1313. *Aroyl Peroxides. Part III.*[1] *The Decomposition of Benzoyl Peroxide in Chlorobenzene and Bromobenzene*

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The kinetics and products of the reactions of benzoyl peroxide with chlorobenzene and with bromobenzene have been studied over a range of initial peroxide concentrations ($[\mathrm{P}]_0$). The rate equation for chlorobenzene depends on the value of $[\mathrm{P}]_0$, and may have the two forms:

$$(a)\quad -\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_1[\mathrm{P}] + k'_1[\mathrm{P}]\ \ ([\mathrm{P}]_0 > 0{\cdot}12\,\mathrm{M})$$
$$(b)\quad -\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_1[\mathrm{P}] + k_{\frac{3}{2}}[\mathrm{P}]^{\frac{3}{2}}\ \ ([\mathrm{P}]_0 < 0{\cdot}11\,\mathrm{M})$$

Equation (*a*) is thought to be characteristic of chain termination between benzoyloxy-radicals and σ-complexes and arises in chlorobenzene at high $[\mathrm{P}]_0$ values, owing to an increase in the relative concentration of benzoyloxy-radicals. Equation (*a*) is the rate equation for the reaction in bromobenzene over the range of concentrations investigated. The apparent difference in mechanism between the solvents is discussed in terms of the greater stability of the benzoyloxy-radical in bromobenzene, probably owing to the formation of a one-electron transfer complex with the solvent.

THE reactions of benzoyl peroxide with chloro- and with bromo-benzene have attracted considerably less attention than the reaction with benzene, since rather more complex mixtures of products are formed in these halogenated solvents. The reaction in a monosubstituted benzene derivative (C_6H_5X) yields the following main products: benzoic acid, carbon dioxide, the monosubstituted biphenyl derivatives (2-, 3-, and 4-$XC_6H_4{\cdot}C_6H_5$), the corresponding isomeric monosubstituted derivatives of phenyl benzoate, and, sometimes, significant quantities of a high-boiling residue, containing, among other compounds, derivatives of terphenyl [2,3] and tetrahydroquaterphenyl.[3,4] A little phenyl benzoate is often formed.[5] Dihydrobiaryls have also been reported [3,6] but these compounds have not previously been isolated from the reaction mixtures.

The kinetics of the reactions in chlorobenzene and bromobenzene have not been investigated in detail. However, Nozaki and Bartlett [7] found that, in other aromatic solvents, the decomposition of the peroxide obeys the rate equation:

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

Confirmation of this conclusion for the reaction in benzene was reported in Part II.[1]

The results of an investigation into the relative efficiency of a number of radical scavengers in the reactions of benzoyl peroxide with chlorobenzene and bromobenzene are also now reported. Among those investigated were methyl methacrylate, 3,4-dichlorostyrene,[8] naphthacene,[9a] acenaphthylene,[9b] 2,2-diphenyl-1-picrylhydrazyl,[10] and "galvinoxyl."[11-13] Certain objections may be levelled against the use of each of these inhibitors, with the exception of galvinoxyl, the superior efficiency and freedom from

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[1] G. B. Gill and G. H. Williams, *J.*, 1965, 995.
[2] D. R. Augood, D. H. Hey, and G. H. Williams, *J.*, 1953, 44.
[3] D. H. Hey, M. J. Perkins, and G. H. Williams, *J.*, 1963, 5604.
[4] B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, 1957, **10**, 165.
[5] D. I. Davies, D. H. Hey, and G. H. Williams, *J.*, 1961, 562.
[6] J. H. Waters, *Diss. Abs.*, 1961, **22**, 432.
[7] K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.
[8] C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.
[9] (*a*) M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949. (*b*) M. Szwarc, Amer. Chem. Soc., Div. Petrol. Chem., Preprints 1, No. 4; "Polycyclic Hydrocarbons," 1956, 49 (*Chem. Abs.*, 1959, **53**, 17,078).
[10] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.
[11] P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, 1962, **84**, 2596.
[12] G. M. Coppinger, *J. Amer. Chem. Soc.*, 1957, **79**, 501.
[13] F. D. Greene, W. Adam, and J. E. Cantrill, *J. Amer. Chem. Soc.*, 1961, **83**, 3461.

side-reactions of which are immediately apparent from the present results. The kinetics of the uninhibited reactions of benzoyl peroxide with those two solvents have also been investigated, together with the rates of formation of benzoic acid and the molar yields of the major reaction products, at a series of initial peroxide concentrations.

EXPERIMENTAL AND RESULTS

Kinetics.—(*a*) *Reactions in the absence of inhibitors.* The method outlined previously [1] was employed for the determination of the total rate of peroxide decomposition, the reactions being carried out at 80·2°. The reaction in bromobenzene was found to be particularly susceptible to inhibition by oxygen, since, if the solvent deaeration or the purification of the nitrogen was neglected, or carried out inefficiently, depressions of the observed rate constant (k_{obs}) of up to 30% were observed.

