Thermal Rearrangement of Diphenyl Carbonate

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The thermal degradation of diphenyl carbonate has been examined in the gas and condensed phases. From a detailed analysis of the products it is suggested that the mechanism involves an initial rearrangement to 2-phenoxy benzoic acid followed by several competing reactions of the acid. The effect of phase is discussed. The thermal behaviour of several compounds involved in the degradation scheme has also been investigated.

THE degradation of dialkyl[1-3] alkyl aryl,[4] and alkyl benzyl[5,6] carbonates has been studied in detail, and it has been established that they undergo homogeneous, unimolecular decomposition (1).

$$RCH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}OR' \xrightarrow{\text{slow}} [R'O{\cdot}CO{\cdot}OH] \xrightarrow{\text{fast}} ROH + CO_2 \qquad + RCH{=}CH_2 \qquad (1)$$

However, from esters where the elimination of olefin is difficult or impossible, *e.g.*, dimethyl carbonate,[7-9] bis(triphenylmethyl) carbonate,[10] methyl 2-naphthyl carbonate,[11] and some cyclic carbonates,[12,13] the corresponding ether and carbon dioxide are formed as major products, *e.g.*,

$$ArO{\cdot}CO{\cdot}OMe \longrightarrow Ar{\cdot}OMe + CO_2 \qquad (2)$$

Tsou and Seligman[14] suggested that in the pyrolysis of carbonates reaction (1) occurs in preference to (2) wherever structurally possible, although the occurrence of (2) to a limited extent in the degradation of diethyl carbonate,[8] ethyl 2-naphthyl carbonate,[14] and cholesteryl 2-naphthyl carbonate[15] suggests that this distinction is not clear-cut.

The thermal degradation of diaryl carbonates has received very little attention. Ritchie[2] pyrolysed diphenyl carbonate at 640—670° and concluded that diaryl carbonates lost carbon dioxide to form the corresponding ether which underwent further pyrolysis. The degradation of diphenyl carbonate in the presence of sodium carbonate was ascribed by Fosse[16] to interaction of two molecules of the ester to form phenyl 2-phenoxybenzoate followed by hydrolysis to the corresponding acid.

As part of a programme to elucidate the mechanisms of degradation of organic polymers, we have examined the thermal decomposition of diphenyl carbonate as a model for the behaviour of the carbonate group in poly-[2,2-propane-bis-(4-phenyl carbonate)].

EXPERIMENTAL

Materials.—The purity of compounds pyrolysed was established by gas chromatography. Diphenyl carbonate (Koch–Light) was purified by sublimation, m. p. 80°. 2-Phenoxybenzoic acid, m. p. 110° (lit.,[16] 113°) was prepared by hydrolysis of phenyl-2-phenoxybenzoate (m. p. 105°) obtained by sodium carbonate catalysed rearrangement of diphenyl carbonate during 48 hr. at 220°. To prepare phenyl *p*-tolyl carbonate, phenyl chloroformate (47 g.) in ether (250 ml.) was added during 2 hr. to a stirred suspension of sodium 4-methylphenoxide (40 g.) in ether (250 ml.). Work-up of the product gave colourless crystals (59·5 g.), m. p. 85°, after two recrystallisations from petroleum (b. p. 40—60°). Repeated fractional crystallisation raised the melting point to 106° but gas chromatography revealed

