Radiolysis and Photolysis of Diphenyl Carbonate

By **A. Davis** * and **J. H. Golden**,† Ministry of Technology, Explosives Research and Development Establishment, Waltham Abbey, Essex

The products of electron and ultraviolet irradiation of diphenyl carbonate and related carbonates have been examined in detail. The origin of the products and the importance of intramolecular cage-recombinations and re-arrangements in the radiation- and photo-induced degradations is discussed.

IT was previously suggested [1] that cage-recombination of radicals could account for some of the products formed during electron irradiation of diphenyl carbonate, and an electron spin resonance study of irradiated diaryl carbonates confirmed [2] the presence of paired radicals. A more detailed examination of the products of irradiation of diphenyl carbonate and substituted diphenyl carbonates has now substantiated the intramolecular nature of the recombination. The reactions involved in radiolysis have been compared with those occurring during ultraviolet irradiation.

EXPERIMENTAL

Compounds for irradiation were purified by preparative gas–liquid chromatography and sublimation: diphenyl carbonate, m.p. 80°; phenyl p-tolyl carbonate, m.p. 67°; di-p-tolyl carbonate, m.p. 115°.[3]

Irradiation.—Ampoules with break-seals and containing

the compounds were degassed (10^{-6} mm.) and sealed. Pyrex ampoules cooled by a water spray were exposed to a linear accelerator electron beam (4 Mev) at a dose rate of 5 Mrads/min. Silica ampoules were exposed 6 in. from a Hanovia UVS 500 mercury vapour arc.

Analyses.—Gases evolved during irradiation were analysed with an A.E.I. MS 2H mass spectrometer. Liquids and solids were analysed using an LKB 9000 combined gas chromatograph and mass spectrometer, and a Perkin-Elmer 801 gas chromatograph. The g.l.c. stationary phase was 20% Apiezon K on Embacel. Detailed analyses of the higher molecular weight ' polymeric ' components were not obtained.

RESULTS

The identified products from electron irradiation of diphenyl carbonate in a vacuum are listed in Table 1. The

[1] J. H. Golden, *Makromol. Chem.*, 1963, **66**, 73.
[2] A. Davis, J. H. Golden, J. A. McRae, and M. C. R. Symons, *Chem. Comm.*, 1967, 398.
[3] A. Davis and J. H. Golden, *J. Chem. Soc. (B)*, 1968, 40.

† *Present address:* Ministry of Technology, Royal Aircraft Establishment, Farnborough, Hants.

retention times are relative to diphenyl carbonate (10·7 min.) at 180° with a nitrogen flow of 60 ml./min. Products were formed linearly with doses up to 500 Mrads, and G-values are in Table 1; G for the diappearance of diphenyl carbonate

TABLE 1

Products from electron irradiation of diphenyl carbonate

Product	G.l.c. retention time *	G(product) †
Carbon monoxide	—	0·90
Carbon dioxide	—	0·36
Phenol	0·047	0·66
Diphenyl ether	0·351	0·07
Biphenyl	0·355	trace
2-Hydroxybiphenyl	0·617	0·008
2-Hydroxydiphenyl ether	0·621	0·24
4-Hydroxydiphenyl ether	1·19	0·050
4-Hydroxybiphenyl	1·26	0·007
Phenyl salicylate	1·55	0·012
2,2′-Dihydroxybiphenyl	2·10	0·060
2,2′-Dihydroxybenzophenone......	2·59	0·007
2,4′-Dihydroxybiphenyl	4·04	0·016
2,4′-Dihydroxybenzophenone......	6·35	0·002

* Relative to diphenyl carbonate = 1·00. † Dose range 0—500 Mrads.

