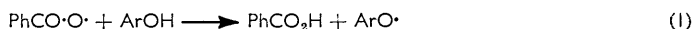


450. The Thermal Decomposition of Some Perbenzoyl Aryl Carbonates in Benzene

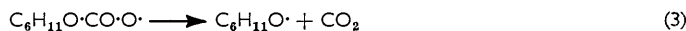
By V. A. DODONOV and WILLIAM A. WATERS

Three perbenzoyl aryl carbonates, $\text{PhCO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{OAr}$, have been prepared, and their homolytic decompositions in dry benzene have been studied. These are first-order reactions which yield (per mol.) 1 mol. of carbon dioxide, 0.5–0.85 mol. of benzoic acid, 0.3–0.4 mol. of aryloxy polymers, and much smaller quantities of simple radical dimers.

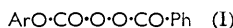
WHILE some reactions between benzoyl peroxide and phenols may involve the formation of aryloxy-radicals by reaction (1),¹⁻³



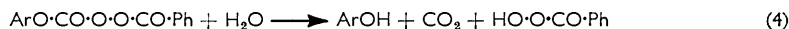
many proceed by a bimolecular "four centre" mechanism not involving free-radical formation.^{4,5} Since alkyloxy-radicals can be obtained directly by the thermal decompositions of percarbonates⁶ and of perbenzoyl alkyl carbonates,⁷ *e.g.*, reactions (2) + (3) ($\text{C}_6\text{H}_{11}\cdot$ = cyclohexyl):



it was of interest to study the decomposition of perbenzoyl aryl carbonates (I), which should simultaneously give free benzoyloxy- and aryloxy-radicals.



These compounds, (I), were made from either phenol, *p*-cresol, or 2,6-xylene-1-ol, through the chloroformate, by condensation with perbenzoic acid at -20 to -30° , using dry pyridine to remove hydrogen chloride. Peroxide analyses, using potassium iodide in dilute aqueous acetic acid, gave low values (70–80%), and small amounts of the corresponding diaryl carbonates were formed. Evidently, under these conditions, some hydrolysis:



occurred (contrast the perbenzoyl alkyl carbonates), and the poor titres were due to the instability of perbenzoic acid, but quantitative peroxide values could be obtained by the use of potassium iodide in acetic acid–acetone.

The thermal decomposition of perbenzoyl phenyl carbonate (I; $\text{Ar} = \text{Ph}$) in benzene proved to be a first-order reaction (see the Figure) with an activation energy of 31.6 kcal. mole⁻¹ (calculated from the data of the Figure). This is decidedly higher than that found⁷ for perbenzoyl cyclohexyl carbonate in benzene or *n*-heptane (24–26 kcal. mole⁻¹), and is explicable on the supposition that the polar effect of the phenoxy-group hinders homolytic fission of the weak O–O bond.⁸

¹ P. D. Bartlett and K. Nozaki, *J. Amer. Chem. Soc.*, 1947, **69**, 2299.

² S. L. Cosgrove and W. A. Waters, (a) *J.*, 1949, 5189; (b) *ibid.*, 1951, 388.

³ N. Inoue, O. Simamura, and K. Takamizawa, *Bull. Chem. Soc. Japan*, 1962, **35**, 1958.

⁴ C. Walling and B. Hodgdon, *J. Amer. Chem. Soc.*, 1958, **80**, 228.

⁵ D. B. Denney and D. Z. Denney, *J. Amer. Chem. Soc.*, 1960, **82**, 1389.

⁶ G. A. Razuvaev and L. M. Terman, *Zhur. obschei. Khim.*, 1960, **30**, 2389.

⁷ G. A. Razuvaev, V. A. Dodonov, and B. N. Moryganov, *Proc. Acad. Sci. (U.S.S.R.)*, 1964, 431.

⁸ W. A. Waters, *J.*, 1942, 153.

The products formed on thermal decompositions of three peroxy-esters in benzene are listed in the Table.

