2 hr. The reaction without mercury required *ca.* 10 hr for completion.

Half of each reaction mixture was taken to dryness under vacuum at room temperature, basified with 20 ml of 5% NaOH, and extracted with benzene. The dried benzene extract was concentrated and used for glc analysis. The other half of each mixture was reduced with zinc and HCl as described above.

Competitive Reactions at 131°. (a) **Pyridine *N*-Oxide.**—Diazoaminobenzene (3.94 g, 0.02 mol) was added to a mixture of 19 g of pyridine *N*-oxide (0.2 mol) and 216 g of anisole (2 mol) under nitrogen at 131 ± 2°. After 24 hr the mixture was cooled and evaporated under vacuum to 100 ml. Hydrochloric acid (50 ml, 0.5 *N*) was added to each of duplicated 10-ml aliquots of this solution, and the mixtures were extracted with ether. The ether extracts, containing methoxybiphenyls, were dried and concentrated for glc analysis. The aqueous phases, containing the phenylpyridines and phenylpyridine *N*-oxides, were reduced with zinc and HCl as above.

Two other 10-ml aliquots of the reaction mixture were acidified, washed with ether to remove methoxybiphenyls, basified, and extracted with benzene to give phenylpyridines in <1% yield. The isomer ratios were found to be between those for phenylation of pyridine and those found for phenylation of pyridine *N*-oxide. The authors therefore found it reasonable to overlook this insignificant amount in calculations.

(b) **Anisole.**—Diazoaminobenzene (3.94 g, 0.02 mol) was dissolved in a cold solution of 108 g of anisole (1 mol) and 78 g of benzene (1 mol) in a Carius tube. The solution was frozen in liquid nitrogen and the tube sealed. The tube and contents were allowed to come to room temperature and then agitated in an oil bath at 131° overnight. The tube was then frozen again; the contents were removed, concentrated to 25 ml and used directly for glc analysis.

Identification and Estimation of Products.—All reaction mixtures were analyzed by gas–liquid partition chromatography (glc). Phenylpyridines and biphenyls were identified by retention times and mass spectroscopy and were collected for verification from melting points and infrared spectra. After completion of reactions containing acetonitrile, the latter was distilled under vacuum at room temperature. In the pyridine reaction dry ether was added to precipitate tetrabutylammonium perchlorate. The ether solution was concentrated under vacuum and used directly for glc analysis. Yields, isomer ratios, total rate ratios, and partial rate factors are mean values of duplicate or triplicate runs.

Glc Columns Used and Retention Times.—It was found that any of the following stationary phases could be used for separation of biphenyl, methoxybiphenyls, and phenylpyridines: ethylene glycol adipate (10%), butanediol succinate (15%), Apiezon L (25%), and QF-1 (20%) [all weight/weight % on Chromosorb WNAW, 60–80 mesh].

QF-1, 6 ft × $^3/_{16}$ in., temperature programming from 70 to 160°, was used to separate phenylpyridines. The retention times for biphenyl and 2-, 3-, and 4-phenylpyridines were 6.5, 16, 17, and 17.5 min, respectively. Apiezon L, 8 ft × $^3/_{16}$ in., temperature programming from 70 to 250° and held at 250°, separated 2-, 3-, and 4-methoxybiphenyls with retention times 28, 30.5, and 31.5 min, respectively.

Registry No.—Pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7.

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The Radical-Induced Decomposition of Aryliodine Dicarboxylates

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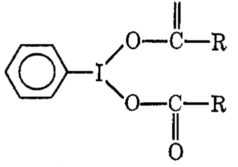
Benzoyl and substituted benzoyl peroxides induce the decomposition of phenyliodine dibenzoate or dianisate in C_6H_5Cl at 80°. The rate of decomposition of the peroxide is slightly diminished, and the yield of chlorobiphenyls from the peroxide is increased as compared to the values in the absence of the iodine compounds. The major products from the iodine compound are iodobenzene and the corresponding carboxylic acid. The product mixture from previously decomposed benzoyl peroxide also accelerates the decomposition of the iodine compound. It is suggested that phenylchlorocyclohexadienyl radicals induce the decomposition of the iodine compound. The catalytic effect of peroxide decomposition products is attributed to substituted tetrahydroquaterphenyls acting as chain-transfer agents.

The thermal decomposition of aryliodine dicarboxylates (**1**) is accelerated both by added radical initiators and by radical chain-transfer agents.[1,2]

The decomposition of phenyliodine dibenzoate[3] (**1a**, R = C_6H_5), accelerated by benzoyl peroxide, continues at an enhanced rate long after the peroxide concentration has been reduced to a negligible value, and indeed a chlorobenzene solution of benzoyl peroxide decomposition products also accelerates the decomposition.[1] Thus benzoyl peroxide not only produces radicals capable of attacking the dibenzoate, but also a chain-transfer agent that increases the effectiveness of the dibenzoate itself as initiator.