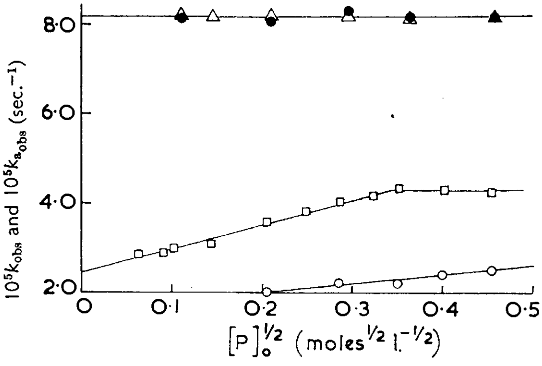
TABLE 1

Rate constants for the decomposition of benzoyl peroxide and formation of benzoic acid, in chlorobenzene and bromobenzene (80·2°)

Chlorobenzene			Bromobenzene		
$[P]_0$ (mole l.$^{-1}$)	10^5k_{obs} (sec.$^{-1}$)	$10^5k_{a_{obs}}$ (sec.$^{-1}$)	$[P]_0$ (mole l.$^{-1}$)	10^5k_{obs} (sec.$^{-1}$)	$10^5k_{a_{obs}}$ (sec.$^{-1}$)
0·2065	4·27	2·52	0·2092	8·15	8·13
0·1614	4·30	2·43	—	—	—
0·1225	4·34	2·21	0·1318	8·12	8·14
0·1042	4·18	—	—	—	—
0·08241	4·04	2·22	0·08749	8·16	8·20
0·06194	3·84	—	—	—	—
0·04112	3·61	2·01	0·04345	8·15	8·02
0·02032	3·10	—	0·02128	8·14	—
0·01023	2·98	—	0·01213	8·15	8·09
0·008147	2·91	—	—	—	—
0·003926	2·85	—	—	—	—

The results are given in Table 1 and the Figure in which k_{obs} is plotted against $[P]_0^{\frac{1}{2}}$.

The formation of benzoic acid was followed by removing aliquot portions (1—25 ml.) of the reaction mixture at convenient times, as for the determination of the peroxide. To each portion, in a three-necked 100-ml. flask, and under oxygen- and carbon dioxide-free nitrogen, were added 50% aqueous methanol (15 ml.) and Thymol Blue solution (0·2 ml.). An antimony or glass electrode and a saturated calomel electrode containing 50% aqueous methanol were fitted into the side-necks of the flask and connected to a Pye "Dynacap" pH meter. The mixture, while being stirred rapidly with a magnetic stirrer in order to effect continuous extraction of the benzoic acid into the aqueous phase, was titrated against 0·02N aqueous potassium hydroxide. The approach of the end-point was signalled by transient coloration of the indicator, and its exact location was determined from the point of zero slope of the differential titration curve. The use of a two-phase titration system in this way ensured that undecomposed



Variation in the rates of decomposition of benzoyl peroxide (k_{obs}) and formation of benzoic acid ($k_{a_{obs}}$) in chlorobenzene and in bromobenzene (80·2°)

Chlorobenzene: □, benzoyl peroxide; ○, benzoic acid

Bromobenzene: △, benzoyl peroxide; ●, benzoic acid peroxide did not interfere with the end-point of the titration, as accurate results could not be obtained in homogeneous media, probably owing to slow hydrolysis of the peroxide.

The results are given in Table 1 and the Figure.

(*b*) *The inhibited decomposition.* The method developed previously [1] for the determination of the rate constant of the inhibited reaction in the presence of galvinoxyl was employed. A similar method was used for the reaction inhibited by 2,3-diphenyl-1-picrylhydrazyl (DPPH). However, the degree of reproducibility achieved with the latter inhibitor was not high and the rate of reaction appeared to depend on the history of the sample of DPPH, and particularly on the solvent from which it was crystallised and the duration and temperature of drying. DPPH is known to form complexes with certain solvents from which it is crystallised,[14] and the observed deviations from the theoretical zero-order reaction have been reported in other instances when DPPH was used as a radical scavenger.[11, 15] Reproducible results (Table 2) were, however, obtained with galvinoxyl.

TABLE 2

Rate constants for the decomposition of benzoyl peroxide in the presence of galvinoxyl (80·2°)

Solvent	10^5[P]$_0$ (mole l.$^{-1}$)	10^6[Galvinoxyl]$_0$ (mole l.$^{-1}$)	[P]$_0$/[Galvinoxyl]$_0$	10^5k_1 (sec.$^{-1}$)
Chlorobenzene	1·672	7·337	2·279	2·40
,, ...	2·424	8·744	2·773	2·36
,, ...	4·120	7·272	5·666	2·33
,, ...	6·986	7·239	9·650	2·32
,, ...	8·263	7·296	11·32	2·41
Bromobenzene	4·137	6·382	6·482	2·19
,, ...	6·567	7·701	8·527	2·20
,, ...	8·310	7·490	11·10	2·18

The experimental procedure employed for the reaction in the presence of polynuclear hydrocarbons and polymerisable monomers was virtually the same as that for the uninhibited reaction, except that the required quantity of the inhibitor was added to the solvent just before the addition of the peroxide. Rate constants were calculated as for the uninhibited reaction. The results are given in Table 3.

