178. *Aroyl Peroxides. Part II.*[1] *The Decomposition of Benzoyl Peroxide in Benzene.*

By G. B. Gill and Gareth H. Williams.

The kinetics and products of the reaction of benzoyl peroxide with benzene have been studied over a range of initial peroxide concentrations. Reactions of order 1 and 1·5 occur simultaneously, as indicated by the rate equation $-d[P]/dt = k_1[P] + k_1[P] + k_{3/2}[P]^{3/2}$, and correspond to primary and induced decomposition of the peroxide. A mechanism is suggested which is consistent with the kinetics and the products of the reaction.

A study of the kinetics and products of the decomposition of benzoyl peroxide in some alkylbenzenes was reported in Part I.[1] The results of a similar, but more detailed, study of the corresponding reaction in benzene are now reported.

At moderate peroxide concentrations (0·01—0·04M), the products of this reaction are known to include carbon dioxide, benzoic acid, biphenyl, dihydrobiphenyl, phenyl benzoate, and the positional and stereo-isomers of tetrahydroquaterphenyl.[2-4] Since, at higher concentrations (0·04—0·10M), the incursion of side-reactions is indicated by the formation of the isomeric quaterphenyls,[3,4] phenylbenzoic acids,[5,6] and terphenyls,[4,5,7] mechanistic studies are best carried out at low concentrations. Further, since oxygen [8,9] and other impurities [3] modify the reaction, the reactions must be carried out in the absence of oxygen, and the purity of the reagents carefully scrutinised.

Nozaki and Bartlett [10] found that the rate of disappearance of the peroxide was given by:

$$-d[P]/dt = k_1[P] + k_{3/2}[P]^{3/2} \qquad (1)$$

where P is the peroxide, and k_1 and $k_{3/2}$ are first- and 1·5-order rate constants, respectively, and considered the first term to represent the unimolecular dissociation of the peroxide:

$$\text{Ph·CO·O·O·CO·Ph} \longrightarrow 2\text{Ph·CO·O·} \qquad (2)$$

This interpretation was supported by the formation of benzoic acid in almost quantitative yield when the reaction was conducted in the presence of iodine and water,[11] indicating that intramolecular decarboxylation of the peroxide, by reaction (3) or (4), is relatively unimportant.

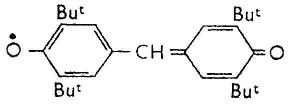
$$\text{Ph·CO·O·CO·Ph} \longrightarrow \text{Ph·} + \text{Ph·CO·O·} + CO_2 \qquad (3)$$

$$\text{Ph·CO·O·CO·Ph} \longrightarrow \text{Ph·CO·OPh} + CO_2 \qquad (4)$$

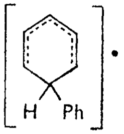
The influence of radical-induced decomposition of the peroxide, represented by the second term of eqn. (1), is also indicated by the acceleration of the reaction by radical-chain initiators [12] and by its retardation by radical scavengers.[11,13-16] Such experiments also afford a method of measurement of the rate constant for reaction (2). Agreement between

[1] Part I, Foster and Williams, *J.*, 1962, 2862.
[2] DeTar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.
[3] DeTar, Long, and Rendleman, personal communication.
[4] Hey, Perkins, and Williams, *J.*, 1964, 3412.
[5] Gelissen and Hermans, *Ber.*, 1925, **58**, 285, 476, 479, 764, 765, 770; 1926, **59**, 63, 662.
[6] Walling and Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 1738.
[7] Razuvaev, Zateev, and Petukhov, *Proc. Acad. Sci.* (*U.S.S.R.*), 1960, **130**, 336.
[8] Eberhardt and Eliel, *J. Org. Chem.*, 1962, **27**, 2289.
[9] Morrison, Cazes, Samkoff, and Howe, *J. Amer. Chem. Soc.*, 1962, **84**, 4152.
[10] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; 1947, **69**, 2299.
[11] Hammond and Soffer, *J. Amer. Chem. Soc.*, 1950, **72**, 4711.
[12] Hammond, Rudesill, and Modic, *J. Amer. Chem. Soc.*, 1951, **73**, 3929.
[13] Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.
[14] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.
[15] Hammond, *J. Amer. Chem. Soc.*, 1950, **72**, 3737.
[16] McGowan and Powell, *J.*, 1960, 238.