was 2·53. Above 500 Mrads consumption of diphenyl carbonate led to decreases in the yields of products (see Figure).
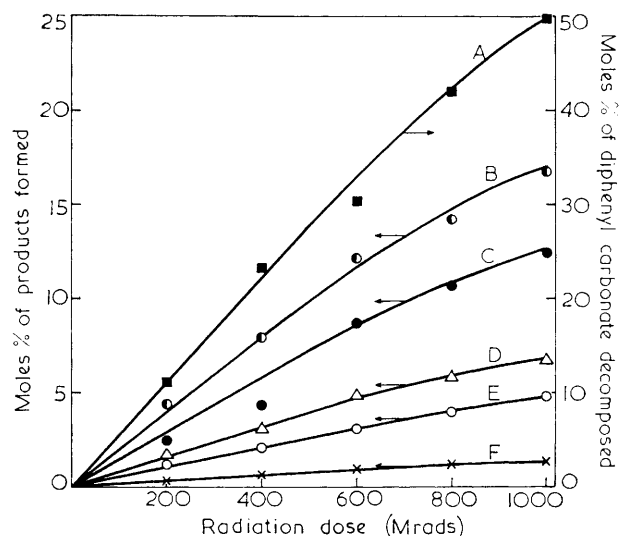
Effect of radiation dose on the decomposition of diphenyl carbonate and the formation of products. A, Diphenyl carbonate; B, carbon monoxide; C, phenol; D, carbon dioxide; E, 2-hydroxydiphenyl ether; F, diphenyl ether. The arrows indicate the relevant ordinate

The products from electron irradiation of phenyl p-tolyl carbonate and di-p-tolyl carbonate were also examined but in less detail. The pattern of products was in each case similar to that for diphenyl carbonate. Diphenyl and di-p-tolyl derivatives were not formed during irradiation of phenyl p-tolyl carbonate.

The non-gaseous products identified from ultraviolet irradiation of diphenyl carbonate are listed in Table 2.

The gas formed at the same time consisted of carbon dioxide (22%) and carbon monoxide (78%).
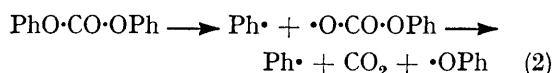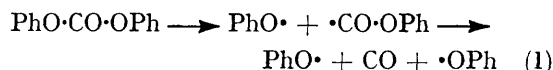
TABLE 2

Non-gaseous products from u.v. irradiation of diphenyl carbonate

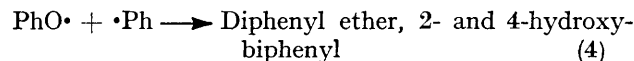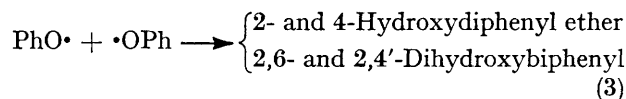| Product	Approx. yield *
Phenol	52·0
Diphenyl ether	2·2
2-Hydroxydiphenyl ether	6·8
Phenyl salicylate	21·2
2,2′-Dihydroxybenzophenone.........	39·4
2,4′-Dihydroxybenzophenone.........	20·9

* After 100 hours' irradiation, expressed as % conversion × 100.

DISCUSSION

Most of the products of electron irradiation of diphenyl carbonate can be attributed to two alternative scission reactions [1] accompanied, or followed, by loss of carbon monoxide and carbon dioxide respectively to yield radical pairs, i.e.,

$$PhO \cdot CO \cdot OPh \longrightarrow PhO \cdot + \cdot CO \cdot OPh \longrightarrow$$
$$PhO \cdot + CO + \cdot OPh \quad (1)$$

$$PhO \cdot CO \cdot OPh \longrightarrow Ph \cdot + \cdot O \cdot CO \cdot OPh \longrightarrow$$
$$Ph \cdot + CO_2 + \cdot OPh \quad (2)$$

The observed ratio (3 : 1) of the yields of CO and CO_2 then indicates the relative importance of reactions (1) and (2). The presence of the phenoxy-radical pair from reaction (1) is consistent with the observed e.s.r. spectrum of irradiated diphenyl carbonate.[2] The presence of the radical pair from reaction (2) cannot be deduced from the e.s.r. spectrum since the appropriate peaks are likely to be masked by those of the more abundant pair from reaction (1). However, the existence of both pairs can be inferred from the final products of degradation which indicate substantial recombination of both pairs according to reactions (3) and (4).

$$PhO \cdot + \cdot OPh \longrightarrow \begin{cases} \text{2- and 4-Hydroxydiphenyl ether} \\ \text{2,6- and 2,4′-Dihydroxybiphenyl} \end{cases} \quad (3)$$

$$PhO \cdot + \cdot Ph \longrightarrow \text{Diphenyl ether, 2- and 4-hydroxy-} \text{biphenyl} \quad (4)$$

The relatively high yields of 2-hydroxydiphenyl ether and diphenyl ether, formed by addition of one member of the pair to the other with minimum movement, indicate that this mode of recombination is preferred, though it is apparent from the range of products that reorientation can occur.