1a, R = C_6H_5
b, R = p-$CH_3OC_6H_4$

The chain-transfer agent is not benzoic acid, phenyl benzoate, biphenyl, iodobenzene, or any of the isomeric chlorobiphenyls, since these substances are produced in substantial amounts by the decomposition of the dibenzoate in the absence of added peroxide and the expected autocatalysis is not observed.

In the present paper we report the results of an investigation of the peroxide-accelerated decomposition of phenyliodine dibenzoate and dianisate in chlorobenzene at 80°. At this temperature the spontaneous decomposition of the phenyliodine dicarboxylate is extremely slow, and its decomposition products are almost exclusively those of the induced reaction.

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(1) J. E. Leffler, W. J. M. Mitchell, and B. C. Menon, *J. Org. Chem.*, **31**, 1153 (1966).

(2) J. E. Leffler and L. J. Story, *J. Amer. Chem. Soc.*, **89**, 2333 (1967).

(3) The *Chemical Abstracts* name is (dihydroxyiodo)benzene dibenzoate.

TABLE I

Initial concn, *M*		Yields, mol/mol[b]						
C_6H_5I-$(OOCR)_2$[a]	$(C_6H_5COO)_2$	C_6H_5I[h,d]	RCOOH[c]	Biphenyls			Esters	
0.005	0.005		1.74	0.44[e,f]	0.04[g,h]		0.016[h,i]	0.012[f,j,k]
	0.010		1.77	0.41[e,f]	0.042[g,h]		0.005[h,i]	0.016[f,j,k]
0.010	0.010	0.98	1.79	0.46[e,f]	0.45[f,l]	0.025[f,m,n]		
	0.020		1.51	0.40[e,f]	0.07[g,h]			0.016[f,j,k]
	0.030	0.97	1.78	0.34[e,f,o]				
0.010[p]	0.010	0.98	1.88[p,q]	0.56[e,f]	0.52[f,l]	0.025[f,m]		
None	0.010			0.23[e]	0.17[l]	0.021[m]		
None	0.010[r]			0.31[e]	0.22[l]	0.008[m]	0.01[j]	

[a] R = *p*-methoxyphenyl unless otherwise stated. [b] Per mole of the iodine compound or the peroxide, whichever is appropriate. [c] Anisic acid. [d] No iodoanisole was found. [e] *o*-Chlorobiphenyl. [f] Yield based on peroxide. [g] 2-Chloro-4′-methoxybiphenyl with traces of the 3- and 4-chloro isomers. [h] Yield based on the iodine compound. [i] Phenyl anisate. [j] Phenyl benzoate. [k] Accompanied by traces of *o*- and *m*-chlorophenyl benzoates. [l] *m*- plus *p*-chlorobiphenyl. [m] Biphenyl. [n] A yield of 0.029 of benzene, based on the peroxide, was also found. [o] A yield of 0.148 of benzene, based on the peroxide, was also found. [p] R = C_6H_5. [q] Includes an estimated 0.04 to 0.10 mol from the peroxide. [r] Data from ref 6.

Reaction Products.—The major products from the phenyliodine dianisate or dibenzoate are iodobenzene (0.98 mol) and 1.5–1.9 mol of the corresponding carboxylic acid. The products from the benzoyl or substituted benzoyl peroxide are qualitatively similar to those formed in the absence of the iodine compound. However, the yield of chlorobiphenyls is considerably greater and increases with increasing relative initial concentration of the phenyliodine dianisate (Table I).

Various other oxidants have been observed to increase the yield of biphenyl from the decomposition of benzoyl peroxide in benzene,[4] probably by abstracting a hydrogen atom from some of the phenylcyclohexadienyl radicals[5] before they have an opportunity to dimerize to tetrahydroquaterphenyl.

The ratio of *o*- to (*m*- plus *p*-) chlorobiphenyls appears to be lower than that recently reported for benzoyl peroxide in chlorobenzene by itself.[6] Only traces of methoxychlorobiphenyls are formed. *p*-Iodoanisole, which would correspond to a product of the spontaneous ion-pair reaction observed at higher temperatures in the absence of peroxide or peroxide decomposition products,[1,7] is not a product of the induced decomposition.

