Mechanism of the Thermal Decomposition of [Di(benzoyloxy)iodo]benzene in Bromobenzene

By **Colin J. Cribb, G. Bryon Gill,* and Harith A. R. El-Jamali,** Department of Chemistry, The University, Nottingham NG7 2RD

The decomposition of [di(benzoyloxy)iodo]benzene in bromobenzene at 145.5 °C is first-order with k_{obs} $(8.48 \pm 0.40) \times 10^{-5}$ s^{-1}. Product studies indicate that concurrent heterolytic and homolytic decomposition of starting material occurs. Heterolysis of the iodo-compound gives phenyl benzoate and benzoyl hypoiodite. The hypoiodite reacts under the experimental conditions to give, as determined from the results of control experiments, 1-bromo-2-iodo- and -4-iodo-benzene by electrophilic iodination of the solvent, and iodobenzene by a Hunsdiecker type of process. The homolytic pathway gives carbon dioxide, benzoic acid, iodobenzene, 2-, 3-, and 4-bromobiphenyl, an involatile residue, and free iodine as major products. Direct evidence for a radical-chain decomposition of [di(benzoyloxy)iodo]benzene was not obtained. Control experiments indicate that such a reaction is possible, whereas the kinetic and product studies indicate that the chain decomposition is likely to be no more than of minor importance. It is proposed that free benzoyloxyl radicals are rapidly decarboxylated at 145.5 °C, and that most of the benzoic acid is derived from the reactions of the benzoyloxy(phenyl)iodo-radical, which behaves essentially as a stabilized benzoyloxyl radical. Control experiments provide circumstantial evidence for the existence of the radical $Ph\dot{I}O_2CPh$. The major reaction pathway is considered to be adequately represented by not less than twelve individual steps. The reactions are highly susceptible to the presence of traces of water, and consistent results could only be obtained under essentially anhydrous conditions.

EARLY work on (diaroyloxyiodo) compounds of the type $Ar'I(O_2CAr)_2$ established that their thermolysis in solution generated aryl radicals Ar•. Thus, decomposition of [di(benzoyloxy)iodo]benzene (DBIB) in monosubstituted benzenoid solvents afforded unsymmetrical biphenyls (all three isomers), phenyl benzoate, benzoic acid, iodobenzene, and carbon dioxide as major products.[1] The ratios of the isomeric biphenyls were similar to those obtained in the reactions of other phenyl radical sources (*e.g.* benzoyl peroxide) with the same solvent. However, there were notable differences between the DBIB and benzoyl peroxide results, in the relative yields of the major products that these reactions have in common. In particular, the yields of benzoic acid and phenyl benzoate appeared to be abnormally high in the DBIB thermolyses, and hydrolysis[2] of the starting material (to give $PhCO_2H$) appeared to be an important side reaction.

In order to clarify the details of the mechanism of the thermal decomposition of DBIB, we studied the reaction in bromobenzene at 145.5 °C. The choice of solvent was conditioned by its availability, ease of purification, inertness to autoxidation, and good thermal stability; the temperature was selected so that the reaction had a half-life of *ca.* 2—3 h. In addition, detailed studies had already been reported for the thermal decomposition of benzoyl peroxide in bromobenzene,[3] thus facilitating direct comparisons between the two systems.

When this initial programme was in progress, Leffler, Mitchell, and Menon published details of their work on DBIB–chlorobenzene–benzoic anhydride;[4] the anhydride was added to re-benzoylate material hydrolysed by adventitious water. Their kinetic results and product studies were interpreted in terms of a complex sequence of reactions, admitted to contain a number of speculative steps, in which benzoic anhydride plays an important and integral role. We had already circumvented the hydrolysis problem by a careful routine of solvent purification so that, as far as possible, reactions were conducted under essentially anhydrous conditions. Hence, our studies are not strictly comparable to those of the above authors since the majority of their proposed reaction scheme will not be applicable under our conditions. However, our results presented below do verify their important conclusion that DBIB decomposes unimolecularly by both radical and heterolytic pathways, and evidence for the formation of benzoyl hypoiodite in the heterolytic decomposition has been obtained.

RESULTS AND DISCUSSION

The reactions listed in the Scheme are regarded as the minimum necessary to explain the experimental observations. Various additional steps demand serious consideration, and these are discussed in the appropriate sections below. All reactions were performed at 145.5 °C unless stated to the contrary.

a $PhI(O_2CPh)_2 \longrightarrow PhO_2CPh + PhCO_2I$
b $PhI(O_2CPh)_2 \longrightarrow Ph\dot{I}O_2CPh + PhCO_2$
c $PhCO_2I \longrightarrow PhCO_2\cdot + I\cdot$
d $PhCO_2I + PhBr \longrightarrow$ *o*- + *p*-$BrC_6H_4I + PhCO_2H$
e $PhCO_2\cdot \longrightarrow Ph\cdot + CO_2$
f $Ph\cdot + PhBr \longrightarrow (PhC_6H_5Br)\cdot$
g $Ph\dot{I}O_2CPh \longrightarrow PhI + PhCO_2\cdot$
h $`R\cdot' + PhI \longrightarrow `RI' + Ph\cdot$
i $[Ph\cdot + I\cdot]_{cage} \longrightarrow PhI$
j $Ph\dot{I}O_2CPh + (PhC_6H_5Br)\cdot \longrightarrow PhI + PhCO_2H + PhC_6H_4Br$
k $2(PhC_6H_5Br)\cdot \longrightarrow$ products of combination or disproportionation
l $2I\cdot + PhBr \longrightarrow I_2 + PhBr$

SCHEME

Kinetics.—Consistent results were obtained only after rigorous precautions had been taken to exclude water

---

[1] D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1956, 1475; B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, 1957, **10**, 329.