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[1] A. S. Gordon and W. P. Norris, *J. Phys. Chem.*, 1965, **69**, 3013.
[2] P. D. Ritchie, *J. Chem. Soc.*, 1937, 1054.
[3] G. L. O'Connor and H. R. Nace, *J. Amer. Chem. Soc.*, 1953, **75**, 2118.
[4] G. G. Smith and B. Kosters, *Chem. Ber.*, 1960, **93**, 2400.
[5] G. G. Smith and B. L. Yates, *J. Org. Chem.*, 1965, **30**, 434.
[6] G. G. Smith, D. A. K. Jones, and R. Taylor, *J. Org. Chem.*, 1963, **28**, 3547.
[7] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, 1959, **63**, 104.
[8] M. H. J. Wignen, *J. Chem. Phys.*, 1961, **34**, 1465.
[9] S. C. S. Thynne and P. Gray, *Trans. Faraday Soc.*, 1962, **58**, 2403.
[10] M. Gomberg, *Ber.*, 1913, **46**, 226.
[11] A. Einhorn and L. Rothlauf, *Annalen*, 1911, **382**, 237.
[12] S. Searles, D. G. Hummel, S. Nukina, and P. E. Throckmorton, *J. Amer. Chem. Soc.*, 1960, **82**, 2928.
[13] E. D. Bergmann and I. Shahak, *J. Chem. Soc.*, 1966, 899.
[14] K. C. Tsou and A. M. Seligman, *J. Amer. Chem. Soc.*, 1954, **76**, 3704.
[15] K. C. Tsou, *J. Amer. Chem. Soc.*, 1954, **76**, 6108.
[16] R. Fosse, *Compt. rend.*, 1903, **136**, 1074.

three components which were subsequently purified by preparative gas chromatography and sublimation: diphenyl carbonate, m. p. 78°; phenyl *p*-tolyl carbonate (Found: C, 74·0; H, 5·3. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%), m. p. 67° (lit., 94°,[17] 49—50°,[18] but these products may have contained traces of the symmetrical carbonates formed during preparation); di-*p*-tolyl carbonate (Found: C, 74·7; H, 6·1. Calc. for $C_{15}H_{14}O_3$: C, 74·4; H, 5·8%), m. p. 115° (lit.,[19] 115°).

Thermal Degradation.—The required quantity of compound was placed in a Pyrex ampoule having a break-seal, and dried in a vacuum (10^{-6} mm.) by heating and, if possible, by sublimation. The ampoule was sealed and placed in a molten-salt bath at the required temperature (±0·5°) for an appropriate period. The contents of the cooled ampoule were analysed quantitatively. The ampoules varied in internal volume from 0·5 to 500 ml. and the surface area was increased in some cases by packing with Pyrex Fenske helices. Ampoules were pretreated with hydrofluoric acid before washing with distilled water.

Analyses.—Gaseous degradation products were analysed by mass spectrometry or gas chromatography. Liquid and solid products were dissolved in acetone, separated by preparative gas chromatography, and identified by microanalysis and infrared spectroscopy. After identification, components were analysed quantitatively using a Perkin-Elmer 801 chromatograph equipped with an all-glass dual inlet and column system. The stationary phase was 20% Apiezon K on Embacel. Solutions containing free acids were pretreated with diazomethane before chromatography as methyl esters

RESULTS

Diphenyl Carbonate.—(a) *Liquid phase.* The products detected after liquid phase degradation of diphenyl carbonate at 360° were carbon dioxide, phenol, xanthone, and phenyl 2-phenoxybenzoate, with smaller quantities of carbon monoxide, diphenyl ether, dibenzofuran, and phenyl 2-phenoxyphenyl carbonate. The rates of formation of the major products, except carbon dioxide, are shown in Figure 1. The yield of gas (99·5% CO_2, 0·5% CO) after 2·6 hr. at 360° was 3·5 × 10^{-2} mol./mol. of diphenyl carbonate.

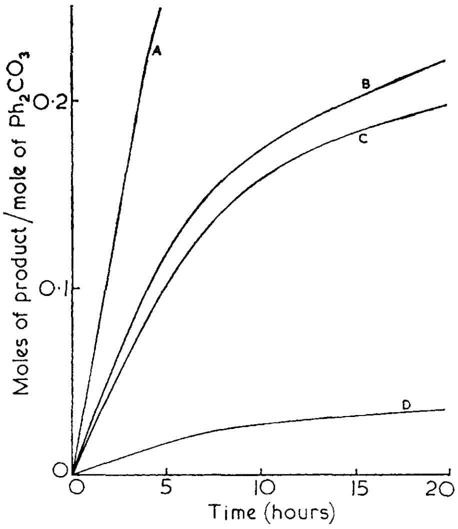

FIGURE 1 Rates of formation of (A) phenol, (B) xanthone, (C) phenyl 2-phenoxybenzoate, and (D) diphenyl ether from diphenyl carbonate in the liquid phase at 360°

