$/s^{-1}	k_{rel}	Acetate $k_{682\ K}$/s^{-1}	k_{rel}	Acetate[4] $k_{676.9\ K}$/s^{-1}	k_{re}
Et	1·42 × 10^{-3}	1	1·42 × 10^{-3}	1		
Pr^i	3·94 × 10^{-2}	28	2·91 × 10^{-2}	21		
Bu^t	2·01	1410	3·72	2620		
Pr^n	1·42 × 10^{-3}	1			1·43 × 10^{-3}	1
Bu^s	5·19 × 10^{-2}	37			2·97 × 10^{-2}	21
t-Pentyl	4·05	2840			7·10	4980

DISCUSSION

Only di-t-butyl carbonate was investigated over the full temperature range of the previous Parts. The agreement between Arrhenius parameters measured in the lower and higher temperature regions is less good than for the primary and secondary carbonates. This could be associated with the radical component identified at low temperature, but such an explanation is not consistent with the higher activation measured in this region. It seems more likely that the 4 kcal mol^{-1} difference represents the extreme of experimental error (±2 kcal mol^{-1}), and that the real value is **36·0** kcal mol^{-1}. The decrease in E_a previously noted on α-methylation is thus accelerated on further α-methylation: diethyl, 47; di-isopropyl, 45; di-t-butyl, 36 kcal mol^{-1}; and di-n-propyl, 47; di-2-butyl, 42; di-t-pentyl, 36 kcal mol^{-1}. In comparison, the corresponding acetates show a range of only 4 kcal mol^{-1} in E_a.[4] A comparison of the relative rate changes of carbonates with those of acetates therefore depends on temperature. The temperatures quoted in Table 2 are so chosen that the rates of pyrolysis of the parent compounds are the same, and therefore $\Delta G^‡$ the same for each. It appears from Table 2 that α-methylation of an n-alkyl carbonate enhances its rate of decomposition more than it affects the corresponding acetate, but that the effect is reversed on dialkylation. The effects are small, however, and indicate a similar degree of polarity in the cleavage of the $C_α$–O bond. This conclusion is in agreement with the similarity of ρ values for the two reactions reported by Smith *et al.*[5,6]

The unsymmetrical carbonates were examined by the flow method only. Under these conditions there was no evidence for alkyl group exchange according to scheme (1), as neither symmetrical carbonate could be detected.

$$2\text{MeO–CO–OR} \rightleftharpoons \text{MeO–CO–OMe} + \text{RO–CO–OR} \qquad (1)$$

Further, since the rates of pyrolysis of the symmetrical carbonates are similar to those of the unsymmetrical ones, one may rule out a scheme such as (2). The rate

$$2A \overset{\text{slow}}{\rightleftharpoons} B + C \longrightarrow \text{products} \qquad (2)$$

constants of Table 1 must therefore refer to the pyrolysis of the unsymmetrical carbonates themselves, the methyl esters having been chosen so that only one of the alkyl groups could undergo pyrolysis. The resulting activ-

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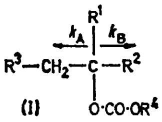
[4] J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.

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

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

ation parameters are indistinguishable from those of the symmetrical carbonates (shown in parentheses in the Table) but the rate constants show measurable differences.

The nature of the second alkyl group has almost no effect on the ratio of olefins produced from the first alkyl group. These ratios can be used to proportion the observed rate constants into separate rate constants, k_A and k_B, for the individual branches of the alkyl group, as in (I). Finally, a statistical correction can be applied by dividing each rate constant by $R \ln x$,[7] where x is the total number of hydrogen atoms available in that branch. The rate per hydrogen atom can be obtained by dividing simply by x. The results of such analyses are shown in Table 3. For both A- and B-branches, there is an increase of rate with increasing length of the β-alkyl group on the A-branch. This situation is paralleled by the acetates,[4] but in both cases while the trend is the same, the size of the increase depends on the temperature. In the present series the effect of alkylation is more marked on the A-branch than on the B-branch, as the effect has to be transmitted *via* the β-CH_2 group to affect the latter.



(I)

$$R^3{-}CH_2{-}\overset{\overset{R^1}{|}}{\underset{\underset{O{\cdot}CO{\cdot}OR^4}{|}}{C}}{-}R^2 \qquad \xleftarrow{k_A} \; \xrightarrow{k_B}$$

When the number of available β-hydrogen atoms is allowed for in this way, isobutyl carbonate,[2] having two β-methyl groups, has 1·1 times the rate of ethyl carbonate. It appears that steric hindrance is outweighing the small stabilisation of the incipient double bond in this case. A similar conclusion can be drawn from the comparison of the rates of methyl and di-t-pentyl carbonates. Thus the rates of methyl n-hexyl and 1-methylpentyl carbonates are about half of those of their symmetrical counterparts, but the two t-pentyl carbonates are very similar in rate. One may predict an ' unhindered ' rate of 6·96 s^{-1} for di-t-pentyl carbonate, with a rate of 4888 relative to di-n-propyl carbonate. Such a value fits the data of Table 2 rather more easily than the experimental value.

TABLE 3

Relative rates of pyrolysis of carbonates at 629 K; A, rate into β-CH_2; B, rate into R^2

R^3 [see structure (I)]	$R^1 = R^2 = H$	$R^1 = H$ $R^2 = Me$		$R^1 = R^2 = Me$	
	A	A	B	A	B
H	1	1	1	1	1
	1	*1*	*1*	*1*	*1*
Me	1·3	1·6	1·4	2·3 (3·9)	1 (1·6)
	1·5	*1·8*	*1·4*	*2·6* (*4·5*)	*0·9*$_5$ (*1·6*)
Et	1·9				
	2·2$_5$				
Pr^n		2·1 (2·3)	1·5 (1·5)		
		2·5 (*2·6*)	*1·5* (*1·8*)		
Bu^t	2·8 (2·1)				
	3·3 (*2·4*)				

Figures in parentheses are calculated from the unsymmetrical carbonates MeO·CO·OR. Ordinary numerals are values of $k/(R \ln x)$ and italic numerals are values of k/x (see text).

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[7] S. W. Benson, ' Thermochemical Kinetics,' Wiley, 1968.