[2] K. H. Pausacker and M. Karelsky, *Austral. J. Chem.*, 1958, **11**, 39.

[3] G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 7127.

[4] J. E. Leffler, W. J. M. Mitchell, and B. C. Menon, *J. Org. Chem.*, 1966, **31**, 1153.

from the reaction mixture. Solutions of DBIB in ' anhydrous ' bromobenzene were stable at room temperature, and the sparingly soluble hydrolysis product, iodosylbenzene, was not detected under these conditions. Studies were limited to the range 0.005—0.03M by the low solubility of DBIB at one extreme, and by solvent expense and problems of analytical accuracy at the other. Two independent investigations indicated reaction to be strictly first-order with a mean rate constant (k_{obs}) of 8.48×10^{-5} s^{-1} (standard deviation σ 0.33_8).* The observed first-order decomposition is consistent with the mechanism set out in the Scheme.

Products.—Typical results are summarised in Table 1, the bottom portion of which gives the product accountability of the various parts of the DBIB molecules; the method of calculation is given in the footnote. Iodine is accounted for quantitatively, within experimental error. The products arising from the phenyl group attached to iodine in DBIB [*i.e.* (k)] are uniformly overestimated by 6—17%, and the products derived from the benzoyloxy-groups [*i.e.* (m)] account for only 57.6—68.8% of the theoretical quantity (excluding the 156 °C results); this last point is considered further below. Hence, in view of the complexity of the product mixture, the figures quoted in Table 1 should be regarded as an indication of relative rather than of absolute yield.

TABLE 1

Products (mol per mol) of the decomposition of [di(benzoyloxy)iodo]benzene in bromobenzene at 145.5 °C

		[DBIB]/M				
		0.029 3	0.0115	0.005 48	0.002 38	0.032 2 *
(a)	PhI	0.90	0.90	0.90	0.90	0.98
(b)	$PhCO_2H$	0.52_6	0.65_7	0.63_2	0.60_1	0.53_4
(c)	$PhCO_2Ph$	0.16_7	0.26_1	0.26_8	0.27_5	0.25_1
(d)	$2\text{-}BrC_6H_4Ph$	0.13_0	0.13_5	0.13_8	0.13_8	0.50_9
(e)	$3\text{-}BrC_6H_4Ph$	0.063_5	0.072_5	0.071_2	0.077_7	0.25_9
(f)	$4\text{-}BrC_6H_4Ph$	0.045_3	0.051_5	0.050_5	0.052_1	0.13_0
(g)	I_2	0.042_3	0.055_6	0.049_5	0.043_4	0.004_0
(h)	$2\text{-}BrC_6H_4I$	0.011_5	0.018_6	0.021_4	0.022_2	Absent
(i)	$4\text{-}BrC_6H_4I$	0.037_3	0.066_0	0.072_5	0.077_1	Absent
(j)	Residue [a]	0.11	0.10	0.050	0.038	0.10_2
(k) [b]	$\mathit{Ph}I(O_2CPh)_2$	1.06_7	1.16_1	1.16_8	1.17_5	1.23_1
(l) [c]	$Ph\mathit{I}(O_2CPh)_2$	1.03_3	1.09_6	1.09_3	1.08_6	0.98_8
(m) [d]	$PhI(O_2C\mathit{Ph})_2$	1.15_2	1.37_7	1.26_0	1.22_0	1.88_7

[a] Assuming it comprises the isomeric dibromotetrahydroquaterphenyls, *M* 468. [b] (k) = (a) + (c); theoretical yield 1 mol per mol. [c] (l) = (a) + 2(g) + (h) + (i); theoretical yield 1 mol per mol. [d] (m) = (b) + (c) + (d) + (e) + (f) + 2(j); theoretical yield 2 mol per mol.

* Results obtained at 156°.

Product studies were also made on the reactions of compounds of the type $ArI(O_2CR)_2$, and the data are presented in Table 2.

Steps a, c, d, e, h, i, *and* l.—Reaction *a* of the Scheme was first proposed by Leffler, Mitchell, and Menon,[4] whose evidence rested with the finding that aryl benzoate is obtained from the thermolysis of [di(benzoyloxy)iodo]arenes. We find that the yield of aryl benzoate (p-$XC_6H_4{\cdot}O_2CPh$) is controlled to some extent by the nature of the substituent X and the inital concentration of [di(benzoyloxy)iodo]arene (Tables 1 and 2). The precise mechanism of step *a* is not clear. The two main contenders are a pericyclic type of transformation, and ion-pair formation and nucleophilic displacement [reaction (i)]. A mechanism based on radical pair formation and

$$\mathrm{PhI(O_2CPh)_2 \rightleftharpoons Ph\overset{+}{I}O_2CPh + {}^{-}O_2CPh \longrightarrow PhO_2CPh + PhCO_2I} \qquad \text{(i)}$$

displacement, the homolytic analogue of (i), appears less likely, although homolytic dissociation of [di(benzoyloxy)-iodo]arene may be a prelude to ion-pair formation, which itself could arise by one-electron transfer.