(b) *Gas phase.* The products of gas phase decomposition of diphenyl carbonate in the range 360—500° were carbon dioxide, phenol, diphenyl ether, dibenzofuran, and xanthone, with traces of carbon monoxide, benzene, phenyl 2-phenoxybenzoate, and phenyl 2-phenoxyphenyl carbonate. The use of packed and unpacked reaction vessels (Table 1) indicated that the major products except diphenyl ether occurred by heterogeneous processes.

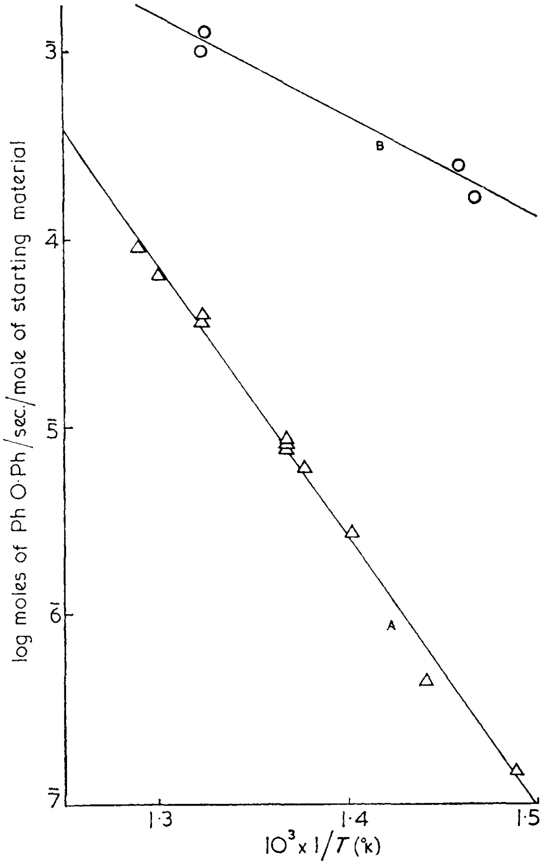

FIGURE 2 Effect of temperature on the first-order rate constants for the gas phase formation of diphenyl ether from (A) diphenyl carbonate and (B) 2-phenoxybenzoic acid

The amounts of phenol, diphenyl ether, and dibenzofuran formed depended on the initial pressure of diphenyl carbonate, whereas the quantity of xanthone appeared to be inversely proportional to the diphenyl carbonate pressure (Table 2). The rates of formation of phenol, diphenyl ether, and dibenzofuran are expressed by the first-order rate constants, *k*, in Table 2, where

$$k = (dx/dt)(1/[Ph_2CO_3])\ \text{sec.}^{-1}$$

The effect of temperature on these rate constants is shown in Figure 2.

Xanthone.—Xanthone was stable in the liquid phase at 360° and yielded only a trace of dibenzofuran in the gas phase at 460°.

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[17] A. Morel, *Bull. Soc. chim. France*, 1899, [3], **21**, 823.

[18] P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 2469.

[19] G. Bender, *Ber.*, 1886, **19**, 2268.

Phenyl 2-Phenoxybenzoate.—Thermal decomposition in the liquid phase at 360° yielded gas (87% CO_2, 13% CO), phenol, diphenyl ether, xanthone, and dibenzofuran. At 460° in the gas phase the same products were formed; the gas composition was 54% CO_2, 46% CO.