TABLE 3

Rate constants (k_{In}) for the inhibited decomposition of benzoyl peroxide in chlorobenzene and in bromobenzene (80·2°)

	Chlorobenzene			Bromobenzene		
Inhibitor (M)	[P]$_0$ (mole l.$^{-1}$)	10^5k_{In} (sec.$^{-1}$)	$t_{\frac{1}{2}}$ (hr.)	[P]$_0$ (mole l.$^{-1}$)	10^5k_{In} (sec.$^{-1}$)	$t_{\frac{1}{2}}$ (hr.)
3,4-Dichlorostyrene (0·215) ...	0·1151	4·07	4·73	0·1195	4·43	4·35
	0·07499	3·85	5·13	0·07638	4·29	4·49
	0·03981	3·69	5·28	0·04140	4·14	4·65
	0·02018	3·52	5·50	0·02005	3·82	5·04
	—	—	—	0·01986	3·85	5·00
	0·009818	3·41	5·63	0·009977	3·84	5·01
Methyl methacrylate (0·094) ...	0·04088	3·26	5·90	—	—	—
	0·02051	2·65	7·30	—	—	—
	0·01354	2·70	7·15	—	—	—
	0·009908	2·62	7·31	0·006637	3·55	5·75
Naphthacene (0·003)	0·1563	3·85	5·13	—	—	—
Acenaphthylene (0·04)	—	—	—	0·04859	4·34	4·44

In the reactions in chlorobenzene with 3,4-dichlorostyrene and methyl methacrylate as inhibitors, the linear graphs of k_{In} against [P]$_0$ were extrapolated to [P]$_0$ = 0. The intercepts then gave limiting values of the rate constants ($k_{\text{extrap.}}$) of $3·37 \times 10^{-5}$ ($\pm 0·03 \times 10^{-5}$) and $2·40 \times 10^{-5}$ ($\pm 0·03 \times 10^{-5}$) sec.$^{-1}$, respectively. Application of a similar procedure to the results for the reaction in bromobenzene in the presence of 3,4-dichlorostyrene gave $k_{\text{extrap.}} = 3·72 \times 10^{-5}$ ($\pm 0·08 \times 10^{-5}$) sec.$^{-1}$.

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[14] J. J. Lothe and G. Eia, *Acta Chem. Scand.*, 1958, **12**, 1535.

[15] P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, 1960, **82**, 1756.

(*c*) *Reaction products.* A method similar to that outlined for the reaction in benzene [1] was used, each reaction being carried out in duplicate. However, the method of estimating the biaryl and dihydrobiaryl yield was necessarily modified owing to the large number of isomers of the dihydro-compound which could be formed. In one series of duplicate reactions (Scheme A) the dihydrobiaryls were converted into biaryls by aerial oxidation, whilst in a second series (scheme B) the biaryls were estimated directly after the removal of the dihydro-compounds by oxidation to *cis*-1,2-diols by reaction with an excess of 2% potassium permanganate in acetone. The dihydrobiaryl yield was obtained from the difference in the biaryl yield between Scheme A and Scheme B duplicates.

Benzoic acid was determined gravimetrically,[1] biphenyl, phenyl benzoate, and the isomeric chloro- and bromo-biphenyls were analysed by gas chromatography using an internal standard (Apiezon L column, 180°, argon carrier). The residues were determined by weight after distilling out the biaryl-ester fraction of the Scheme A reactions, and assumed to consist entirely of the appropriate derivatives of tetrahydroquaterphenyl. The isomeric chloro- and bromo-phenyl benzoates were determined as benzoic acid after alkaline hydrolysis of the biaryl-ester distillates,[16] since analysis by gas chromatography proved difficult.

The results are given in Tables 4 and 5, in which the yields of the various products are compared with the function f described previously,[1] and defined by equations (7) and (8) (*q.v.*).

TABLE 4

Molar yields of products of the decomposition of benzoyl peroxide in chlorobenzene (80·2°)

$[P]_0$ (mole l.$^{-1}$)	0·1652	0·0826	0·0413	0·0206	0·0103
Benzoic acid (a)	0·420	0·335	0·282	0·208	0·170
Chlorobiphenyls (b)	0·493	0·524	0·562	0·552	0·536
Ratio of isomers (2- : 3- : 4-) Scheme A	59·1 : 26·0 : 14·9	59·0 : 24·6 : 16·4	57·5 : 24·8 : 17·7	58·2 : 25·3 : 16·5	58·1 : 23·8 : 18·1
Ratio of isomers (2- : 3- : 4) Scheme B	59·1 : 26·2 : 14·7	58·0 : 25·1 : 16·9	56·4 : 25·7 : 17·9	57·8 : 24·8 : 17·4	58·2 : 24·9 : 16·9
Dihydrobiphenyls (c)	0·000	0·003	0·031	0·060	0·080
Chlorophenyl benzoates * (d)	0·061	0·060	0·065	0·068	0·064
Biphenyl (e)	0·009	0·008	0·007	0·008	0·008
Residue † (h)	0·332	0·345	0·420	0·490	0·548
$(1 - f)$	0·451	0·301	0·235	0·181	0·141
f ‡	0·549	0·699	0·765	0·819	0·859
$\frac{1}{2}(a + b)$	0·457	0·430	0·422	0·380	0·353
$\frac{1}{2}(a + b + d + e)$	0·492	0·464	0·458	0·418	0·389
$\frac{1}{2}(b + d + e - a) + \frac{1}{2}c + h = g$	0·404	0·475	0·612	0·730	0·804

* Shown by g.l.c. to contain ~20% phenyl benzoate. † As dichlorotetrahydroquaterphenyls. ‡ Calculated from equations (7) or (8) as appropriate.