TABLE 2

Products (mol per mol) of the decomposition of [di(benzoyloxy)iodo]arenes in bromobenzene at 145.5°

	$[4\text{-}XC_6H_4I(O_2CPh)_2]$/M		
	X = Me	X = MeO	X = Cl
	0.019 2	0.016 0	0.026 2
$4\text{-}XC_6H_4I$	0.88	0.91	0.93
PhI	0.029_4	0.009 4	0.010_4
$PhCO_2H$	1.03	*a*	*a*
$4\text{-}XC_6H_4O_2CPh$	0.12_3	0.076_4	0.081_1
$2\text{-}BrC_6H_4Ph$	0.16_4 [b]	0.15_8	0.28_8
$3\text{-}BrC_6H_4Ph$	0.11_1	0.076_4	0.12_9
$4\text{-}BrC_6H_4Ph$	0.063_8	0.036_7	0.073_6
I_2 [c]	0.038_4	0.012_4	0.023_8
$2\text{-}BrC_6H_4I$	0.012_6	$0.006\,9_0$	0.012_4
$4\text{-}BrC_6H_4I$	0.035_4	0.020_5	0.030_5
Residue [d]	0.032	*a*	0.009 2
$\mathit{Ar}I(O_2CPh)_2$ *	1.00_3	0.986_4	1.01_2
$Ar\mathit{I}(O_2CPh)_2$ *	1.03_4	0.971_6	1.03_1
$ArI(O_2C\mathit{Ph})_2$ *	1.58_5		

[a] Not determined. [b] The isomeric 2-, 3-, and 4-bromo-4′-methylbiphenyls (*ca.* 6×10^{-4} mol per mol) also detected. [c] Decomposition of $PhI(O_2CMe)_2$ (0.027 4M) and of $PhI(O_2C{\cdot}CF_3)_2$ (0.021 3M) gave, respectively, 0.020_7 and 0.032_3 mol per mol of iodine. [d] Assuming *M* 468.

* See footnotes to Table 1 for method of calculation.

No evidence for the intermediacy of benzoyl hypoiodite, the postulated co-product of step *a*, has been reported hitherto. Careful g.l.c. analysis of the reaction mixtures revealed the presence of *o*- and *p*-bromoiodobenzene (Tables 1 and 2), but no *meta*-isomer was detected. These products are the expected result of the electrophilic iodination of the solvent, step *d*.

The reaction of mercury(II) benzoate with iodine (1 : 1 molar ratio) in bromobenzene at 145.5 °C yielded iodobenzene, benzoic acid, and *o*- and *p*-bromoiodobenzene (*m*-isomer not detected); these conditions parallel those employed for the generation of acetyl hypoiodite.[6] No iodine remained at the end of the reaction, and the basic reaction course was largely unaffected by the co-addition of the major DBIB thermolysis products (Table 1) or of benzoic anhydride (*cf.* ref. 4). At the reflux (156 °C)

---

* From t-distribution small-sample statistics,[5] the 99% confidence limits are given by $k_{\mathrm{obs}} = (8.48 \pm 0.40) \times 10^{-5}$ s^{-1}.

[5] J. M. Smith, ' Scientific Analysis on the Pocket Calculator,' Wiley-Interscience, New York, 1975, p. 265.

[6] E. M. Chen, R. M. Keefer, and L. J. Andrews, *J. Amer. Chem. Soc.*, 1967, **89**, 428.

temperature of the solvent, however, the iodine colouration disappeared fairly rapidly and iodobenzene was the only significant non-polar volatile product detected. A similar feature was observed in the decomposition of DBIB at 156 °C; the bromoiodobenzenes were no longer detected among the products (Table 1). The formation of a common intermediate (benzoyl hypoiodite) in the control and DBIB reactions is further suggested by the close correspondence of the *o*- to *p*-bromoiodobenzene isomer ratios, respectively 1 : 3.36 and 1 : 3.35—3.55. In the analogous decompositions of [di(benzoyloxy)iodo]arenes (Table 2) the ratio was 1 : 2.45—3.0. These results support the formulation of steps *a* and *d* (bromoiodobenzene formation) and steps *c*, *e*, and *i* (non-chain Hunsdiecker-type decomposition); the homolytic pathway assumes an almost exclusive role in the higher temperature (156 °C) reactions.

Reaction *l* of the Scheme is necessary to explain the formation of the free iodine obtained in all the reactions studied (Tables 1 and 2). Step *h* is reasonable in view of the known abnormally high reactivity that aryl iodides exhibit to iodine transfer on attack by radicals.[7,8] The radical ' R· ' in the Scheme is most frequently likely to be phenyl. Aryl–iodine bond homolysis of the benzoyloxy(phenyl)iodo-radical, equation (ii), was considered to be a possible reaction in the DBIB decomposition – a

$$^{*}\mathrm{Ph\dot{I}O_2CPh} \longrightarrow {}^{*}\mathrm{Ph\cdot} + \mathrm{IO_2CPh} \qquad \text{(ii)}$$