TABLE 1

Analysis of products (millimoles) from the gas phase decomposition of diphenyl carbonate (0·330 mmole) at 460° for 40 min., (a) in a packed vessel and (b) in an unpacked vessel

Gas (% CO_2, % CO)	Phenol	Diphenyl ether	Dibenzofuran	Xanthone
(a) 0·133 (80, 20)	0·032	0·0067	0·0033	0·032
(b) 0·013 (78, 22)	0·008	0·0065	0·0009	0·0012

2-Phenoxybenzoic Acid.—Analyses of the degradation products in the condensed phase at 360° and in the gas phase at several temperatures are in Table 3. The gas evolved was composed of carbon dioxide and significant quantities of water, but the relative amounts were not determined.

TABLE 2

Formation of products during the gas phase degradation of diphenyl carbonate at 460° for 90 min.

Initial Ph_2CO_3 (mmoles)	Products (millimoles)									
	CO_2	CO	Phenol	Diphenyl ether	Dibenzofuran	Xanthone	$k_{\text{phenol}} \times 10^6$	$k_{\text{ether}} \times 10^6$	$k_{\text{dibenzofuran}} \times 10^6$	Xanthone × Ph_2CO_3 × 10^6
0·175	0·017	0·0034	0·0045	0·0073	0·001	0·0050	4·8	7·8	1·06	0·9
0·329	0·029	0·0058	0·0172	0·0146	0·002	0·0026	9·7	8·2	1·24	0·9
1·105	0·109	0·022	0·054	0·049	0·007	0·0013	9·1	8·2	1·23	1·4

TABLE 3

Analysis of products from the decomposition of 2-phenoxybenzoic acid

Run	Phase	Temp. (°C)	Time (min.)	Acid initially (mmoles)	Products (millimoles)			
					Gas	Diphenyl ether	Xanthone	Phenyl 2-phenoxybenzoate
C134	Liquid	360	60	0·283	0·128	0·0507	0·145	0·004
C136	Gas	460	10	0·135	0·094	0·084	0·008	0·002
C137	Gas	460	10	0·135	0·100	0·100	0·014	0·003
C141	Gas	414	20	0·205	0·116	0·073	0·100	0·005
C138	Gas	410	40	0·495	0·188	0·204	0·007	

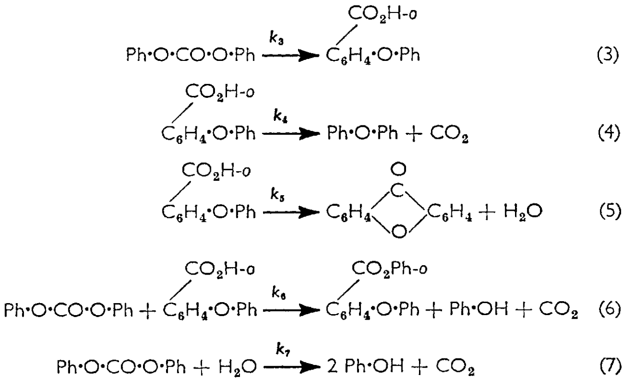
The effect of changing the surface-to-volume ratio was investigated in runs C136 (8-mm. tube, volume 6 ml., surface area 30 cm.^{2}) and C137 (bulb volume 520 ml., surface area 95 cm.^{2}).

Phenyl p-*Tolyl Carbonate.*—Phenyl *p*-tolyl carbonate pyrolysed in the gas phase at 460° for 1 hr. yielded a range of products including diphenyl ether, phenyl *p*-tolyl ether, and di-*p*-tolyl ether in the approximate ratio 1 : 2 : 1, and diphenyl carbonate, phenyl *p*-tolyl carbonate, and di-*p*-tolyl carbonate in the same ratio. A similar pyrolysis at 540° for 6 min. yielded the same products but both of the above ratios became 1 : 10 : 1.