Reagents.—Nitrogen was purified as previously described.[1] Chloro- and bromo-benzene were purified by standard methods and finally dried by allowing them to stand for 3—7 days over 4-Å molecular-sieve material in a 4-ft. column under nitrogen. The solvents, which were run off slowly as required, were shown by gas chromatography to be chemically homogeneous and found to contain $\not>$10 p.p.m. of water, by Karl Fischer non-aqueous titration.

Acenaphthylene, biphenyl, 4-bromobiphenyl, 4-chlorobiphenyl, naphthacene, and phenyl benzoate were crystallised to constant m. p. from ethanol. 2-Bromobiphenyl, after fractional distillation, had b. p. 160—161°/11 mm., and n_D^{20} 1·6283. Methyl methacrylate, after fractional distillation, had b. p. 100—101°/760 mm. Diphenylmethane was fractionally frozen to constant m. p. 26—27°. Benzoyl peroxide was purified and estimated as described previously [1] (m. p. 105·5°, purity 99·98% ± 0·02%).

3,4-Dichloroacetophenone (m. p. 76°) was prepared by Roberts and Turner's method,[17] and converted into 3,4-dichlorostyrene (b. p. 69—70°/4 mm., n_D^{20} 1·5858) by Brooks's method.[18]

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[16] W. R. Foster and G. H. Williams, *J.*, 1962, 2862.

[17] E. Roberts and E. E. Turner, *J.*, 1927, 1832.

[18] L. A. Brooks, *J. Amer. Chem. Soc.*, 1944, **66**, 1295.

TABLE 5

Molar yields of products of the decomposition of benzoyl peroxide in bromobenzene (80·2°)

$[P]_0$ (mole $l.^{-1}$)	0·1652	0·0826	0·0413	0·0206	0·0103
Benzoic acid (*a*)	0·962	0·982	0·972	0·955	0·941
Bromobiphenyls (*b*)	0·833	0·883	0·730	0·660	0·653
Ratio of isomers (2- : 3- : 4-) Scheme A	—	—	—	—	53·3 : 31·0 : 15·7
Ratio of isomers (2- : 3- : 4-) Scheme B	57·1 : 27·2 : 15·7	56·1 : 28·1 : 15·8	55·2 : 29·1 : 15·7	55·8 : 29·7 : 14·5	54·5 : 29·8 : 15·7
Bromophenyl benzoates * (*c*)	0·021	0·025	0·032	0·039	0·021
Residue † (*d*)	0·059	0·085	0·112	0·150	0·199
$(1 - f)$	0·731	0·731	0·731	0·731	0·731
f ‡	0·269	0·269	0·269	0·269	0·269
$\frac{1}{2}(a + b + c) - 0{\cdot}731 + d = g$	0·236	0·299	0·248	0·246	0·276

* Contain a trace of phenyl benzoate (g.l.c.). † As dibromotetrahydroquaterphenyls. ‡ Calculated from equation (7).

2-Chlorobiphenyl was prepared by the decomposition of *o*-chlorobenzoyl peroxide in benzene containing 0·1% of *m*-dinitrobenzene, as described by Hey, Perkins, and Williams,[19] to improve the yield. It was obtained in 51·3% yield and had m. p. 32°. 3-Chloro- and 3-bromo-biphenyl were prepared by analogous methods. They were obtained in 51·8 and 63·6% yield, and had b. p. 79°/0·05 mm. and 82°/0·05 mm., and n_D^{20} 1·6197 and 1·6405, respectively. All the biphenyl derivatives were shown to be chemically homogeneous by gas chromatography. 2,2-Diphenyl-1-picrylhydrazyl was prepared by Poirer, Kahler, and Benington's method,[20] and had m. p. 127—129°, and $\lambda_{max.}$ 520 mμ in ethanol. Galvinoxyl was prepared as described previously.[1]

DISCUSSION

The general mechanism proposed in Part II [1] [equation 2, where R· is the benzoyloxy-, and R'· the phenyl, radical, σ· and σ'· are the corresponding σ-complexes for benzoyloxylation and phenylation, respectively, and k_1—k_6 are the specific rate constants for reactions (2i)—(2vi), respectively], is capable of accommodating the observed kinetics and product distribution.

$$\begin{array}{rlll}
\text{(i)} & P \longrightarrow 2R\cdot & (k_1) & \\
\text{(ii)} & R\cdot \longrightarrow R'\cdot + CO_2 & (k_2) & \\
\text{(iiia)} & R\cdot + PhX \longrightarrow \sigma\cdot & \multirow{2}{*}{$\left.\right\}(k_3)$} & \\
\text{(iiib)} & R'\cdot + PhX \longrightarrow \sigma'\cdot & & \\
\text{(iv)} & \sigma\cdot + P \longrightarrow R\cdot + PhR + PhCO_2H & \multirow{2}{*}{$\left.\right\}(k_4)$} & (2) \\
 & \sigma'\cdot + P \longrightarrow R\cdot + PhR' + PhCO_2H & & \\
\text{(v)} & 2\sigma\cdot \text{ or } 2\sigma'\cdot \longrightarrow \text{Dimerisation and disproportionation products} & (k_5) & \\
\text{(vi)} & \sigma\cdot + R\cdot \longrightarrow PhR + PhCO_2H & \multirow{2}{*}{$\left.\right\}(k_6)$} & \\
 & \sigma'\cdot + R\cdot \longrightarrow PhR' + PhCO_2H & &
\end{array}$$