k_1 and this result would indicate the absence of any first-order induced reactions, which can in principle occur under certain conditions of chain-termination,[1,13] while the difference, if any, between these two rate constants should be the rate constant of the first-order induced reaction. A number of radical scavengers has been described,[13-19] but the unreliability [17,20-23] of most of them renders the results obtained of doubtful validity. The kinetics of the inhibited reaction have therefore been re-investigated, using, as a radical scavenger, the 2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxo-2,5-cyclohexa-2,5-dienylidene)-4-tolyloxy-radical [18] (" galvinoxyl ") (I), whose efficiency as an acceptor for a wide variety of radicals has been demonstrated.[17,19] The kinetics of the reaction, in the absence of inhibitors, has also been studied over a wide range of initial peroxide concentrations and by using improved analytical techniques, in order to obtain reliable values of k_1 and $k_{3/2}$.



(I)



(II)

It was shown in Part I [1] that deductions concerning the reaction mechanism could be made by comparison of the yields of the various reaction products, over a range of initial peroxide concentrations $[P]_0$, with the kinetic results. Some of the necessary data on product yields are already available,[4] and we now report the results of studies designed to complete this survey, so as to enable a detailed comparison to be made with the kinetics, and the reaction mechanism to be deduced.

EXPERIMENTAL METHODS AND RESULTS

Kinetics.—The uninhibited reaction. Before each experiment, the solvent (100—1000 ml.) was freed from dissolved oxygen by boiling it under reflux in a stream of dry, oxygen-free nitrogen for 4—12 hr. Reactions were conducted, under dry oxygen-free nitrogen, in three-necked flasks fitted with reflux condensers and immersed in a thermostat bath at 78·0°. Samples (2—50 ml.) were withdrawn at intervals into chilled receivers, care being taken that no air was admitted into the reaction vessel. The peroxide content of each sample was determined iodometrically by a modification of the " dead-stop " method, using polarised electrodes.[24] Each peroxide estimation was carried out in duplicate, and each experiment was also duplicated. The values of k_1 and $k_{3/2}$ were obtained, as described in Part I,[1] by the use of eqn. (5):

$$k_{\text{total}} = k_1 + k_{3/2}[\text{P}]_0^{0\cdot5}. \qquad (5)$$

The results obtained are given in Table 1.

TABLE 1.

Rate of decomposition of benzoyl peroxide in benzene at 78·0°.

$[\text{P}]_0$ (mole l.$^{-1}$)	$[\text{P}]_0^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$)	10^5k_{total} (sec.$^{-1}$)	$[\text{P}]_0$ (mole l.$^{-1}$)	$[\text{P}]_0^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$)	10^5k_{total} (sec.$^{-1}$)
0·2175	0·4664	3·62	0·04355	0·2094	2·64
0·1281	0·3579	3·20	0·02208	0·1486	2·39
0·08640	0·2939	3·00	0·01056	0·1028	2·30

Hence, $k_1 = 1{\cdot}88 \times 10^{-5}$ sec.$^{-1}$ ($\pm 0{\cdot}02 \times 10^{-5}$ sec.$^{-1}$), and $k_{3/2} = 3{\cdot}74 \times 10^{-5}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$ ($\pm 0{\cdot}04 \times 10^{-5}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$).

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[17] Bartlett and Funahashi, *J. Amer. Chem. Soc.*, 1962, **84**, 2596.
[18] Coppinger, *J. Amer. Chem. Soc.*, 1957, **79**, 501.
[19] Greene, Adam, and Cantrill, *J. Amer. Chem. Soc.*, 1961, **83**, 3461.
[20] Bartlett and Rüchardt, *J. Amer. Chem. Soc.*, 1960, **82**, 1756.
[21] Wild, *Discuss. Faraday Soc.*, 1952, **12**, 127.
[22] Griffith, U.S. Atomic Energy Commission, Report No. UCRL 3422 (1956).
[23] Lothe and Eia, *Acta Chem. Scand.*, 1958, **12**, 1535.
[24] Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045.