process that would escape detection under normal circumstances. However, careful g.l.c. analysis of the products of reaction of 4-[di(benzoyloxy)iodo]toluene with bromobenzene revealed the presence of small quantities of the 4-methyl-*x*′-bromobiphenyls. These compounds could have resulted from the attack of *p*-tolyl radicals [formed in the analogue of reaction (ii)] on solvent and subsequent hydrogen transfer. Similar results were obtained with other [di(benzoyloxy)iodo]arenes. Alternatively, the *p*-tolyl radicals could have been generated in an iodine abstraction attack on *p*-iodotoluene. The addition of *p*-iodobiphenyl to the DBIB–PhBr reaction resulted in the formation (g.l.c. detection) of 4-bromo-*p*-terphenyl, and similar addition of *p*-bromoiodobenzene gave 4,4′-dibromobiphenyl (the isomeric biaryls, also expected to be formed, were not specifically analysed since positive identification would have been more difficult). These results prove that iodine abstraction does occur, so that reaction (ii), if it occurs at all, will be masked. In any event, the formation of phenyl radicals by direct or subsequent phenyl–iodine bond cleavage is not a major process in the general scheme, but was studied in an attempt to demonstrate the presence of the benzoyloxy(phenyl)iodo-radical in these reactions.

Steps b, f, g, j, *and* k.—The proportions of 2-, 3-, and 4-bromobiphenyls formed (53, 28, and 19%, respectively) are indicative of homolytic phenylation [steps *e* and *f*, followed probably by *j* (see later)].[3] The conclusion that benzoyloxyl radicals are formed by step *b* rather than by fission of both I–O bonds [equation (iii)] is supported by circumstantial evidence for the existence of the radical $\mathrm{Ph\dot{I}O_2CPh}$, obtained by comparison of the photolytic reactions of DBIB and of benzoyl peroxide with 2,3-dimethylbutane. Both reactions produce the alkyl benzoates, namely 2,3-dimethylbutyl benzoate (*p*) and 1,1,2-trimethylpropyl benzoate (*t*), but in markedly different ratio: benzoyl peroxide, $p : t$ 1 : 2.2; [di(benzoyloxy)iodo]benzene, $p : t \leq 1 : 200$. Findings such as these have been used frequently as a measure of differences in radical selectivity, but these interpretations are not without ambiguity. The [di(benzoyloxy)iodo]benzene and the peroxide should, upon homolysis,

$$\mathrm{PhI(O_2CPh)_2} \longrightarrow \mathrm{PhI} + 2\mathrm{PhCO_2\cdot} \qquad \text{(iii)}$$

produce the same radical species (benzoyloxyl and phenyl) if step *b* is inoperative and reaction (iii) operative. Other things being equal, it is then expected that the $p : t$ values would be very similar. Since the $p : t$ ratios are widely different, the main active radical species in the [di(benzoyloxy)iodo]benzene photolysis may be the less reactive, more selective benzoyloxy(phenyl)iodo-radical (*i.e.* less energy is required to abstract hydrogen from a tertiary than a primary C–H bond). However, the final $p : t$ ratio does not necessarily mean that the primary and tertiary alkyl radicals are initially produced in the same ($p : t$) ratio; if interception of these radicals (*e.g.* by starting material) is inefficient, then the ratio will be altered by radical transfer reactions with the solvent reaction (iv). Hence, the widely different $p : t$ values

$$\mathrm{Me_2CH{\cdot}CHMe{\cdot}\dot{C}H_2} + \mathrm{Me_2CH{\cdot}CHMe_2} \longrightarrow \mathrm{Me_2CH{\cdot}CHMe_2} + \mathrm{Me_2CH{\cdot}\dot{C}Me_2} \qquad \text{(iv)}$$

mean that the benzoyloxy(phenyl)iodo-radical is a *possible* intermediate of the reaction; the result is not sufficiently definitive for one to be sure that it is a definite intermediate. The implications of these results are considered further in the context of an induced decomposition (see below).

If the benzoyloxy(phenyl)iodo-radical is to be a kinetically significant intermediate, as would be required for the operation of step *j* of the Scheme, it would need to be an appreciably more stable species than the benzoyloxyl radical. Otherwise step *g* should be very fast such that steps *b* and *g* occur in rapid sequence [*i.e.* to give, in effect, reaction (iii)]. It is also pertinent to examine the probable stability of the benzoyloxyl radical under the reaction conditions. The rate constant for decarboxylation of the benzoyloxyl radical (step *e*; k_e) has been estimated as 2.4×10^4 s^{-1} at 80 °C,[9] and data from two distinct sources put the activation energy, E_a, equal to 14 [9] and 15 kcal mol^{-1}.[10] Simple calculation by using the Arrhenius equation and $E_a = 14.5$ kcal mol^{-1} gives k_e

---

[7] D. L. Brydon and J. I. G. Cadogan, *J. Chem. Soc.* (*C*), 1968, 819.

[8] M. M. Schwartz and J. E. Leffler, *J. Amer. Chem. Soc.*, 1968, **90**, 1368.

[9] J. C. Bevington and J. Toole, *J. Polymer Sci.*, 1958, **28**, 413.

[10] T. Suehiro and M. Ishida, *Bull. Chem. Soc. Japan*, 1971, **44**, 1692.