DISCUSSION

Mechanism of Thermal Degradation of Diphenyl Carbonate.—The present study has shown that degradation of diphenyl carbonate produces carbon dioxide, phenol, diphenyl ether, xanthone, and phenyl 2-phenoxybenzoate, with minor quantities of carbon monoxide, dibenzofuran, and 2-phenoxyphenyl phenyl carbonate. The relative amounts formed in the condensed phase at 360° are different from those in the gas phase at 360—500°. Since the products could arise from either inter- or intra-molecular reactions, the relative importance of such reactions was examined by degradation of the unsymmetrical phenyl *p*-tolyl carbonate. Gas phase pyrolysis at 460° for 1 hour yielded amongst the products, diphenyl, phenyl *p*-tolyl, and di-*p*-tolyl ethers in the approximate ratio 1 : 2 : 1. However, as the pyrolysate also contained diphenyl, phenyl *p*-tolyl, and di-*p*-tolyl carbonate in the same ratio, transesterification had clearly occurred. To minimise the importance of the latter process, which should have a low activation energy, the carbonate was pyrolysed at 540° for 6 minutes. Under these conditions the three ethers and three carbonates were again formed, but in the ratio 1 : 10 : 1. These results point to an intramolecular process, as the ethers would be expected in the ratio 1 : 2 : 1 from a scission process followed by recombination. The ratios of the respective dibenzofurans and xanthones, again 1 : 10 : 1, indicate that these products also result from intramolecular processes.

The major products of the condensed and gas phase decompositions of diphenyl carbonate can be accounted for by postulating a rearrangement of diphenyl carbonate to 2-phenoxybenzoic acid [reaction (3)] followed by reactions (4)—(7). Attempts to confirm reaction (3)



$$\mathrm{Ph{\cdot}O{\cdot}CO{\cdot}O{\cdot}Ph} \xrightarrow{k_3} \overset{\mathrm{CO_2H}\text{-}o}{\mathrm{C_6H_4{\cdot}O{\cdot}Ph}} \quad (3)$$

$$\overset{\mathrm{CO_2H}\text{-}o}{\mathrm{C_6H_4{\cdot}O{\cdot}Ph}} \xrightarrow{k_4} \mathrm{Ph{\cdot}O{\cdot}Ph + CO_2} \quad (4)$$

$$\overset{\mathrm{CO_2H}\text{-}o}{\mathrm{C_6H_4{\cdot}O{\cdot}Ph}} \xrightarrow{k_5} \mathrm{C_6H_4}\genfrac{}{}{0pt}{}{\overset{\mathrm{O}}{\mathrm{C}}}{\mathrm{O}}\mathrm{C_6H_4 + H_2O} \quad (5)$$

$$\mathrm{Ph{\cdot}O{\cdot}CO{\cdot}O{\cdot}Ph} + \overset{\mathrm{CO_2H}\text{-}o}{\mathrm{C_6H_4{\cdot}O{\cdot}Ph}} \xrightarrow{k_6} \overset{\mathrm{CO_2Ph}\text{-}o}{\mathrm{C_6H_4{\cdot}O{\cdot}Ph}} + \mathrm{Ph{\cdot}OH + CO_2} \quad (6)$$

$$\mathrm{Ph{\cdot}O{\cdot}CO{\cdot}O{\cdot}Ph + H_2O} \xrightarrow{k_7} \mathrm{2\,Ph{\cdot}OH + CO_2} \quad (7)$$

directly, by isolation of 2-phenoxybenzoic acid, were unsuccessful. It is to be expected, however, that esterification of the acid [reaction (6)] will occur with relative ease to give the phenyl 2-phenoxybenzoate found as a product. Formation of the ester is consistent with the complete conversion of diphenyl carbonate into phenyl 2-phenoxybenzoate and phenol [*i.e.*, reactions (3) and (6)] which occurs during 18 hours at 230° when catalysed by the addition (5% w/w) of sodium carbonate or sodium hydrogen carbonate. In the absence of such catalysts we have found that the conversion of diphenyl carbonate into products under the above conditions is negligible and unaffected by the addition of (5% w/w) of sodium chloride, sodium iodide, pyridine, or copper-bronze.