The inhibited decomposition. The solvent (75—100 ml.) was freed from oxygen as before. Weighed amounts of benzoyl peroxide (4—20 mg.) and galvinoxyl (3—4 mg.) were added to the solvent, and samples (2—3 ml.) removed as before. To each sample was added a small chip of solid carbon dioxide, and the solution was allowed to attain room temperature. An aliquot portion (1 ml.) of each sample was diluted to 25 ml. with oxygen-free ethanol or 2,2,4-trimethylpentane, and the optical density at 431 mμ determined by using 1-cm. silica cells, in a Unicam S.P. 500 spectrophotometer with the solvent in the reference cell. The products of the reaction absorbed only weakly at this wavelength. Each determination was duplicated, as also was each run.

Solutions of galvinoxyl in ethanol or 2,2,4-trimethylpentane obeyed Beer's Law over a 25-fold concentration range, and showed an intense absorption maximum at 431 mμ ($\varepsilon_{\text{max.}} = 154 \times 10^3$).

The inhibited reaction may be shown to be of zero order by arguments similar to those employed by Bawn and Halford,[25] if the inhibitor (Z) reacts with the radicals R· produced by the thermal dissociation of the –O–O– bond of the benzoyl peroxide:

$$\text{Ph·CO·O·O·CO·Ph} \longrightarrow 2\text{Ph·CO·O·} \quad \text{(slow)} \qquad (2)$$

$$\text{Ph·CO·O·} + \text{Z·} \longrightarrow \text{Ph·CO·O·Z} \quad \text{(fast)} \qquad (6)$$

The rate of disappearance of the inhibitor is then given by

$$-\text{d}[\text{Z}]/\text{d}t = 2k_1[(\text{Ph·CO·O})_2] = \text{constant}, \qquad (7)$$

since the concentration of peroxide may be regarded as constant if it is present in large excess over the inhibitor. Such conditions lead to reactions of very short duration, which can be conveniently followed only by a continuous-reading optical system.[14] Under different stoicheiometric conditions, a more general equation, of which eqn. (7) is a special case, may be derived, as follows.

If D_0 is the optical density at time $t = 0$, and D_t that at time t, then the fraction of the inhibitor that has reacted is $(D_0 - D_t)/D_0$, and hence the fraction of the peroxide decomposed is given by:

$$(1/2j)[(D_0 - D_t)/D_0] = x/a \qquad (8)$$

where a is the initial amount of the peroxide, x the fraction decomposed in time t, and j the ratio of the initial concentrations of peroxide and inhibitor, *i.e.*,

$$j = [\text{P}]_0/[\text{Z}]_0 \qquad (9)$$

Since the first-order rate constant, k_1, for the unimolecular fission of the peroxide is given by:

$$k_1 = (2{\cdot}303/t)\,[\log_{10} a/(a - x)] \qquad (10)$$

it follows that, in the presence of the inhibitor,

$$k_1 = \frac{2{\cdot}303}{t} \,.\, \log_{10}\left[\frac{2jD_0}{D_0(2j - 1) + D_t}\right]. \qquad (11)$$

The values of D_0 were obtained by the extrapolation, to zero time, of the linear plots of $\log_{10}(I_0/I)$ against time. Substitution of these values into eqn. (11) and plotting $\log_{10}[D_0(2j - 1) + D_t]$ against time afforded straight lines of slope $k_1/2{\cdot}303$ sec.$^{-1}$. These lines were usually fairly steep, since j was generally selected to lie within the range 2—15, and sharp breaks in the slopes occurred at the points in time equivalent to the total disappearance of the inhibitor. After these breaks, the values of $\log_{10}(I_0/I)$ were virtually constant, indicating only a very slow reaction between the products and the radicals derived from the peroxide.

The value of j must be known precisely, and this requires that the purity of the peroxide

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[25] Bawn and Halford, *Trans. Faraday Soc.*, 1955, **51**, 780.

and of the galvinoxyl are accurately known. The purity of these compounds is conveniently determined by iodometric titration, as outlined elsewhere in this section.

The results are given in Table 2.

TABLE 2.

The inhibited decomposition of benzoyl peroxide in benzene at 78·0°.

Peroxide (moles)	Galvinoxyl (moles)	*j*	$10^5 k_1$ (sec.$^{-1}$)
$2·0271 \times 10^{-5}$	$6·3221 \times 10^{-6}$	3·2064	1·72
$4·1984 \times 10^{-5}$	$6·2571 \times 10^{-6}$	6·7098	1·65
$5·7961 \times 10^{-5}$	$6·7774 \times 10^{-6}$	8·5523	1·65

Hence, k_1 (mean) = $1·67 \times 10^{-5}$ sec.$^{-1}$ ($\pm 0·05 \times 10^{-5}$ sec.$^{-1}$).