Kinetics.—In both solvents, the lowest, and therefore the most reliable, estimate of k_1 is obtained by the use of galvinoxyl as an inhibitor, even if the values of k_1 obtained with the other inhibitors (polynuclear hydrocarbons and polymerisable monomers) are extrapolated to $[P]_0 = 0$. It is probable, therefore, that radicals derived from these inhibitors themselves take part in the induced reaction, leading to erroneous results.

For chlorobenzene, since k_1 (galvinoxyl) $\sim k_1$ (extrap.), no first-order induced reaction occurs at $[P]_0 < 0{\cdot}11$M. At $[P]_0 > 0{\cdot}12$M the induced process was first-order and no 1·5-order reaction could be detected, although the kinetic analysis is probably insensitive to intermediate reaction orders, particularly if the difference from either limiting value is small.

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[19] D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. and Ind.*, 1963, 83.

[20] R. H. Poirer, E. J. Kahler, and F. Benington, *J. Org. Chem.*, 1952, **17**, 1437.

In bromobenzene, on the other hand, extensive first-order induced decomposition occurs over the whole concentration range. The occurrence of a first-order induced process has not previously been reported for this reaction.

Termination by reaction (2v) leads to the kinetics described by equation (1)$[k_{\frac{3}{2}} = k_4(2k_1/k_5)^{\frac{1}{2}}]$, and observed for the reaction in chlorobenzene at $[P]_0 < 0{\cdot}11$—$0{\cdot}12$M (Figure), while termination by (2vi) leads to kinetics described by equation (3):

$$-d[P]/dt = k_1[P] + k_1'[P] \qquad (3)$$

where

$$k_1' = \tfrac{1}{2}\{-k_1 + k_1^{\frac{1}{2}}k_6^{-\frac{1}{2}}[k_1k_6 + 4k_4(k_2 + k_3)]^{\frac{1}{2}}\}.$$

The high value of the extrapolated first-order constant in bromobenzene arises from the fact that $k_{\text{extrap.}}(\text{PhBr}) = k_1 + k_1'$, whereas $k_{\text{extrap.}}(\text{PhCl}) = k_1$. The rate-constant $k_{\frac{3}{2}}$ (which depends on k_1, k_4, and k_5) is concentration-dependent, and is zero at $[P]_0 = 0$. The constant k_1' (which depends on k_1, k_2, k_3, k_4, and k_6) is a first-order constant, and being consequently independent of concentration, increases the magnitude of $k_{\text{extrap.}}(\text{PhBr})$. Kinetics of this type were observed for the reaction in chlorobenzene ($[P]_0 > 0{\cdot}11$—$0{\cdot}12$M) and bromobenzene (Figure). The observed yield and the rate of formation of benzoic acid in bromobenzene are also consistent with termination by reaction (2vi), the rate being given by equation (3) (cf. Figure). In the case of chlorobenzene, however, the observed rate of benzoic acid formation, which takes the form of equation (1), differs from the "steady-state" equation derived from treatment of reactions (2i)—(2v), *viz.*,

$$-d[P]/dt = k_{\frac{3}{2}}[P]^{\frac{3}{2}} \qquad (4)$$

This anomaly is regarded as an artefact arising from the known inaccuracy of the experimental determination in chlorobenzene media since both the yield and rate of formation of benzoic acid are particularly low in this solvent. As $[P]_0 \longrightarrow 0$, however, the acid yield also approaches zero, and this is consistent with equations (2) and (4).

The kinetic results are summarised in Table 6, which includes the values of the first- and 1·5-order rate constants k_{a_1} and $k_{a_{3/2}}$ for the formation of benzoic acid in chlorobenzene, and the corresponding extrapolated rate-constant, $k_{a_{\text{extrap.}}}$, for the reaction in bromobenzene.

TABLE 6

Rate constants for the decomposition of benzoyl peroxide in chlorobenzene and in bromobenzene (80·2°)

Chlorobenzene	10^5k_1 (sec.$^{-1}$) (by extrapolation)	$2{\cdot}43 \pm 0{\cdot}04$
,, ...	$10^5k_{\frac{3}{2}}$ (sec.$^{-1}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$) ($[P]_0 < 0{\cdot}11$M)	$5{\cdot}53 \pm 0{\cdot}08$
,, ...	$10^5k_1'$ (sec.$^{-1}$) ($[P]_0 > 0{\cdot}12$M)	$1{\cdot}87 \pm 0{\cdot}05$
,, ...	10^5k_1 (sec.$^{-1}$) (galvinoxyl inhibition)	$2{\cdot}36 \pm 0{\cdot}05$
,, ...	$10^5k_{a_1}$ (sec.$^{-1}$)	$1{\cdot}66 \pm 0{\cdot}08$
,, ...	$10^5k_{a_{\frac{3}{2}}}$ (sec.$^{-1}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$)	$1{\cdot}90 \pm 0{\cdot}09$
Bromobenzene	$10^5k_{\text{extrap.}}$ (sec.$^{-1}$)	$8{\cdot}15 \pm 0{\cdot}08$
,, ...	10^5k_1 (sec.$^{-1}$)	$2{\cdot}19 \pm 0{\cdot}04$
,, ...	$10^5k_1'$ (sec.$^{-1}$)	$5{\cdot}96 \pm 0{\cdot}12$
,, ...	$10^5k_{a_{\text{extrap.}}}$ (sec.$^{-1}$)	$8{\cdot}13 \pm 0{\cdot}10$