The suggested mechanism requires that 2-phenoxybenzoic acid should decompose according to reactions (4) and (5). Examination of the thermal degradation of this acid showed that water, carbon dioxide, diphenyl ether, xanthone, and traces of phenyl 2-phenoxybenzoate were formed in both the condensed and the gas phase (Table 3). At low temperatures in the condensed phase, xanthone and water were the major products, whereas at high temperatures in the gas phase diphenyl ether and carbon dioxide predominated. These results are consistent with the postulate that the degradation of 2-phenoxybenzoic acid involves a competition between reactions (4) and (5).

Kinetics of the Condensed Phase Thermal Degradation of Diphenyl Carbonate.—Quantitative estimation of the major products of degradation of diphenyl carbonate made an analysis of the mechanism possible.

From the suggested mechanism, if attainment of steady-state conditions is assumed in the condensed phase degradation, the rate of formation of phenol is given by

$$\begin{array}{ccccc} d[\text{Phenol}]/dt & = & 2d[\text{Xanthone}]/dt & + & d[\text{Benzoate}]/dt \\ 1{\cdot}54 \times 10^{-5} & & 2(0{\cdot}55 \times 10^{-5}) & & 0{\cdot}55 \times 10^{-5} \end{array}$$

where benzoate refers to phenyl 2-phenoxybenzoate. The values (mmole sec.$^{-1}$ mmole Ph_2CO_3) shown for the nitial rates were determined from Figure 1.

Similarly, the rate of formation of carbon dioxide is given by

$$d[CO_2]/dt = d[\text{Ether}]/dt + d[\text{Benzoate}]/dt + d[\text{Xanthone}]/dt$$

where 'ether' refers to diphenyl ether, which is consistent with the values of d[Benzoate]/dt and d[Xanthone]/dt given above, and d[Ether]/d$t \sim 0{\cdot}7 \times 10^{-6}$ from the initial rate (Figure 1) and d[CO_2]/d$t = 0{\cdot}97 \times 10^{-5}$ mmole sec.$^{-1}$ mmole Ph_2CO_3 determined from the amount of carbon dioxide, $3{\cdot}5 \times 10^{-2}$ mmole/mmole of diphenyl carbonate, evolved after 2·6 hours at 360°.

Further, the reaction scheme predicts that

$$d[\text{Xanthone}]/d[\text{Benzoate}] = k_5/k_6[Ph_2CO_3]$$

which, assuming a density of 1·1 for diphenyl carbonate and expressing concentration in millimoles/c.c., can be expressed as

$$d[\text{Xanthone}]/d[\text{Benzoate}] = 200k_5/k_6 \sim 1 \text{ (from Figure 1)}$$

Hence,

$$k_6 \sim 200k_5$$

It also follows from the reaction scheme that

$$d[\text{Xanthone}]/d[\text{Ether}] = k_5/k_4 \sim 8 \text{ (from Figure 1)}$$

whence

$$8k_4 \sim k_5$$

which is in reasonable agreement with the ratio of k_4 to k_5 (1 : 3) found in the degradation of 2-phenoxybenzoic acid. From the breakdown of the acid (Table 3), by assuming first-order kinetics, k_4 and k_5 were calculated to be 3×10^{-3} and 9×10^{-3} sec.$^{-1}$, respectively, at 360° in the condensed phase. If we apply this value for k_5 to diphenyl carbonate, then

$$k_6 \sim 1{\cdot}8 \text{ c.c. mmole}^{-1} \text{ sec.}^{-1}$$

Similarly, at 360°, k_3 was determined as 5×10^{-3} sec.$^{-1}$ from

$$d[\text{Xanthone}]/dt = k_3k_5[Ph_2CO_3]/(k_4 + k_5 + k_6[Ph_2CO_3])$$

and the steady-state concentration of 2-phenoxybenzoic acid was calculated to be 5×10^{-6} mol./mol. of Ph_2CO_3 from

$$[\text{Acid}] = k_3[Ph_2CO_3]/(k_4 + k_5 + k_6[Ph_2CO_3])$$

Kinetics of the Gas phase Thermal Degradation of Diphenyl Carbonate.—The products of the gas phase decomposition of diphenyl carbonate at 460° included all those found in the liquid phase. However, the relative amounts differed (Table 2); in particular, only a trace of 2-phenoxyphenyl benzoate was formed. Also, the gas phase reaction produced dibenzofuran; this, with carbon monoxide, carbon dioxide, phenol, xanthone, and phenyl 2-phenoxybenzoate, appear to result from heterogeneous processes.