Reaction Products.—Benzoyl peroxide (2 g.) was allowed to decompose in deaerated benzene (100—800 ml.) under pure dry nitrogen at 78·0° for 72 hr. The resulting mixtures were analysed by a modification of the method of Hey, Perkins, and Williams,[4] as follows. The pale yellow reaction mixture, after cooling, and after the addition of bibenzyl (0·4882 g.) and 10% palladium in charcoal (*ca.* 200 mg.), was shaken with hydrogen at atmospheric pressure. Hydrogenation generally proceeded sluggishly, but was usually complete in 4—8 hr. After removal of the catalyst, the solution was extracted with saturated aqueous sodium hydrogen carbonate solution (6 × 50 ml.), and the extracts were washed with a little benzene (2 × 10 ml.), which was added to the organic layer. The alkaline extracts were acidified with concentrated hydrochloric acid and extracted with dichloromethane (6 × 20 ml.). The resulting extract was dried ($CaCl_2$) and filtered. The filter pad was washed with a little dichloromethane (15 ml.) and the combined organic solutions were allowed to evaporate at room temperature. The residual benzoic acid (m. p. 119—122°) was dried *in vacuo* and weighed.

The organic layer from the alkaline extraction was dried ($CaCl_2$), filtered, and the filter pad washed with a little benzene. The excess of solvent was then removed by fractional distillation until *ca.* 10 ml. of solution remained. It was shown, by means of gas chromatography, that the distillate contained only negligible quantities of binuclear products. The distillation column was washed with a little benzene (*ca.* 5 ml.) and the contents of the flask were diluted to 20 ml. with benzene. The binuclear reaction products contained in the resulting solution were analysed by means of gas chromatography at 170°, using a column packed with Apiezon " L " grease on Celite 545, and a high-sensitivity β-ionisation detector with argon as the carrier gas, the flow-rate being 75 ml. min.$^{-1}$. The heights of the various component-peaks were measured relative to the internal standard (bibenzyl), and the following relative retention times were recorded: phenylcyclohexane, 0·38; biphenyl, 0·54; bibenzyl, 1·00; phenyl benzoate, 1·79. The yields of the various components of the reaction mixtures were determined by reference to the linear calibration graphs of solutions (20 ml.) of phenylcyclohexane, biphenyl, and phenyl benzoate in benzene, each of which also contained bibenzyl (0·4882 g.). Control experiments showed the results to be accurate to within ±2·0—2·5%.

After the removal of the small quantity of the reaction mixture required for the gas-chromatographic analysis (*ca.* 0·5 µl.), the remaining solvent was removed by fractional distillation and the products boiling below 150° were distilled *in vacuo* (b. p. 35—150°/0·01 mm.). The residue was weighed and assumed to consist entirely of the isomeric dodecahydroquaterphenyls, formed by hydrogenation of hydroaromatic tetranuclear products.[3,4]

In order that reliable results should be obtained, the dihydrobiphenyls must be quantitatively reduced to phenylcyclohexane,[3] and must not suffer irreversible hydrogen transfer (cf. 2,3-dihydrobiphenyl [26]). Moreover, pyrolysis of the quaterphenyl fraction to binuclear compounds on the chromatography column must be avoided. Control experiments with 1,4-dihydrobiphenyl indicated that the hydrogenation in benzene solution was quantitative to within experimental error. Pyrolysis of the dodecahydroquaterphenyls at moderately high temperatures has been shown not to occur,[3,4] although the parent tetrahydroquaterphenyls decomposed appreciably above about 130°.[4]

The results, together with those previously reported,[4] are given in Table 3, in which the molar yields at various initial peroxide concentrations are also correlated with a quantity *f*, whose significance is discussed below.

[26] Woods, Bolgiano, and Duggan, *J. Amer. Chem. Soc.*, 1955, **77**, 1800.

TABLE 3.

Molar yields of products of decomposition of benzoyl peroxide in benzene at 78°.