Products.—The individual components of the residue were not isolated in the present work owing to experimental difficulty, but their identity is beyond doubt. They may be considered, with little error, particularly at low values of $[P]_0$, to consist entirely of the appropriate derivatives of tetrahydroquaterphenyl, and are formed by reaction (2v) by dimerisation of σ-complexes.[3,4,21] The analogous reaction involving hydrogen transfer between σ-complexes (2v) yields the dihydrobiaryls.[3,21] The low yield of residue and the apparent absence of dihydrobiaryls in the reaction in bromobenzene indicates that the reactions (2v) are unimportant in this solvent. In chlorobenzene, on the other hand, the formation of dihydrobiaryls and a large yield of residue is consistent with the prediction, from the kinetics, that termination is entirely by reaction (2v). This mode of termination is

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[21] D. F. De Tar and R. A. J. Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.

clearly also important at high $[P]_0$ values, although this is not indicated by the kinetics, probably owing to non-ideality in these concentrated solutions.

The high biaryl and benzoic acid yields in bromobenzene indicate that these products are formed in both propagation (2iv) and termination (2vi) reactions. The decrease in biaryl yield at low $[P]_0$ values (with a concomitant increase in the residue yield) indicates, however, that at these concentrations, reaction (2v) assumes some minor importance. In chlorobenzene, the yield of benzoic acid is very much lower and approaches zero as $[P]_0 \longrightarrow 0$, as would be expected of a product formed entirely by reaction (2iv), whereas the biaryls show little variation and must result from reactions (2iv) and (2v). In both solvents, the lack of variation in the proportions of isomeric chloro- and bromo-biphenyls, although the biaryl yields are not constant in either solvent, confirms the conclusion previously reached by Morrison, Cazes, Samkoff, and Howe,[22] and by Hey, Perkins, and Williams,[19] that the isomeric σ-complexes are not selectively removed by dimerisation and disproportionation. The biaryl isomer ratios therefore correctly represent the proportions in which the isomeric σ-complexes are formed, and the incursion of reaction (2v) does not affect the validity of previously determined partial rate factors for homolytic phenylation (cf. Williams [23]).

Chloro- and bromo-phenyl benzoates are formed in low yield by benzoyloxylation in a manner analogous to the corresponding biaryls. The yields of these esters are so low that variations in them are hardly significant. They are, however, accompanied by very small amounts (0·01 mole/mole of peroxide) of phenyl benzoate, which may be formed in an

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{(Ph{\cdot}CO{\cdot}O)_2} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OPh} + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{CO_2} \qquad (5)$$

$$\mathrm{(Ph{\cdot}CO{\cdot}O)_2} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}OPh} + \mathrm{CO_2} \qquad (6)$$

induced reaction (5), or by " cage " recombination of phenyl and benzoyloxy-radicals, or conceivably by intramolecular decarboxylation of the peroxide (6).

Very small amounts (~0·008 mole/mole of peroxide) of biphenyl formed in the reaction in chlorobenzene are unlikely to arise by dimerisation of phenyl radicals since their stationary concentration must be extremely low, but probably result from the attack of phenyl radicals on the 1-position of the chlorobenzene molecule. The resulting σ-complex may then undergo hydrogen- or chlorine-transfer [cf. reaction (2v)], followed by dehydrochlorination of the hydroaromatic products to biphenyl and hydrogen chloride. Hydrogen chloride is known to be formed in the reaction, although it may also be formed by another route.[3] The fact that no biphenyl could be detected in the reaction in bromobenzene is consistent with the comparatively large size of the bromine atom, and the low probability of reactions of the type of (2v) in bromobenzene.

Correlation of Rate-constants and Product Yields.—In Tables 4 and 5 the yields of the various products are correlated with a function f, defined by equations (7) and (8), (where $K = k_{\frac{3}{2}}/k_1$) according as the induced reaction is of order 1 or 1·5, respectively.

$$f = k_1/(k_1 + k'_1) \qquad (7)$$

$$= 2\{K[P]_0^{\frac{1}{2}} - \ln(1 + [P]_0^{\frac{1}{2}})\}K^2[P]_0 \qquad (8)$$

This quantity represents the fraction of the peroxide which decomposes by primary fission at any given value of $[P]_0$, and should be related directly to the molar yield of the termination products.[16] The molar yields of the various products, or portions thereof, which have been considered in the foregoing discussion to be formed in termination reactions, are included in the sum g given in Tables 4 and 5, which may be compared with f. (The sum g is calculated in such a way as to allow for the formation of either one or two molecules of dimerisation or disproportionation products, as appropriate.) As may be seen from Table 4, the correlation between f and g for the reaction in chlorobenzene is good at

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[22] R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Amer. Chem. Soc.*, 1962, **84**, 4152.