The formation of diphenyl ether, a major product, is apparently the only homogeneous process and is first-order with respect to diphenyl carbonate. From Figure 2 the rate constant can be expressed as

$$k_{\text{ether}} = 9{\cdot}7 \times 10^{13}e^{-64{,}000/RT}$$

Assuming that conversion of carbonate into ether proceeds by reactions (3) and (4), then, since the rate of formation of ether depends on the first power of the diphenyl carbonate concentration, the entire process must have attained a steady state. Hence, if for simplicity other reactions of the acid are neglected, the rate of reaction (3) should be approximately that of the overall conversion into ether, *i.e.*,

$$k_3 \sim 10^{14}e^{-54{,}000/RT} \text{ sec.}^{-1}$$

Now, in the gas phase decomposition of 2-phenoxybenzoic acid, reaction (4) appears to be homogeneous, and an Arrhenius plot for the production of ether (Figure 2) gives

$$k_4 = 2 \times 10^{11}e^{-48,000/RT} \text{ sec.}^{-1}$$

If we assume this value to be valid for the gas phase decomposition of diphenyl carbonate, then, from Figure 2, $k_4 \sim 100k_3$ at 460°. Therefore the steady-state concentration of 2-phenoxybenzoic acid, given approximately by $(k_3/k_4)[Ph_2CO_3]$, has a value at 460° about 0·8% that of diphenyl carbonate.

The other products of the gas phase reaction appear to result from heterogeneous processes (Table 1). The rates of formation of carbon monoxide, carbon dioxide (less the amount equivalent to diphenyl ether), phenol, and dibenzofuran seem to depend on the first power of the diphenyl carbonate pressure (Table 2, Figures 3 and 4). There is a ratio of about 2 : 1 in the yield of carbon monoxide to that of dibenzofuran, and of carbon dioxide to phenol. The heterogeneous nature of the reactions leads to some scatter of results (Figures 3 and 4), and prevents precise determination of activation energies. A reasonable average activation energy for formation of all four products is 65 kcal./mole, although there is some indication that the values for carbon monoxide and dibenzofuran are higher and those for carbon dioxide and phenol are lower than this average. It is significant that the activation energy for formation of these products is similar to that for formation of diphenyl ether. If, as suggested, formation of 2-phenoxybenzoic acid is the rate-determining step in the production of diphenyl ether, the acid is probably a common intermediate for all five products in accordance with reactions (3)—(7).

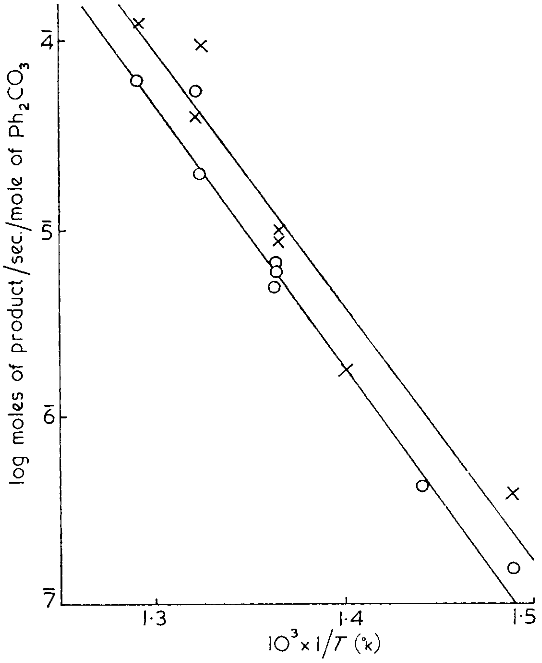


FIGURE 3 Effect of temperature on the first-order rate constants for formation of phenol (×) and carbon dioxide (○) from diphenyl carbonate in the gas phase. The carbon dioxide results represent the difference between the total carbon dioxide and that equivalent to the diphenyl ether formed