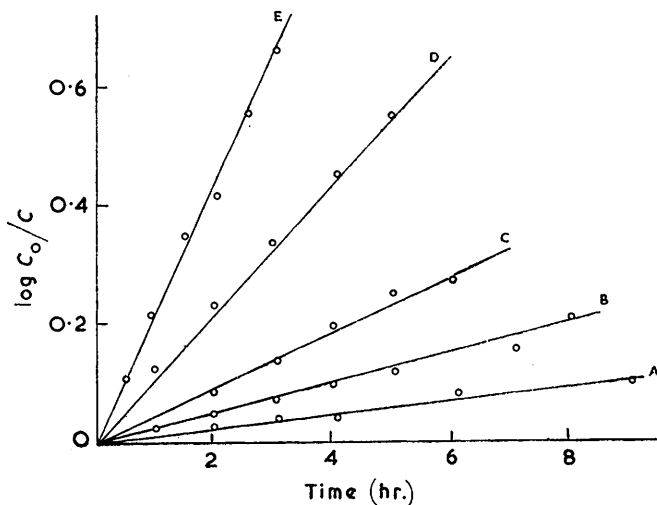
Products of the decomposition of perbenzoyl aryl carbonates in benzene, and their yields (moles product/mole peroxide)

Per-ester (I)	Ar = Ph	Ar = <i>p</i> -Me·C ₆ H ₄	Ar = 2,6-Me ₂ -C ₆ H ₃
Carbon dioxide	1.07	0.96	0.91
Benzoic acid	0.89	0.8	0.51
Phenol	0.09	Trace	—
Polymer	0.28—0.30	0.30—0.32	0.35—0.38
Others	Ph·Ph, 0.1	(III), 0.24 (II), 0.03	(IV), 0.1 (V), 0.16 (VI), 0.08

From the Table, it is evident that the decompositions involve homolyses similar to reaction (2), and that the subsequent reaction (6), which yields aryloxy-radicals, is nearly quantitative



Again, the high recovery of benzoic acid shows that the benzoyloxy-radicals mainly act as dehydrogenators of aryloxy-radicals or their condensation products. There must be very little decomposition of benzoyloxy-radicals to free phenyl. With (I; Ar = Ph), decomposition in carbon-14-labelled benzene showed that the small yield of biphenyl arose mainly by interaction of phenyl radicals with the solvent.

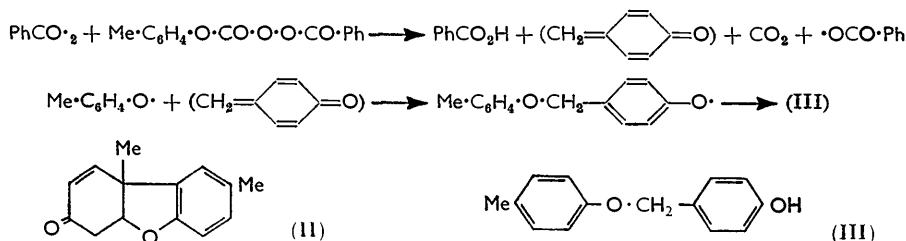


The rate of decomposition of perbenzoyl phenyl carbonate in benzene, at various temperatures

A, 45°. B, 50°. C, 55°. D, 60°. E, 65°.

In each case, polymers of molecular weight in the range 600—800 made up quite 30% of the reaction product. These polymers are probably similar to those formed by the oxidation of the corresponding phenols with alkaline ferricyanide,⁹ for they had high infrared absorptions near 1260 cm.⁻¹, corresponding to the Ar—O stretching vibration. From (I; Ar = *p*-Me-C₆H₄), there was a small yield of Pummerer's ketone (see ref. 9), and a larger yield of an isomer, 4-hydroxybenzyl *p*-tolyl ether (III), which could possibly have been formed as shown below, or by homolytic reactions of a similar type.

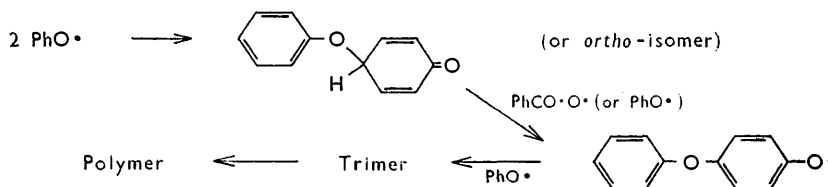
⁹ C. G. Haynes, A. H. Turner, and W. A. Waters, *J.*, 1956, 2823.



From (I; Ar = 2,6-Me₂-C₆H₃), 3,3',5,5'-tetramethyl-4,4'-diphenylquinone (IV) and 4-benzoyloxy-2,6-dimethylphenol (V) are clearly formed from the 2,6-dimethylphenoxy-radical, the latter by consumption of the benzoyloxy-radicals. A green product (VI) must, from its reactions, be closely related to (IV); one possibility is the tautomer (VII) of the bisphenol (VIII), whilst another is that it is the quinhydrone of (IV) and (VIII).