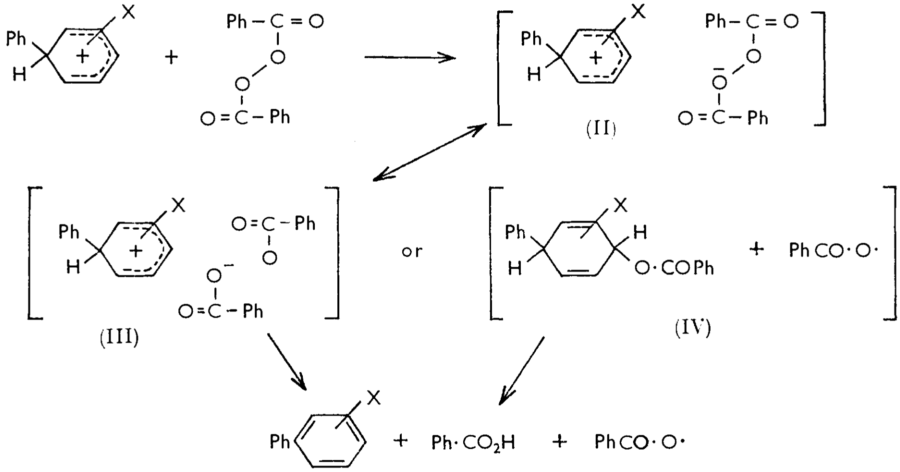
[23] G. H. Williams, *Chem. and Ind.*, 1961, 1286.

low values of $[P]_0$, but the parameters diverge increasingly at higher concentrations. This probably arises from the increasing incursion of side reactions such as the addition of radicals to hydroaromatic nuclei, leading to degradation of the dihydrobiaryls and the residue. Moreover, in the range $[P]_0 > 0{\cdot}12\text{M}$, where f is calculated from equation (7), the formation of appreciable amounts of residue shows equation (3) to be a rather inadequate description of the reaction (*q.v.*), and a close correlation of f and g would not be expected.

The closer agreement between f and g for the reaction in bromobenzene (Table 5) reflects the reduced importance of side reactions in this solvent, in which the reactive hydroaromatic products are formed in much lower yield.

Reaction Mechanism.—It is concluded from the foregoing discussion that, apart from the incursion of side reactions at high concentrations in chlorobenzene, equation (2) provides a reasonably accurate description of the reaction in both solvents, and that in bromobenzene, termination of chains occurs mainly by reaction (2vi), whereas in chlorobenzene, as in benzene,[1] the chains are terminated almost entirely by reaction (2v) except at high concentrations, where reaction (2vi) begins to become important.

Two matters remain for discussion, namely the detailed mechanisms of the propagation stage (2iv) of the induced reaction, and the reason for the different behaviour of chlorobenzene and bromobenzene. In the induced decomposition, radical attack (by σ-complexes) may occur on the carbonyl oxygen [8] or, more probably, on peroxidic oxygen.[24] Attack of the second type was recently formulated by Simamura [24] as arising from interaction of the charge-transfer type, involving the highest occupied molecular orbital of the attacking radical and the vacant $2p\sigma_u$ antibonding orbital around the oxygen–oxygen bond of the peroxide. The influence of the carbonyl group was regarded as subordinate. The sequence of reactions of which reaction (2iv) is a summary, is probably best represented by equation (9) [cf. ref. 24]. It would appear, on the basis of the present evidence, that the transition state schematically represented by structures (II) and (III) is more probable than the alternative [(II) and (IV)], since it is difficult to see why at least some of the hydroaromatic ester (IV) should not survive the relatively mild reaction conditions. The alternative would require that compound (IV) decomposes almost completely to biaryl and benzoic acid in a reaction of low activation energy and with a rate several times faster than that of hydrogen abstraction by radicals, since this process would give high-boiling esters rather than biaryls.



(9)

The main difference between the reactions in bromobenzene on the one hand, and benzene and chlorobenzene on the other, is that in bromobenzene the σ-complexes react

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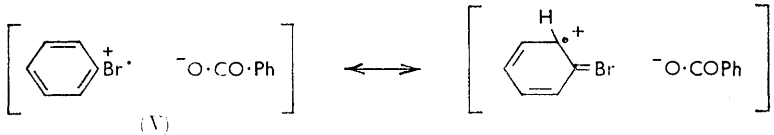
[24] K. Tokumaru and O. Simamura, *Bull. Chem. Soc. Japan*, 1963, **36**, 333.

mainly with benzoyloxy-radicals rather than by dimerisation and disproportionation. This significant difference is unlikely to arise from the small structural difference between the σ-complexes derived from chlorobenzene and bromobenzene, respectively. It is, however, explicable if it can be assumed that the effective stationary concentration of benzoyloxy-radicals is higher in the latter solvent. It is therefore suggested that complexes are formed between these radicals and the solvents, and that such complexes are formed more readily with bromobenzene. Such complexes are more likely to be of the π- rather than of the σ-type, and may involve interaction between the highest occupied molecular orbital of the radical and the lowest unoccupied orbital around the bromine atom. Such interaction may or may not involve the actual transfer of one electron to the acceptor radical giving the complex (V) (cf. iodosobenzene $PhI^+—O^-$), in which delocalisation of the odd electron is possible in the radical-cation so formed.