$[P]_0$ (mole $l.^{-1}$)	0·1652	0·0826	0·0413	0·0206	0·0103
Benzoic acid (*a*)	0·319	0·248	0·193, 0·18 *	0·150	0·110
Biphenyl (*b*)	0·372	0·371 *	0·346 *	0·320 *	0·297 *
Dihydrobiphenyl (*c*)	0·029	0·068	0·080, 0·100 *	0·131 *	0·117, 0·162 *
Phenyl benzoate (*d*)	0·013, 0·020	0·023 *	0·024, 0·025 *	0·026	0·023, 0·027 *
Residue (as dodecahydroquaterphenyl) (*e*)	0·331	0·404	0·468	0·530	0·603
$(1 - f)$	0·339	0·269	0·207	0·157	0·116
f	0·661	0·731	0·793	0·843	0·884
$\frac{1}{2}(b - a) + \frac{1}{2}c + \frac{1}{2}d + e = g$	0·383	0·511	0·608	0·694	0·792
Phenyl radicals accounted for (%) †	70·8	77·0	80·4	85·7	90·1

* From ref. 4. † It is assumed that the residue is comprised entirely of the dodecahydroquaterphenyls, and thus contains two peroxide-derived nuclei per molecule. This is known to be an underestimate.[27]

Preparation and Purification of Materials.—" White spot " nitrogen was freed from oxygen, and dried by passing it through chromous sulphate solution and zinc amalgam,[28] and then through concentrated sulphuric acid. Acid spray and the last traces of water were removed by tubes packed with activated alumina and 4-Å molecular sieve, respectively.

Benzene was purified by standard methods, and finally distilled from sodium through a 5-ft. column. The course of the distillation was followed by means of gas-chromatographic analysis of the distillate (polyethylene glycol column at 38°, argon flow-rate of 75 ml. min.$^{-1}$), and the middle fraction (b. p. 80·5°, n_D^{20} 1·50119) which was retained, contained a small quantity ($<$0·05%) of cyclohexane. The cyclohexane content of the solvent recovered from the above reactions with benzoyl peroxide did not appear to differ significantly from this, and identical rate constants were obtained for equivalent reactions carried out in either the original or recovered solvent, indicating that the cyclohexane impurity does not react preferentially with the radicals derived from the peroxide.

Before use, the solvent was passed through a 4-ft. column containing 4-Å molecular sieve material in which it had previously been stored for a minimum of seven days. The water content was found, by Karl Fischer titration, to be 4—8 p.p.m.

Phenylcyclohexane (B.D.H.) was fractionally distilled; it had b. p. 127—128°/30 mm., n_D^{20} 1·5334.

Biphenyl, bibenzyl, and phenyl benzoate (all B.D.H.) were recrystallised from ethanol to constant m. p. (70, 51·5, and 71°, respectively).

Benzoyl peroxide, purified by standard methods, had m. p. 105·5°. Estimation of its purity by the " dead-stop " method [24] gave a value of 99·98 ± 0·02%.

1,4-Dihydrobiphenyl was prepared by the reduction of biphenyl with sodium in liquid ammonia at −78°,[29] and was purified by fractional freezing. It was shown, by means of gas chromatography, to contain 20% of biphenyl. The product was stored under carbon dioxide in a bottle fitted with a serum cap.

The 2,6-di-t-butyl-α-(3,5-di-t-butyl-4-oxocyclohexa-2,5-dienylidene)-4-tolyloxy-radical (" Galvinoxyl ") was prepared from 4,4′-dihydroxy-3,5,3′,5′-tetra-t-butyldiphenylmethane [30] by Coppinger's method,[18] except that benzene was used as the solvent. The m. p. of a sample of 96·0% purity (determined by iodometric titration [31]) was 153·5—154° (lit. values: 157·5°,[30] 153°,[18] 153·2—153·6° [17]); it had $\lambda_{max.}$ (in 2,2,4-trimethylpentane) 280, 289, 407, 431 ($\varepsilon_{max.}$ 154 × 10^3), and 772·5 mμ. The solid galvinoxyl was stored under carbon dioxide, since it decomposed slowly in air. Solutions of galvinoxyl in benzene, 2,2,4-trimethylpentane, and ethanol decomposed rapidly on exposure to air, contrary to a previous report.[30]

DISCUSSION

The linearity of the plot of k_{total} against $[P]_0^{\frac{1}{2}}$ indicates that the reaction can be described by eqn. (1). However, the value of k_{total} at zero initial peroxide concentration,

