Pyrolysis of Carbonates. Part II.[1] The Gas-phase Pyrolysis of Some Symmetrical 1-Methylalkyl Carbonates. Kinetic Deuterium Isotope Effect

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The similarity observed in the pyrolyses of primary alkyl carbonates and acetates extends to the 1-methylalkyl series.

IN Part I, the rates of pyrolysis of some symmetrical di-n-alkyl carbonates were reported, and were compared with literature data for the corresponding acetates.[1] The change in rate of pyrolysis with structure was very similar for the two series, and the ratio of the rate of decomposition of carbonate to that of acetate fell within the range 24—26 for all the compounds studied. We now report the results of our observations of some secondary carbonates.

EXPERIMENTAL

The carbonates were prepared by passing a known weight of phosgene into a solution of the appropriate alcohol in equal parts of benzene and pyridine.[2] The products had the following physical constants: di-isopropyl carbonate, b.p. 143—145°, n_D^{23} 1·3910 (lit.,[3] b.p. 146·1—146·7°, $n_D^{20\cdot6}$ 1·3906); bis-1-methylpropyl carbonate, b.p. 33° at 1·3 mmHg, n_D^{17} 1·4068 (lit.,[4] b.p. 73—76° at 18 mmHg, n_D^{20} 1·4039); bis-1-methylpentyl carbonate, b.p. 87—88° at 0·5 mmHg, n_D^{17} 1·4224; di-[1,3-$^2H_6$]isopropyl carbonate, b.p. 48·5° at 20·2 mmHg, $n_D^{17\cdot2}$ 1·3917. The alcohol for the last carbonate was obtained by reduction of commercial hexadeuterioacetone with lithium aluminium hydride.

Stoicheiometry.—The products were measured fully for only bis-1-methyl-propyl and -pentyl carbonates. The yields of alcohol and carbon dioxide were measured as previously described:[1] bis-1-methylpropyl carbonate, CO_2, 96·3; butan-2-ol, 102·1; and butenes, 96·0%; bis-1-methylpropyl carbonate, CO_2, 98·7; hexan-2-ol, 96·5; and hexenes, 96·0%. The estimation of the olefins was complicated by their isomerisation under the conditions of the experiment (*ca.* 280°). There is a loss of hex-1-ene and a gain of the *cis*-2-isomer up to about 75% pyrolysis of the carbonate. The true olefin ratios may be obtained by extrapolating to zero reaction (*trans*-hex-2-ene, 37; *cis*-hex-2-ene, 14; and hex-1-ene, 49%). A similar result is given by the packed pyrolysis tube[5] where the product molecules are separated by solvent or nitrogen molecules (*trans*-hex-2-ene, 36·9; *cis*-hex-2-ene, 15·1; and hex-1-ene, 48·0%). The ratios listed in the Results section were obtained by the latter method.

RESULTS

Only bis-1-methylpropyl carbonate was studied by the sealed tube method, the disappearance of carbonate being estimated by g.l.c. The reaction was of the first order in runs taken to *ca.* 70% completion. Runs performed in the presence of 200 mole % of cyclohexene, or in tubes packed with helices (surface : volume ratio increased 500%) showed no significant differences. An Arrhenius plot over the range 489—540° gave a good straight line, yielding the following parameters: bis-1-methylpropyl carbonate, E_a = 40·8 kcal mol^{-1}, $A = 9\cdot07 \times 10^{12}$ s^{-1}, and $\Delta S^{\ddagger}_{550\,K} = -2\cdot5$ cal K^{-1} mol^{-1}. The Arrhenius equation gave a value of $k_{629\,K} = 6\cdot09 \times 10^{-2}$ s^{-1} in satisfactory agreement with that calculated from the flow method (Table 1, $k_{629\,K} = 5\cdot25 \times 10^{-2}$ s^{-1}).

Table 1 shows the results of flow-tube experiments, and Table 2 the results of tests of homogeneity in these experiments. The olefin ratios obtained are compared with those from acetates in Table 3.

TABLE 1

Activation parameters for the pyrolysis of secondary carbonates by the flow-tube method (593—648 K)

Carbonate	E_a/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}	$10^2k_{629\,K}$/ s^{-1}
Di-[1,3-$^2H_6$]isopropyl	46·5	3·8	1·66
Di-isopropyl	45·3	3·6	3·99
Bis-1-methylpropyl	41·6	−1·8	5·25
Bis-1-methylpentyl	40·3	−3·4	6·29

TABLE 2

Tests for homogeneity in flow-tube pyrolysis of carbonates (629 K)

Carbonate	10^2k/s^{-1} (unpacked)	10^2k/s^{-1} (packed)	10^2k/s^{-1} (cyclohexene)
Di-isopropyl	3·94	4·01	4·10
Bis-1-methylpropyl	4·61	4·86	4·51