(V)

Interaction of the benzoyloxy-radical with the π-electrons of the bromobenzene nucleus would appear less likely since it would be difficult on this basis to account for the marked difference in behaviour between bromobenzene on the one hand, and benzene and chlorobenzene on the other. A complex such as (V), however, would be expected to be more readily formed by bromobenzene.[25] Formation of structure (V) should stabilise the benzoyloxy-radical, particularly since the transfer of one electron to this radical results in the formation of the benzoate anion, a species far less likely to lose carbon dioxide under the experimental conditions, owing to the greater strength of the C(1)–CO bond. The result should be a higher stationary concentration of (complexed) benzoyloxy-radicals, and a lower stationary concentration of σ-complexes in bromobenzene than in chlorobenzene. The latter effect arises from the increased reluctance of complexed benzoyloxy-radicals to undergo decarboxylation to phenyl radicals, which are the necessary precursors of σ-complexes, as well as from the more efficient oxidation of σ-complexes by reaction (2vi). Thus, for example, at $[P]_0 = 0{\cdot}103$M, the number of σ-complexes formed in chlorobenzene compared with the number formed in bromobenzene, as calculated from the molar yields of biaryls, dihydrobiaryls, and tetrahydroquaterphenyl derivatives obtained in these solvents, is in the ratio 1 : 0·6. Both these above factors are linked with the greater incidence of reaction (2v), the rate of which depends on the square of the concentration of σ-complexes, and which does not involve benzoyloxy-radicals, in chlorobenzene.

The proposed mechanism (2) should therefore be modified for the reaction in bromobenzene by replacement of reaction (2iii*a*) by (10) and (11),

$$R\cdot + PhBr \rightleftharpoons (V) \tag{10}$$

$$(V) \longrightarrow \sigma\cdot \tag{11}$$

and of reaction (2vi) by (12). Mutual combination of complexes, (13), is

$$\left.\begin{array}{l} (V) + \sigma\cdot \longrightarrow PhR + PhCO_2H + PhBr \\ (V) + \sigma\cdot' \longrightarrow PhR' + PhCO_2H + PhBr \end{array}\right\} \tag{12}$$

$$2(V) \longrightarrow PhCO{\cdot}O{\cdot}O{\cdot}CO{\cdot}Ph + 2PhBr \tag{13}$$

unlikely to be important. The inclusion of reactions (10)—(12) does not alter the consequences upon the kinetics already discussed, the rate of decomposition of the peroxide and the rate of formation of benzoic acid still being given in general form by equation (3), although k_1' is given by a more complex expression.

The small but significant increase in the yield of the residue which becomes apparent in bromobenzene at low concentrations of benzoyl peroxide, and which is not accompanied

[25] P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, 1963, **85**, 2849.

by a corresponding decrease in the yield of benzoic acid, may be due to incursion of reactions (14)—(17) at these concentrations owing to the relatively high concentration of complexed benzoyloxy-radicals (V).

$$2\sigma\cdot \longrightarrow \text{Hydroaromatic residue } (\text{AH})_2 \tag{14}$$

$$\text{AH}_2 + (\text{V}) \longrightarrow \text{PhBr} + \text{Ph·CO}_2\text{H} + \text{AH·} \tag{15}$$

$$\text{AH·} + (\text{Ph·CO·O})_2 \longrightarrow \text{A} + \text{Ph·CO}_2\text{H} + \text{Ph·CO·O·} \tag{16}$$

$$\text{AH·} + (\text{V}) \longrightarrow \text{A} + \text{PhBr} + \text{Ph·CO}_2\text{H} \tag{17}$$

The change in form of the rate expression for the reaction in chlorobenzene at high peroxide concentrations does not provide evidence for the formation of a complex of the benzoyloxy-radical with chlorobenzene (although this is not precluded), since reaction (2vi) would in any case be expected to increase in importance at high peroxide concentrations. This arises since, as can be seen from equations (18) and (19), the steady-state concentration of benzoyloxy-radicals varies as a higher power of the initial peroxide concentration than that of the σ-complex. Increased participation of benzoyloxy-

$$[\text{Ph·CO·O·}] = \frac{2k_1}{(k_2 + k_3)}[\text{P}]_0 + \frac{k_4}{k_2}\kappa[\text{P}]_0^{\frac{3}{2}} \tag{18}$$

$$[\sigma'\cdot] = \kappa[\text{P}]^{\frac{1}{2}} \tag{19}$$

where $$\kappa = [2k_1k_2^2/(2k_3k_5 + k_3^2k_5 + k_2^2k_5)]^{\frac{1}{2}}$$

radicals in termination reactions at higher peroxide concentrations is therefore to be expected, and, in the reaction in chlorobenzene, causes the change in kinetic form to occur within the concentration range studied.

Thanks are accorded to the D.S.I.R. for the award of a grant to G. B. G.

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[*Received, November* 30*th*, **1964**.]