The products from radiolysis of phenyl p-tolyl carbonate did not include diphenyl ether or di-p-tolyl ether and similar products expected from intermolecular reactions. As the e.s.r. spectrum again reveals the existence of

radicals pairs, the available evidence suggests that the scission–recombination process is essentially intramolecular.

From Table 1 it can be seen that, for the recombination products from reactions (3) and (4), G is 0·45. Since $G(CO + CO_2)$ is 1·26, it appears that only 36% of the possible recombination occurs, and that the remaining phenyl and phenoxy-radicals escape from the cage and undergo addition or abstraction reactions. Thus, if we assume that phenoxy-radicals are formed only in accordance with reactions (1) and (2), G(phenoxy-radicals escaping) is given by:

$$2\{G(CO) - G \text{ [recombination products from (1)]}\} + \{G(CO_2) - G \text{ [recombination products from (2)]}\} = 1·34$$

Similarly, G(phenyl radicals escaping) = 0·28. If we assume that these radicals attack the diphenyl carbonate substrate, the possible products are phenol (G 0·66) and benzene (not detected) by hydrogen abstraction, or high molecular weight products by addition (detected but not identified). The formation of only a trace of biphenyl, presumably by combination of two phenyl radicals derived from reaction (2), shows that the probability that a phenyl or phenoxy-radical will survive long enough to meet a second escaping radical is very low. Loss of diphenyl carbonate by radical attack accounts for the discrepancy between the observed loss (G 2·53) and that calculated from the combined gas yield (G 1·26). The consumption of diphenyl carbonate is probably responsible for the increasing departure from linearity of the yields of products (Figure) with radiation dose above 500 Mrads.

The formation of phenyl salicylate and 2,2′- and 2,4′-dihydroxybenzophenone can be attributed to Fries rearrangements of diphenyl carbonate. These rearrangements had been observed [4] during photolysis of diphenyl carbonate solutions, the second step occurring more rapidly than the first.

The present results for photolysis of solid diphenyl carbonate show a reversal of the relative importance of the scission and Fries rearrangement reactions observed during radiolysis. Thus, high yields of phenyl salicylate and 2,2′- and 2,4′-dihydroxybenzophenone are formed with only minor quantities of products resulting from scission reactions. E.s.r. examination [5] was in accord with a low yield of trapped phenoxy-radicals but the spectrum was too weak to establish the existence of radical pairs although their presence is probable from the observed pattern of products (Results section). It has been suggested [6-8] that the photo-Fries rearrangement is preceded by a photodissociation of the ester into a pair of radicals which are retained in a solvent cage for long enough to allow recombination. Migration of some radicals from the cage is postulated to account for the formation of intractable 'polymer' and for the production of the corresponding phenol by hydrogen abstraction. Thus, it appears that ionising radiation causes scission accompanied or followed by expulsion of CO or CO_2 followed by recombination of the resulting radicals, whereas u.v. irradiation causes scission which is followed immediately by recombination. This difference could be a result of the energy of the bombarding particle rather than a basic difference in overall mechanism.

In contrast to the above, thermal degradation of the ester causes rearrangement to o-phenoxybenzoic acid followed by a series of reactions including decarboxylation to diphenyl ether.[3] The mass spectrum of diphenyl carbonate contains a major peak attributed to the molecular ion of diphenyl ether, and postulated to result from rearrangement of diphenyl carbonate followed by elimination of carbon dioxide.[9,10] Thus, the reactions involved during mass spectrometry resemble those of thermal rather than radiation-induced breakdown. Thermal rearrangement and formation of diphenyl ether might occur prior to ionisation during the measurement of the mass spectrum, as has been observed in other cases.[11]

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[5] J. A. McRae, and M. C. R. Symons, following paper.
[6] H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293.
[7] R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters*, 1963, 365.
[8] R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015.

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[11] R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, *Austral. J. Chem.*, 1967, **20**, 139.