6.1×10^5 s^{-1} at 145.5 °C, indicating a half life of only 10^{-6}s for the radical at the higher temperature. At 0.01M initial concentration of benzoyl peroxide, it has been shown that greater than 90% of all benzoyloxyl radicals formed in benzene suffer decarboxylation at 80 °C.[11] Since k_e (145.5 °C)/k_e (80 °C) $\simeq$ 25.4, the extent of the decarboxylation of free benzoyloxyl radicals at 145.5 °C must be appreciably greater than at 80 °C so that their stationary concentration will be extremely low. By making the simplifying assumption that reaction (iii) is the only source of benzoyloxyl radicals, the rate constant being about $\frac{2}{3}$ k_{obs}, and step *e* is the only process in which benzoyloxyl radicals are destroyed, then the stationary concentration of these radicals is given by equation (v) if the steady state limitations can be applied. Using [DBIB] = 0.01M, then appropriate numerical substitution gives $[PhCO_2\cdot] \simeq 2 \times 10^{-12}$M. Even allowing for an error factor of up to 10^{2-3}, the concentration of benzoyl-

$$[PhCO_2\cdot] = 4\ k_{obs}[DBIB]/3k_e \qquad (v)$$

oxyl radicals is so low that their involvement in radical termination is very unlikely, even at a diffusion-controlled rate.

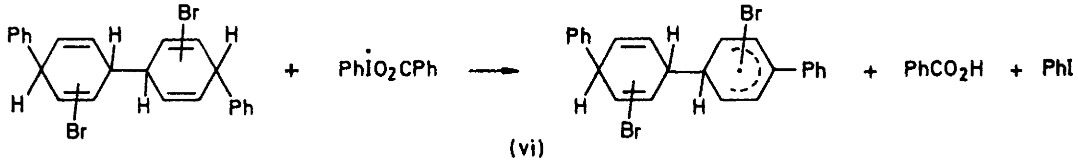
As it appears very unlikely that benzoic acid is formed in appreciable quantity in any reaction featuring direct involvement of benzoyloxyl radicals, there arises the problem of the mode of genesis of this material.* We believe the simplest and most self-consistent explanation for benzoic acid formation lies in the operation of step *j*, which in turn requires the formulation of steps *b* and *g* of the Scheme. Indications that the benzoyloxy(phenyl)-iodo-radical is a chemically reasonable proposal comes from several sources. First, the general ability of the iodine atom in aryl iodides to stabilise electronegative ligands is well known (*e.g.* stable existence of $PhIX_2$). This stabilisation tendency is so well developed that *p*-nitrobenzoyl peroxide reacts with iodobenzene to give [bis-(*p*-nitrobenzoyloxy)iodo]benzene.[7] The complexation of benzoyloxyl radicals by the bromine atom of bromobenzene has been proposed to explain the high yield of benzoic acid formed in the thermolysis of benzoyl peroxide in that solvent.[3] The association of benzoyloxyl radicals with iodine in the benzoyloxylation of benzene derivatives by benzoyl peroxide and iodine has also been invoked to explain the observed results.[12]

The diaryliodonium salts (*e.g.* $Ar\overset{+}{I}Ar'\ X^-$) provide evidence for a p_π–d_π bonding interaction between the aryl ring C(1) atoms and the iodine atom,[13] and it seems probable that benzoyloxy(phenyl)iodo-radicals could be stabilised by a similar electronic mechanism. In addition, iodine abstraction from aryl iodides by aryl radicals might well proceed by way of a species $Ar\dot{I}Ar'$, which is an intermediate rather than a transition state.[7] The *p*-methoxybenzoyloxy(phenyl)iodo-radical has been proposed[14] as an intermediate in the induced decomposition of [bis(*p*-methoxybenzoyloxy)iodo]benzene by radicals generated from the thermolysis of benzoyl peroxide in chlorobenzene at 80 °C, a temperature at which the thermal decomposition of the iodine compound itself is extremely slow. The change in reaction behaviour of (diacetoxyiodo)benzene upon the introduction of phenyl groups into its acetoxy-moieties has been interpreted in terms of an enhancement of a radical process leading to the production of radicals $Ph\dot{I}O_2CR$.[15] These radicals were regarded as being more stable than the t-butoxyl radical.

These considerations, taken together with the above results on the DBIB photolysis in 2,3-dimethylbutane, and the need to formulate the presence of stabilized benzoyloxyl radicals, lends support to the conclusion that the radical $Ph\dot{I}O_2CPh$ is involved in the reactions under scrutiny.

Oxidation of the substituted phenylcyclohexadienyl radicals by $Ph\dot{I}O_2CPh$ in step *j* should lead to equal amounts of benzoic acid and bromobiphenyl. If an induced decomposition reaction occurs (see below), both of these products should again be formed concurrently and in equal quantities. Table 1 reveals that the benzoic acid yield is always well in excess of that for bromobiphenyl, and hence there must be other routes to the acid. Hydrolysis of starting material is ruled out by the absence of the necessary co-products iodosylbenzene and iodylbenzene, which are sparingly soluble under our conditions; in any case, hydrolysis would require the converse of the observed trend in acid yield with DBIB concentration.

A reasonable source for the additional benzoic acid is reaction (vi) and its analogues. It has been established for the benzoyl peroxide thermolysis in benzene that phenylcyclohexadienyl radicals combine to form involatile tetrahydroquaterphenyls;[11] the phenylbromocyclohexadienyl radicals are expected[3] to combine in



(vi)

---

* Hydrogen abstraction from the aromatic nucleus of the solvent molecules by benzoyloxyl radicals is generally not regarded as an important reaction, and there is no evidence supporting such a process in the present system.