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[27] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 40.
[28] Stone and Beeson, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 188.
[29] Hückel and Schwen, *Chem. Ber.*, 1956, **89**, 150.
[30] Kharasch and Joshi, *J. Org. Chem.*, 1957, **22**, 1435.
[31] Müller and Ley, *Chem. Ber.*, 1954, **87**, 922.

namely, 1·8 × 10^{-5} sec.$^{-1}$ (±1%), is greater than the value of k_1 determined in the presence of galvinoxyl [1·67 × 10^{-5} sec.$^{-1}$ (±3%)], the difference between the two values being greater than the experimental error. A more precise equation describing the reaction of benzoyl peroxide with benzene, eqn. (12), may therefore be written:

$$-\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_1[\mathrm{P}] + k_{\mathrm{I}}[\mathrm{P}] + k_{3/2}[\mathrm{P}]^{3/2} \qquad (12)$$

However, since k_{I} is small ($10^5 k_{\mathrm{I}} = 0{\cdot}20 \pm 0{\cdot}05$ sec.$^{-1}$) it may be neglected for most purposes, and eqn. (1) taken to represent the reaction. The occurrence of this small term, representing a first-order induced reaction, is significant, however, since it explains the formation of the small quantities of benzoic acid which are formed in the reaction even in very dilute solution.[32] A first-order induced reaction can arise if chain-termination occurs by combination of two dissimilar radicals, *e.g.*, a benzoyloxy-radical and a σ-complex (II) [reaction (13)].

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + [\mathrm{PhPhH}]{\cdot} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OH} + \mathrm{PhPh} \qquad (13)$$

Termination by combination of two like radicals (σ-complexes) gives rise to 1·5-order kinetics:

$$2[\mathrm{PhPhH}]{\cdot} \longrightarrow \text{Products} \qquad (14)$$

Indeed, reaction (14) has been shown to be the source of the isomeric tetrahydroquaterphenyls and dihydrobiphenyls (the products of combination and disproportionation of σ-complexes), particularly in dilute solution.[2–4,27,33]

Reactions (13) and (14) are therefore consistent with the products formed by the reaction in dilute solution, and, under certain conditions of induced reaction, are also consistent with the reaction kinetics. The induced reaction is important even at values of $[\mathrm{P}]_0$ as low as 10^{-2}M, where approximately 20% of the peroxide is decomposed in this way.

It is clear that the induced reaction arises from radical attack upon the peroxide,[12] and the products formed thereby should reflect the nature of the attacking radical. It is unrealistic to consider the phenyl radical in this context, because its stationary concentration is extremely low (*ca.* 10^{-10}M at $[\mathrm{P}]_0 = 10^{-2}$M [3]), and also because the thermal decomposition of a labelled symmetrical diaroyl peroxide yields only trace amounts of biaryls labelled in both nuclei.[34–39] Similar objections have been levelled against attack on the peroxide by benzoyloxy-radicals, eqn. (15).

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + (\mathrm{Ph{\cdot}CO{\cdot}O})_2 \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OPh} + \mathrm{CO_2} + \mathrm{PhCO{\cdot}O{\cdot}} \qquad (15)$$

However, the decomposition of benzoyl peroxide in benzene derivatives often yields small but significant amounts of phenyl benzoate. Reaction (15) would therefore appear to occur to a small extent, since reactions of the type (16) may be discounted on statistical grounds,[3] except at high dilution.

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{Ph{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OPh} \qquad (16)$$

The remaining radical present in solution is the σ-complex, and in view of its considerable stability, and consequently higher stationary concentration, it is reasonable to consider that, in benzene, as in alkylbenzenes,[1] the major part of the induced reaction arises from its interaction with the peroxide (17).

$$[\mathrm{PhPhH}]{\cdot} + (\mathrm{PhCO{\cdot}O})_2 \longrightarrow \mathrm{PhPh} + \mathrm{Ph{\cdot}CO{\cdot}OH} + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \qquad (17)$$

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[32] Barson and Bevington, *J. Polymer Sci.*, 1956, **20**, 133.
[33] Walling, " Free Radicals in Solution," Wiley, New York, 1957, p. 483.
[34] DeTar, *J. Amer. Chem. Soc.*, 1950, **72**, 1028.
[35] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.
[36] Hey, Pengilly, and Williams, *J.*, 1956, 1463.
[37] Wieland, Schapiro, and Metzger, *Annalen*, 1934, **513**, 93.
[38] Augood, Hey, and Williams, *J.*, 1952, 2094.
[39] Chang Shih, Ph.D. Thesis, London, 1958.