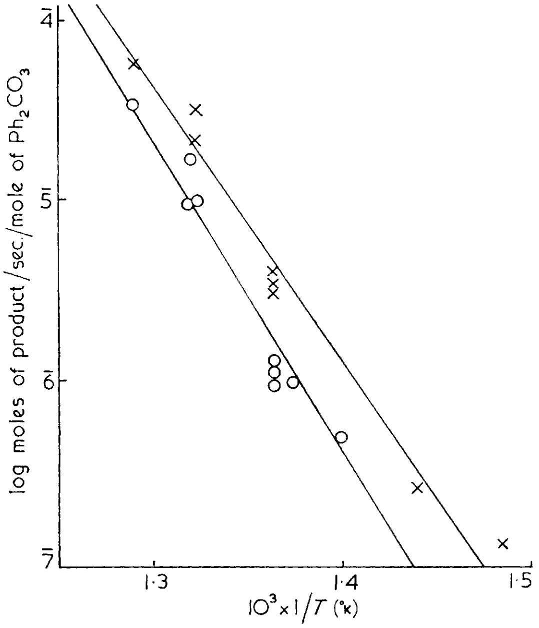


FIGURE 4 Effect of temperature on the first-order rate constants for formation of dibenzofuran (○) and carbon monoxide (×)

The yields of phenol and carbon dioxide exceed those predicted [reactions (3)—(7)] from the combined yields of xanthone and phenyl 2-phenoxybenzoate. This suggested that some of the xanthone and phenyl 2-phenoxybenzoate formed subsequently decomposed; this was confirmed by an examination of the behaviour of these compounds at 460°. Xanthone partly decomposed to dibenzofuran and carbon monoxide. Phenyl 2-phenoxybenzoate yielded xanthone, dibenzofuran, phenol, and carbon monoxide, suggesting formation of dibenzofuran, carbon monoxide, and phenol, in one reaction, and of xanthone and phenol in another. However, the decomposition of this ester is almost certainly more complex than suggested, since a study of phenyl benzoate [20] has shown that thermal rearrangement to 2-phenylbenzoic acid is possible and results in a sequence of reactions analogous to those suggested for 2-phenoxybenzoic acid. In the case of phenyl 2-phenoxybenzoate such reactions would yield trinuclear products consistent with the minor quantities of unidentified high molecular weight products from the decomposition of diphenyl carbonate detected by gas chromatography during the present work. The reactions of xanthone and phenyl 2-phenoxybenzoate can thus account for the presence of carbon monoxide and dibenzofuran as products of the degradation of diphenyl carbonate.

Further reactions of the initial products of degradation

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[20] A. Davis and J. H. Golden, unpublished work.

of diphenyl carbonate can therefore provide a reasonable explanation for observed discrepancies in the mass balance expected from reactions (3)—(7) but make a complete kinetic analysis difficult. Despite this, the suggested mechanism accounts both qualitatively and semiquantitatively for the principal features of the thermal decomposition of diphenyl carbonate in the gas and condensed phases. It appears likely that the degradation [11] of methyl 2-naphthyl carbonate, in which methyl 2-naphthyl ether is a major product, also involves intramolecular rearrangement to a labile acid followed by decarboxylation, rather than the suggested homolytic 1,3-migration of the methyl group with simultaneous elimination of carbon dioxide. It is conceivable that the suggested mechanism could be extended to other carbonates which yield the corresponding ether as a product, that is, those in which reaction (1) is structurally impossible or in which competition with reaction (1) could occur.

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