The chief outcome of this Paper is the demonstration that, even when aryloxy-radicals are formed in a non-polar solvent, they do not principally react to give dimers, but preferably form polymers of low molecular weight (*ca.* 5–6 aryloxy-units). The formation of these polymers can be ascribed to the ease of oxygen-carbon bond formation and to the ease of homolytic dehydrogenation of hydroxy-diphenyl ethers or their tautomers.



Similar polymerisations of phenols can be achieved by other reactions that undoubtedly involve aryloxy-radicals.⁹⁻¹¹

EXPERIMENTAL

***p*-Tolyl Chloroformate.**—Dimethylaniline (69 g.) was added dropwise, with rapid stirring, to a mixture, at -5° , of *p*-cresol (62 g.) and phosgene (57 g.) in dry benzene (500 ml.), the temperature throughout being kept below 0° . The resulting mixture was washed successively with water, 5% sulphuric acid, 2% sodium hydroxide, and water, and was then dried (CaCl₂). After removal of the benzene, the *p*-tolyl chloroformate was distilled at 55–56°/0.2 mm. (quantitative yield) (Found: C, 57.1; H, 4.3; Cl, 20.2. C₈H₇ClO₂ requires C, 56.8; H, 4.1; Cl, 20.8%).

2,6-Dimethylphenyl Chloroformate.—This ester was prepared similarly, having b. p. 56–57°/0.8 mm. (Found: C, 59.7; H, 5.2; Cl, 18.9. C₉H₉ClO₂ requires C, 58.5; H, 4.9; Cl, 19.3%). Phenyl chloroformate had b. p. 66–67°/3 mm.

Perbenzoyl Phenyl Carbonate.—This was prepared by the reaction of phenylchloroformate with barium perbenzoate, in ether suspension at 0° , as previously described.¹² It was crystallised from light petroleum (b. p. 40–60°) at -10° , and had m. p. 60° (Found: C, 65.4; H, 4.0; active O, 6.18. Calc. for C₁₄H₁₀O₅: C, 65.2; H, 3.9; active O, 6.21%).

Perbenzoyl *p*-Tolyl Carbonate.—*p*-Tolyl chloroformate (5.5 g.) was added to a solution of perbenzoic acid (4.8 g.) in methylene chloride (75 ml.) at -20° , and to this a solution of dry

¹⁰ A. H. Hay, *J. Polymer Sci.*, 1962, **58**, 581; G. F. Endres and J. Kwiatek, *ibid.*, p. 593.

¹¹ T. J. Stone and W. A. Waters, *J.*, 1964, 213.

¹² G. A. Razuvaev, V. A. Dodonov, and V. S. Ellis, *Proc. Acad. Sci. (U.S.S.R.)*, 1964, 426.

pyridine (4 ml.) in methylene chloride (25 ml.) was added during 2 min. The peroxide solution was washed with 1% sulphuric acid, then ice-water, and was dried (Na_2SO_4). After removal of the methylene chloride under a vacuum, the residue was crystallised from light petroleum to give *perbenzoyl p-tolyl carbonate* (80%), m. p. 84° (Found: C, 65.6; H, 4.6; active O, 5.86. $\text{C}_{15}\text{H}_{12}\text{O}_5$ requires C, 66.1; H, 4.4; active O, 5.88%).

Perbenzoyl 2,6-Dimethylphenyl Carbonate.—This was prepared similarly in methylene chloride at -35° . Its solution in methylene chloride was dried at -30° , the solvent evaporated, and the residue washed with cold light petroleum to give the *product* (73%), m. p. 49° (Found: C, 67.4; H, 5.0; active O, 5.39. $\text{C}_{16}\text{H}_{14}\text{O}_5$ requires C, 67.2; H, 4.9; active O, 5.59%).

Peroxide Analysis.—The peroxide (0.10–0.15 g.) was added to a saturated solution (15 ml.) of potassium iodide in acetone, to which had been added acetic acid (2 ml.). The liberated iodine was titrated immediately with standard thiosulphate solution.

Kinetic Measurements.—For each measurement, a 0.02M-solution (15 ml.) of perbenzoyl phenyl carbonate was placed in a glass ampoule fitted with a stopcock. The ampoule was then cooled in liquid nitrogen, evacuated to 10^{-3} mm. pressure, the stopcock closed, and the solid allowed to warm to the m. p. of the benzene. This operation was repeated 3 times, after which the closed ampoule was placed in a thermostat at the required temperature (to 0.1°). After definite intervals, each ampoule was removed from the thermostat, cooled immediately in acetone-carbon dioxide, opened, and immediately analysed as described above.