The evidence for the existence of the phenylcyclohexadienyl radical, or σ-complex, is based on the unsaturated products formed,[2-4] the effect of oxygen on the reaction,[40] and the absence of an isotope effect in the nuclear substitution process.[41] More recently, substituted cyclohexadienyl radicals have been recognised in other systems, by means of electron spin resonance spectroscopy.[42]

Further evidence in favour of the above hypothesis can be sought by attempting to make a quantitative correlation between the reaction kinetics and the molar yields of the reaction products. As pointed out in Part I,[1] such a correlation can be made by the comparison of the yields of the reaction products with a function f, defined in eqn. (18)

$$f = 2\{K[\mathrm{P}]_0^{\frac{1}{2}} - \ln(1 + K[\mathrm{P}]_0^{\frac{1}{2}})\}/K^2[\mathrm{P}]_0 \qquad (18)$$

where $K = k_{3/2}/k_1$, $[\mathrm{P}]_0$ is the initial peroxide concentration, and f is the fraction of the initial molar concentration of the peroxide which decomposes by primary fission. Since, in the induced decomposition, one radical is consumed for each radical formed, the number of radicals consumed in termination reactions must equal the number formed by primary fission of the peroxide. The fission of each molecule of peroxide gives two radicals, and it follows that the molar yield of termination products is either equal to or double the fraction f, according as these products are formed by combination or by disproportionation of radicals. The dimerisation of σ-complexes to yield tetrahydroquaterphenyl molecules is a reaction of the first type, while the hydrogen-transfer reactions between σ-complexes, or between a σ-complex and a benzoyloxy-radical, are of the second type, and lead to the formation of dihydrobiphenyl and biphenyl, or benzoic acid and biphenyl. The yields of these products may be compared with f, as in Table 3. Since the yield of benzoic acid tends toward zero at infinite dilution, this product may, as a first approximation, be considered primarily as a product of the induced reaction, and may therefore be correlated with $(1 - f)$. From Table 3, it may be seen that the yield of benzoic acid (a) closely parallels $(1 - f)$, and it may therefore be inferred that the amount of benzoic acid formed in chain-termination reactions is almost insignificant. This is consistent with the low value of k_{I}. The suggested chain-transfer stage (17) requires the formation of an equimolar amount of biphenyl concomitantly with the benzoic acid. Thus, the amount of biphenyl in excess of a [*i.e.*, (b—a)] must be formed in a termination reaction. Similarly, the yield of dihydrobiphenyl should be equal to (b—a). Table 3 shows a marked parallel between the dihydrobiphenyl yield and the difference (b—a), the values showing convergence at low values of $[\mathrm{P}]_0$. Indeed, as expected, the molar yields of biphenyl and dihydrobiphenyl also converge as $[\mathrm{P}]_0$ approaches zero. At all finite peroxide concentrations, however, the biphenyl yield exceeds the sum of the dihydrobiphenyl and benzoic acid yields. This is probably due to further radical attack upon the reactive diene, either by hydrogen abstraction or by addition to a double bond. Eberhardt and Eliel[40] have shown that the addition of 1,4-dihydrobiphenyl to a reaction in benzene results in the formation of rather more biphenyl than in its absence, indicating that the hydrogen-abstraction reaction does occur to some extent; moreover, their results show an apparent loss of material, particularly at high initial peroxide concentrations, and this may well be due to removal of the reactive 1,4-dihydrobiphenyl by radical polymerisation.

It seems probable that phenyl benzoate is formed in reactions [eqns. (19) and (20)] similar to those in which biphenyl is formed, the radical intermediate in this case being a benzoyloxycyclohexadienyl radical, [Ph·CO·O·PhH]·.

$$[\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}PhH}]{\cdot} + (\mathrm{Ph{\cdot}CO{\cdot}O})_2 \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OPh} + \mathrm{Ph{\cdot}CO{\cdot}OH} + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \qquad (19)$$

$$[\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}PhH}]{\cdot} + [\mathrm{PhPhH}]{\cdot} \longrightarrow \text{Products of combination and disproportionation} \qquad (20)$$

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[40] Eberhardt and Eliel, *J. Org. Chem.*, 1962, **27**, 2289.