[11] D. F. DeTar, *J. Amer. Chem. Soc.*, 1967, **89**, 4058, and references cited therein.

[12] P. Kovacic, C. G. Reid, and M. J. Brittain, *J. Org. Chem.*, 1970, **35**, 2152.

[13] F. M. Beringer and I. Lillien, *J. Amer. Chem. Soc.*, 1960, **82**, 5135.

[14] T. T. Wang and J. E. Leffler, *J. Org. Chem.*, 1971, **36**, 1531.

[15] J. E. Leffler, D. C. Ward, and A. Burduroglu, *J. Amer. Chem. Soc.*, 1972, **94**, 5339.

similar fashion (step *k*). Reaction (vi) involves the abstraction of allylic H from such molecules, and should be a fast process of low activation energy. Additional benzoic acid is probably formed (without biaryls) by progressive dehydrogenation of σ-complex dimers (formed in step *k*) by $\mathrm{Ph\dot{I}O_2CPh}$. Reaction (vi) is the first stage of this process, which can lead ultimately to dibromoquaterphenyls. DBIB itself may be implicated in such oxidations, giving benzoic acid and benzoyloxylated high molecular weight material. In fact the reaction residues always exhibited intense i.r. absorptions at 1 730 cm^{-1}, and the rate of decomposition of $\mathrm{PhI(O_2C{\cdot}C_6H_4{\cdot}OMe\text{-}\mathit{p})_2}$ is known to be enhanced in the presence of tetrahydroquaterphenyls.[14]

Nevertheless the yield of benzoic acid is much less than is found in benzoyl peroxide thermolyses in bromobenzene at 80 °C,[3] and is considerably less than the yield of anisic acid from the reaction of [bis-(*p*-methoxybenzoyloxy)iodo]benzene with benzoyl peroxide in chlorobenzene at 80 °C.[14] These are further indications that step *e* is a much more important process at the higher temperatures of the present reactions.

Various alternative pathways to benzoic acid can be visualised if hydrogen iodide is a product (*e.g.* see ref. 12), since reduction of benzoyl hypoiodite or of DBIB may then occur. However, our studies do not reveal firm evidence for the presence of such processes, as iodine (the expected co-product in the redox reaction) is present in only very low concentration during the DBIB decomposition; it may well be formed entirely by step *l*.

The Possibility of Induced Decomposition.—In a large number of radical processes it is known that chain mechanisms are important; that is, starting material is destroyed in a radical-transfer step. In the decomposition of benzoyl peroxide at 80 °C in benzene, chlorobenzene, and bromobenzene the amounts consumed in induced decomposition at 0.01M peroxide concentration are respectively *ca.* 17,[16] 19,[3] and 73%.[3] Hence radical attack on DBIB must be considered seriously, particularly in view of its possession of relatively weak, easily polarised I–O bonds and the likelihood that such reaction would produce relatively stable radicals (*i.e.* $\mathrm{Ph\dot{I}O_2CPh}$). Indeed, the rates of decomposition of (diaroyloxyiodo)arenes are known to be accelerated by peroxides.[14,17]

We found that the addition of triphenylmethyl radical dimer to a solution of DBIB in bromobenzene at 145.5 °C caused an immediate and large increase in the rate of decomposition of DBIB, and triphenylmethyl benzoate was detected among the products. The stoicheiometry of the reaction with enhanced rate *very roughly* corresponded to 1.5 mol DBIB per mol of radical dimer (see Experimental section). However, DBIB and radical dimer reacted together only sluggishly at room temperature; hence if induced decomposition is involved it requires appreciable activation or an appreciable concentration of radicals in the present system.

Unequivocal proof of an induced decomposition normally only follows from a demonstration that k_{obs} is *decreased* in the presence of a radical scavenger. Unfortunately, we find that the reaction system is not amenable to this type of experiment. The addition of galvinoxyl (*cf.* ref. 3) did not prevent biaryl formation, indicating that benzoyloxyl radicals were not being efficiently trapped, but rather that step *e* and subsequent reactions were taking place. Galvinoxyl was consumed in the reaction, probably in the oxidation of phenylbromocyclohexadienyl radicals (*cf.* step *j*) or possibly by direct reaction with DBIB. Nitro-compounds, polymerisable monomers, and other types of radical inhibitor were not thought likely to be more successful than galvinoxyl, since Leffler and Story[17] have reported that such molecules actually increase the rate of decomposition of (diacetoxyiodo)benzene.