The Thermal Decomposition of Perbenzoyl Phenyl Carbonate in Benzene.—A solution of (I; Ar = Ph) (5.4 g.) in dry benzene (100 ml.), in a flask fitted with a reflux condenser, was cooled in acetone-carbon dioxide. After evacuation, the system was filled with dry nitrogen, and the solution was then heated for 40 hr. at 55 – 60° . A slow stream of nitrogen was maintained, to allow the collection of carbon dioxide in barium hydroxide. The deep red solution was then washed with aqueous sodium hydrogen carbonate solution to remove benzoic acid (2.38 g., 0.89 mol.; m. p. 119°), whereupon the benzene solution became yellow. After drying (Na_2SO_4), part of the benzene was evaporated in a vacuum, and the remaining solution was added dropwise to n-hexane (50 ml.). A polymeric product was precipitated (C, 71.2; H, 4.4%; *M*, Rast 581), fractions of which, when separated by thin-layer chromatography, all had similar infrared spectra. After removal of the polymer, the remaining solution was washed with 1% sodium hydroxide, which removed phenol (0.16 g., collected and weighed as tribromophenol, m. p. 87°). Steam distillation of the remaining neutral products removed biphenyl (0.33 g.), leaving a yellow resin which became red on treatment with dilute alkali.

A separate sample (2.08 g.) was decomposed at 60° in carbon-14-labelled benzene (25 ml.; activity, 1908 units/min.). After separation of the products, as above, the activity of the polymer was 24 units/min., and of the biphenyl 654 units/min.

Thermal Decomposition of Perbenzoyl p-Tolyl Carbonate in Benzene.—The decomposition, as above, of (I; Ar = *p*-Me- C_6H_4) (3.2 g.) in benzene (50 ml.) at 55 – 57° gave carbon dioxide (0.508 g.; 0.96 mol.) and benzoic acid (1.17 g.; 0.8 mol.). The dried solution was evaporated to 15 ml. and poured on to hexane (50 ml.), when polymer (30%) (C, 74.5; H, 4.9%; *M*, 558) was precipitated. Steam distillation of part of the remaining hexane solution, and extraction of the distillate with methylene chloride, gave 4-hydroxybenzyl *p*-tolyl ether (III) (estimated total yield, 0.24 mol.) (Found: C, 78.0; H, 6.5%; active H, 0.465%; *M*, 201. Calc. for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.5; H, 6.55, active H, 0.467%; *M*, 214). Its infrared spectrum showed bands at 2930 and 1455 cm^{-1} characteristic of the $-\text{CH}_2-$ group. With phenyl isocyanate, it formed a *phenylurethane*, m. p. 146.5 – 148° (Found: C, 75.9; H, 6.2. $\text{C}_{21}\text{H}_{20}\text{NO}_2$ requires C, 75.7; H, 5.7%). Another portion of the hexane, on chromatography on alumina, gave a solid, m. p. 111° , having an infrared spectrum identical with that of Pummerer's ketone (II) (see ref. 9).

Thermal Decomposition of Perbenzoyl 2,6-Dimethylphenyl Carbonate in Benzene.—Decomposition of the carbonate (3 g.) in benzene (50 ml.) for 30 hr. at 60° , and concentration of the solution, gave solid 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (IV) (0.26 g., 0.1 mol.), m. p. and mixed m. p.^{2b} 209° , having an infrared spectrum identical with that of an authentic specimen. After removal of benzoic acid (0.62 g.; 0.51 mol.) with dilute alkali, the benzene solution was evaporated and the residue dissolved in n-hexane-n-heptane (6 : 4). A green product, possibly (VII), was precipitated by cooling to -70° , and, after crystallisation from light petroleum, had m. p. 108 – 109° (Found: C, 78.4; H, 7.0%, *M*, 232. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 78.9; H, 7.4%, *M*, 242). Oxidation of this with potassium ferricyanide or lead dioxide gave the diphenoquinone (IV), m. p. and mixed m. p. 210° , whilst treatment with zinc dust in acetic acid gave

4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (VIII), m. p. and mixed m. p. 218—219°, having an infrared spectrum identical with that of an authentic specimen.^{2b}

After removal of (VII), evaporation of the solution left 4-benzoyloxy-2,6-dimethylphenol (V) (0.38 g., 0.16 mol.), m. p. 139—149° (lit.,^{2b} m. p. 140°) (Found: C, 74.8; H, 5.8. Calc. for C₁₅H₁₄O₃: C, 74.3; H, 5.9%). Polymeric products (0.4 g.; *M*, 690), insoluble in alkali but soluble in organic solvents, were also formed.

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