TABLE 3

Olefins from carbonate and ester pyrolysis

Carbonate	Olefin (%)	Acetate[6]	Olefin (%)
Bis-1-methylpropyl	But-1-ene 53 *cis*-But-2-ene 18 *trans*-But-2-ene 29	1-Methylpropyl	But-1-ene 57 *cis*-But-2-ene 15 *trans*-But-2-ene 28
Bis-1-methylpentyl	Hex-1-ene 48 *cis*-Hex-2-ene 15 *trans*-Hex-2-ene 37	1-Methylbutyl	Pent-1-ene 55 Pent-2-enes 45
		1-Methyl pentyl	Hept-1-ene 54 *cis*-Hept-2-ene 17 *trans*-Hept-2-ene 29

DISCUSSION

All the reactions were homogeneous and of the first order. A unimolecular mechanism is therefore implicated. The good agreement between the activation

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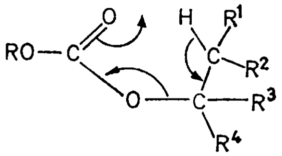
parameters measured at low and high temperature for bis-1-methylpropyl carbonate ($R^1 = R^3 = H$, $R^2 = R^4 = Me$) indicates a continuity of mechanism over some 150°.



The ratio of olefins obtained by the pyrolysis of carbonates is very similar to that obtained from the corresponding acetates. In both cases the statistical percentages should have been: 1-ene, 60; *cis*-2-ene, 20; and *trans*-2-ene, 20%. Table 3 shows that the ratios are distorted by a greater tendency for the formation of the more thermodynamically stable olefins and that this distortion is greater in the case of the carbonates. The isomerisation of the olefins in sealed-tube experiments, referred to in the Experimental section, was unexpected. There was very slight isomerisation in the primary alkyl carbonates,[1] and none with the pure olefins either alone or in the presence of alcohol. We cannot offer an explanation at this time, unless it is associated with the agency of the half-ester of carbonic acid (RO·CO·OH). Although such esters have not been isolated, they might have an unusually long life in the gas phase if there is no mechanism through which they can decompose. Decomposition by an ionic mechanism, for example, would presumably require interaction with a polar site on the wall.

The activation parameters shown in Table 1 are not likely to be highly reliable.[6] In particular the positive value for $\Delta S^\ddagger$ obtained for di-isopropyl carbonate ($R^1 = R^2 = R^3 = H$, $R^4 = Me$) seems unlikely for a reaction involving a six-centre transition state. Nevertheless Scheer *et al.*[6] obtained $\Delta S^\ddagger = -7{\cdot}4$ cal K^{-1} mol^{-1} for n-propyl acetate and $\Delta S^\ddagger = -2{\cdot}9$ for isopropyl acetate. Adding this difference to the value we obtained for di-n-propyl carbonate [1] gives a predicted value of $+4{\cdot}5$ cal K^{-1} mol^{-1} for di-isopropyl carbonate. The more positive value for both isopropyl compounds must reflect the increase in number of available β-hydrogen atoms from two to six together with possible steric effects.

With both primary and secondary carbonates there is a decrease in E_a with increased chain length on the β-carbon atom. There is also a trend to more negative values of $\Delta S^\ddagger$. In comparing the two series, the introduction of an α-methyl group reduces E_a by some 2—3 kcal mol^{-1}, which is expected from stabilisation of the developing olefinic bond.

The rate constants, calculated from the Arrhenius equations are more reliable than the activation parameters. We have chosen 629 K as a temperature most nearly experimentally accessible to primary, secondary, and tertiary carbonates. The rates of the secondary carbonates no longer follow those of the acetates with the precision of the primary alkyl series. Using the data of Scheer *et al.*[6] to calculate k_{acetate} at 629 K (where $R = k_{\text{carbonate}}/k_{\text{acetate}}$) gives values for isopropyl, $1{\cdot}6 \times 10^{-3}$ s^{-1}, $R = 25$; for 1-methylpropyl, $1{\cdot}9 \times 10^{-3}$ s^{-1}, $R = 27$; and for 1-methylbutyl, $3{\cdot}7 \times 10^{-3}$ s^{-1} and 1-methylpentyl, $4{\cdot}0 \times 10^{-3}$ s^{-1}, $R_{\text{av.}} = 16$.

At 684 K, the temperature used for the acetates, the ratios are: isopropyl, 26; 1-methylpropyl, 16; and 1-methylpentyl, 14. The agreement is good but for the 1-methylpropyl case. Here Scheer *et al.* report an inexplicably high value for E_a, and the slopes for carbonate and acetate must be quite different. The decrease in R with substitution on the β-carbon atom may be caused by steric hindrance, which should build up much the more rapidly in the carbonates.

The deuterium kinetic isotope effect of 2·38 at 629 K is of similar magnitude to that found previously in acetates[7] (2·6 at 673 K).

Both the olefin distributions referred to earlier and the deuterium isotope effect imply very similar transition states for acetate and carbonate pyrolysis. However, since both are basically functions of the alkyl group, the similarity is expected once a multicentre elimination is established as operative in each reaction. Neither of these types of evidence can be used to distinguish between ether or carbonyl oxygen attack in the carbonates.

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