The alternative kinetic test for induced decomposition, namely the rate dependence on initial concentration of starting material, is not a sensitive probe for the chain mechanism. If induced decomposition takes the form of reaction (vii), then the consistency of the Scheme plus

$$\mathrm{(PhC_6H_5Br)\cdot + PhI(O_2CPh)_2 \longrightarrow PhC_6H_4Br + PhCO_2H + Ph\dot{I}O_2CPh} \quad \text{(vii)}$$

reaction (vii) with the observed kinetics largely depends upon the relative importance of both step *k* and reaction (vii).[3] Table 1 does reveal that the residues (formed in step *k*) are obtained in low yield. However, the accountancy for benzoate-derived phenyl groups [the quantity (m) in Table 1] is dependent upon the reaction temperature. The material imbalance [*i.e.* 2 − (m)] in the 145.5 °C reactions is presumably due to residue pyrolysis during the removal, by distillation, of the volatile products. The distillation operation necessarily follows *after* the g.l.c. analysis of the volatile components because of the employment of g.l.c. internal standards; thus, formation of additional volatile material by residue pyrolysis escapes quantitative detection. The results obtained at 156 °C (Table 1, final column) support these conclusions. Although the residue yield is still low, the value of (m) is 94.4% of the theoretical quantity owing very largely to an appreciable increase in bromobiphenyl yield. Hence, the dibromotetrahydroquaterphenyls are labile, and the residue yields underestimate the importance of step *k* because of its reversibility. Accordingly, in view of the lack of dependence of k_{obs} on initial DBIB concentration, reaction (vii) can be of only minor importance, if it occurs at all in the present system. Likewise, the close similarity of the bromobiphenyl isomer ratios to those observed from the thermolysis of benzoyl peroxide in bromobenzene[3] also suggests that bromocyclohexadienyl radicals are not, in the main, dehydrogenated by reaction with a sterically crowded oxidant such as DBIB (*cf.* ref. 14), thereby also militating against reaction (vii) as a process of major importance.

---

[16] G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, 995.

[17] J. E. Leffler and L. J. Story, *J. Amer. Chem. Soc.*, 1967, **89**, 2333.

EXPERIMENTAL

Optical densities were determined by using a Unicam SP 500 spectrophotometer, and i.r. spectra with a Unicam SP 200 spectrometer. A Nester–Faust type NF-120 or a Perkin-Elmer type NFT-51 spinning band column was used for fractional distillations. M.p.s were determined with a Kofler hot-stage apparatus. G.l.c. analyses were performed with a Perkin-Elmer 800 dual-column chromatograph.

Bromobenzene.—The reagent grade solvent was purified and dried in the usual way,[3] and stored under an inert atmosphere in a column packed with freshly baked-out type 5 Å molecular sieves. The column rig was so designed that solvent could be transferred into the reaction vessel under an inert atmosphere, thus minimising contamination by adventitious water. Karl Fisher titrations [18] did not give a reliable guide to the residual water content of the solvent.

Starting Materials and Reference Compounds.—The [di(aroyloxy)iodo]benzenes and reference compounds cited were prepared according to standard procedures, or modifications thereof.[1,5,19-27] Reagent grade materials were purified by crystallisation or by fractional distillation.

Kinetics.—The purified bromobenzene was deoxygenated under dry nitrogen in a three-necked reaction vessel which was then placed in an oil thermostat regulated to 145.5 ± 0.05°. After thermal equilibration, a weighed quantity of [di(benzoyloxy)iodo]benzene was added and the mixture swirled to ensure rapid and complete dissolution. Samples were withdrawn as appropriate with a semiautomatic sampling device that maintained the barrier to atmospheric water and oxygen, and allowed sample collection in chilled nitrogen-filled receivers. The substrate concentration was determined by iodimetric analysis; reactions were generally followed to about two half-lives, and consistent results were only obtained by scrupulous attention to experimental technique, particularly with regard to the exclusion of water.

The first-order rate constants were determined by graphical or least-squares analysis, without significant alteration of the results; the correlation coefficients (r) for the points determining the linear slopes were generally better than 0.998.

Iodimetric Analysis.—The analysis depended upon the quantitative liberation of iodine on treatment of the samples with sodium iodide in spectroscopic grade ethanol. Complete liberation of iodine was allowed to occur under nitrogen in the dark and, after dilution with ethanol, the optical densities of the solutions were determined at 435 nm in duplicate. The appropriate calibration experiments showed that the system obeyed Beer's law, irrespective of whether or not iodine or I_3^- ion formed complexes with bromobenzene or ethanol. Accuracy was generally as good or better than could be achieved by the dead-stop potentiometric procedure [16] at the low concentrations of the [di(benzoyloxy)iodo]benzene employed.

Analysis of the Products.—Reactions were conducted as for the kinetic runs, and were allowed to proceed to completion at 145.5 or 156 °C (*ca.* 3 days). Free iodine was estimated from the optical density of the solutions at 435 and 495 nm. After addition of weighed specific quantities of the g.l.c. internal standards (diphenylmethane and nitrobenzene), benzoic acid was extracted into saturated aqueous sodium hydrogen carbonate, isolated from the aqueous phase in the usual way,[3] and weighed. Free iodine was removed by extraction with aqueous sodium thiosulphate and, after a further extraction with water, the bromobenzene phase was dried ($CaCl_2$) and most of the solvent removed by fractional distillation through an efficient spinning-band column; the residual mixture was diluted with bromobenzene to the standard volume (*i.e.* 20 ml) employed throughout the g.l.c. analyses. Product yields were determined from the ratios of their peak areas to that of the internal standard with the nearest retention volume, by reference to the previously obtained linear calibration graphs of relative peak area *versus* weight of compound in 20 ml of bromobenzene. Analyses were rejected in which the actual height of the internal standard peaks varied by more than ±5% about convenient pre-set values in order to minimise non-linearity in the detector response. For all analyses we employed one of a matched pair of 2 m × $\frac{1}{8}$ in o.d. stainless steel columns containing 15% Apiezon L on 80—100 mesh Chromosorb W with 2.1 °C min^{-1} linear programming from 90 to 180 °C and a nitrogen inlet pressure of 30 lb in^{-2}. The retention volumes of the compounds thus analysed [(a), (c)—(f), (h), and (i); Table 1] were respectively 383, 1 718, 1 538, 2 025, 2 122, 1 080, and 1 072 ml. Various other columns were also used to check the resolution of the above components, and to search for the presence of other compounds. Trace components (*e.g.* biphenyl) were not analysed quantitatively.