[41] Eliel, Meyerson, Welvart, and Wilen, *J. Amer. Chem. Soc.*, 1960, **82**, 2936.

[42] Dixon and Norman, *Proc. Chem. Soc.*, 1963, 97.

Some phenyl benzoate, however, may also be formed in reaction (15), but, since the amount cannot be large, the contribution of (15) may be neglected. The yield of phenyl benzoate is nearly independent of $[\mathrm{P}]_0$, indicating that it is formed in both propagation and termination reactions. The amount formed in either process is difficult to estimate at any particular value of $[\mathrm{P}]_0$, but, since at low values of $[\mathrm{P}]_0$, the larger part of the phenyl benzoate must be derived from termination reactions, for simplicity of calculation, the yield of this product (d) is included in the sum of the yields of termination products (g).

Table **3** shows that $g[= \frac{1}{2}(b - a) + \frac{1}{2}c + \frac{1}{2}d + e]$ is less than f, but that the functions converge at low values of $[\mathrm{P}]_0$; hence, at these low values, the various termination reactions which have been considered would appear to describe adequately the actual termination processes. The discrepancy between g and f, particularly at high values of $[\mathrm{P}]_0$, probably arises from the interaction of the reactive radical intermediates with the primary reaction products, particularly since the residue is known to contain benzoate groups attached to non-aromatic nuclei,[27] and the isomeric terphenyls [4,5] and *p*-phenylbenzoic acid [5,6] are also formed as minor products.

The suggested mechanism for the thermal decomposition of benzoyl peroxide in benzene is set out in the simplified scheme below:

$$
\begin{array}{rcll}
\mathrm{P} & \longrightarrow & 2\mathrm{R}\cdot & \qquad (k_1) \\[2ex]
\left.\begin{array}{r} \mathrm{R}\cdot \\ \mathrm{R}\cdot + \mathrm{PhH} \\ \mathrm{R}'\cdot + \mathrm{PhH} \end{array}\right. & \begin{array}{c} \longrightarrow \\ \longrightarrow \\ \longrightarrow \end{array} & \left.\begin{array}{l} \mathrm{R}'\cdot + \mathrm{CO}_2 \\ \sigma\cdot \\ \sigma'\cdot \end{array}\right\} & \qquad (k_2) \\[4ex]
\begin{array}{r} \sigma\cdot + \mathrm{P} \\ \sigma'\cdot + \mathrm{P} \end{array} & \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} & \left.\begin{array}{l} \mathrm{Products} + \mathrm{R}\cdot \\ \mathrm{Products} + \mathrm{R}\cdot \end{array}\right\} & \qquad (k_3) \\[3ex]
\begin{array}{r} \sigma'\cdot + \sigma'\cdot \\ \sigma\cdot + \sigma'\cdot \end{array} & \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} & \left.\begin{array}{l} \mathrm{Products} \\ \mathrm{Products} \end{array}\right\} & \qquad (k_4) \\[3ex]
\begin{array}{r} (\sigma'\cdot + \mathrm{R} \\ (\sigma'\cdot + \mathrm{R} \end{array} & \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} & \left.\begin{array}{l} \mathrm{Products}) \\ \mathrm{Products}) \end{array}\right\} & \qquad (k_5)
\end{array}
$$

where P is the peroxide, R$\cdot$ a benzoyloxy radical, R$'\cdot$ a phenyl radical, $\sigma\cdot$ and $\sigma'\cdot$ are the corresponding σ-complexes derived from R$\cdot$ and R$'\cdot$ and a solvent molecule, and k_1—k_5 the specific rate constants for the various reactions as indicated above.

The application of the " steady-state " hypothesis to the above scheme (omitting the reactions in parentheses) leads to eqn. (1), and the scheme adequately describes the observed kinetics, provided that k_{I} can be neglected. If k_{I} is regarded as significant, however, then the additional reactions in parentheses must be included in the reaction scheme. The " steady-state " treatment of the resulting scheme leads to an extremely complex equation which is incapable of exact solution, but which can be shown, by the use of various approximations, to conform, at least qualitatively, to the observed kinetics. The above scheme is therefore consistent, to a reasonable degree of approximation, with both the products and the kinetics of the reaction, and may be regarded as a reasonable interpretation of it, particularly in dilute solution, where complications arising from subsequent reactions of some of the primary products are reduced to a minimum.

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