Effects of Additives on [Di(benzoyloxy)iodo]benzene Decomposition.—Reactions were conducted as outlined above. The addition of triphenylmethyl radical dimer (0.322 g in 8 ml of bromobenzene) to a solution of [di(benzoyloxy)iodo]benzene (0.525 g) in bromobenzene (76 ml) that had been decomposing at 145.5 °C for 28 min caused a rapid increase in decomposition rate. After 58 min the rate of decomposition had resumed its normal value, and roughly 1.5 mol of substrate per mol of radical dimer had reacted in this time. No detectable reaction between these two compounds was found at room temperature in 2.5 h as assessed by the constancy of the iodimetric analysis. The reaction of [di(benzoyloxy)iodo]benzene (0.944 g) with triphenylmethyl radical dimer (1.88 g) in bromobenzene (76 ml) at 145.5 °C for 6 days produced triphenylmethyl benzoate (g.l.c.).

Decomposition of [di(benzoyloxy)iodo]benzene (0.994 g) in bromobenzene (76 ml) at 145.5 °C was conducted in the presence of three different amounts of 4-iodobiphenyl (0.921, 0.554, or 0.227 g). In each case g.l.c. analysis revealed the presence of 4-bromo-*p*-terphenyl. A similar reaction of [di(benzoyloxy)iodo]benzene (0.994 g) in bromobenzene (76 ml) with *p*-bromoiodobenzene (0.622 g) produced 4,4′-dibromobiphenyl (g.l.c.).

Photolysis of [Di(benzoyloxy)iodo]benzene and of Benzoyl Peroxide in the Presence of an Excess of 2,3-*Dimethylbutane.*—

---

[18] J. Mitchell, jun., *Analyt. Chem.*, 1951, **23**, 1069.

[19] K. H. Pausacker, *J. Chem. Soc.*, 1953, 107.

[20] N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 1963, 4103.

[21] M. Gomberg and J. C. Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.

[22] J. A. Cade and A. Pilbeam, *J. Chem. Soc.*, 1964, 117; see also T. Nozaki and Y. Harada, *Bull. Chem. Soc. Japan*, 1962, **35**, 1783.

[23] R. E. Buckles and N. G. Wheeler, *Org. Synth.*, 1951, **31**, 29.

[24] G. S. Hammond, A. Ravve, and J. F. Modic, *Analyt. Chem.*, 1952, **24**, 1373; H. Lankamp, W. T. Nauta, and C. Maclean, *Tetrahedron Letters*, 1968, 249.

[25] W. von E. Doering, K. Okamoto, and H. Krauch, *J. Amer. Chem. Soc.*, 1960, **82**, 3579.

[26] W. H. Perkin, *J. Chem. Soc.*, 1896, **69**, 1457.

[27] S. Sarel and M. S. Newman, *J. Amer. Chem. Soc.*, 1956, **78**, 5416.

Benzoyl peroxide and [di(benzoyloxy)iodo]benzene (*ca.* 2×10^{-3} mol) were separately irradiated in Pyrex apparatus in the presence of an excess of 2,3-dimethylbutane at 40 °C with a Philips Ultraphil health lamp (KL 2866; 300 W). The reactions were complete (negative NaI test) in 6 h and overnight, respectively. The 2,3-dimethylbutan-1-ol and 2,3-dimethylbutan-2-ol benzoate esters were identified from retention volume data on several columns, and g.l.c. analysis (APL column; 130 °C) gave the following ratios: benzoyl peroxide reaction, primary to tertiary benzoate 1 : 2.2; [di(benzoyloxy)iodo]benzene photolysis, primary to tertiary benzoate $\leqslant$ 1 : 200.

Reaction of Benzoyl Hypoiodite with Bromobenzene.— Equimolar amounts (1.3×10^{-3} mol) of mercury(II) benzoate and iodine were added to bromobenzene (80 ml) at 145.5 °C, and the reaction was allowed to proceed for 12 h, as above, after which the mixture was colourless. Benzoic acid and mercury compounds were extracted into aqueous sodium hydroxide, the bromobenzene layer was further washed with water, dried ($CaCl_2$), and filtered, and the excess of solvent removed by fractional distillation. G.l.c. analysis, as above, revealed the following ratios: PhI to 2- + 4-BrC_6H_4I, 1 : 1.54; 2-BrC_6H_4I to 4-BrC_6H_4I, 1 : 3.36. No *meta*-isomer was detected on any of several g.l.c. columns. The addition, at the outset of the reaction, of benzoic anhydride, benzoic acid, phenyl benzoate, or the three bromobiphenyls was without effect.

When the reaction was conducted at 156 °C the iodine colour had disappeared after 15 min; only iodobenzene was then detected in the g.l.c. analysis.

One of us (C. J. C.) thanks the S.R.C. for a maintenance grant.

[6/1520 *Received, 3rd August,* 1976]