Kinetics. The Peroxide.—The rate law and first-order rate constant for the disappearance of benzoyl peroxide in the presence of phenyliodine dicarboxylate are very nearly the same as in the absence of the iodine compound. The first-order rate constant (k_{1p}, Table II) increases slightly with increasing initial peroxide concentration and decreases slightly during a run. For 0.01 *M* peroxide, k_{1p} in the absence of phenyliodine dicarboxylate is about 18% higher than in the presence of the iodine compound. This is to be expected if reaction with the phenyliodine dicarboxylate consumes radicals that would otherwise induce the decomposition of the peroxide. The data of Gill and Williams indicate about 19% induced decomposition at a peroxide concentration of 0.01 *M* in chlorobenzene, based on inhibition by galvinoxyl.[6]

The Iodine Compounds.—The rate of the spontaneous decomposition of 0.01 *M* phenyliodine dianisate in chlorobenzene at 80° is about 10^{-10} *M* sec^{-1}, and most of this is probably the ion-pair reaction[1,7] leading to phenyl anisate and iodoanisole rather than a dissociation into radicals. At 130° the first-order rate constant for the spontaneous decomposition is 8.5 × 10^{-7} sec^{-1}.[7]

TABLE II

PEROXIDE DECOMPOSITION RATE CONSTANTS IN C_6H_5Cl AT 79.8°

Initial concn, *M*		$10^5 \times k_{1p}$, sec^{-1}	Initial concn, *M*		$10^5 \times k_{1p}$, sec^{-1}
$\phi I(OOC{-}R)_2$[a]	$(ArCOO)_2$[b]		$\phi I(OOCR)_2$[a]	$(ArCOO)_2$[b]	
0	0.0050	3.50[c]	0.0100	0.0103[d]	2.01
0	0.0103	3.59[c]	0.0102	0.0102[e]	10.1
0.0100	0.00345	2.92	0.0	0.0104[e]	10.1
0.0148	0.00509	2.92			
0.0100	0.0102	2.99			
0.0100	0.0301	3.17			

[a] R = *p*-$CH_3OC_6H_4$ unless otherwise noted. [b] Ar = C_6H_5 unless otherwise noted. [c] Reference 6 (80.2°) gives k_{1p} = 2.98 × 10^{-5} sec^{-1}, initial concn 0.01 *M*, and 2.85 × 10^{-5} sec^{-1}, initial concn 0.0039 *M*. K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946), report values near 3.7 × 10^{-5} in aromatic solvents at 0.01 *M*. [d] Bis(*p*-bromobenzoyl) peroxide at 78.5°. [e] Anisoyl peroxide.

When a chlorobenzene solution of decomposition products from 0.01 *M* benzoyl peroxide is used as the solvent instead of pure chlorobenzene, the rate of decomposition of phenyliodine dianisate at 80° increases by about two orders of magnitude, to 4 × 10^{-8} *M* sec^{-1}.

The behavior of typical runs in which the solvent initially contains a low concentration of benzoyl peroxide rather than peroxide decomposition products is shown in Figure 1. The short induction period noticeable in the figure is somewhat longer in runs that have not been carefully degassed. After the induction period (1 or 2 hr), the disappearance of the phenyliodine dianisate becomes more rapid *and remains rapid for quite a few half-lives of the peroxide.* The half-life of benzoyl peroxide under these conditions is 6.0–6.5 hr depending on the initial concentrations.

Figure 2 summarizes the relationship between the maximum rate of dianisate decomposition attained in each run and the rate of decomposition of the added benzoyl peroxide. The peroxide decomposition rates were changed by varying the initial concentration of the peroxide. Since the peroxide decomposition rate decreases during the run (first-order rate law), the value at the end of the first peroxide half-life was chosen arbitrarily to represent the rate. As can be

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(4) G. R. Chalfont, D. H. Hey, Kathrine S. Y. Liang, and M. Perkins, *Chem. Commun.*, 367 (1967).

(5) D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).

(6) G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 7127 (1965).

(7) J. Y.-C. Chu, this laboratory.

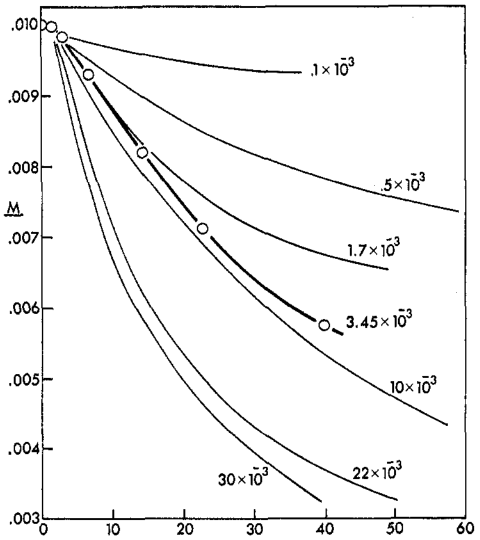


Figure 1.—Decomposition of 0.01 *M* phenyliodine dianisate in the presence of varying initial concentrations of benzoyl peroxide in C_6H_5Cl at 79.8°. For clarity, the experimental points are shown only for one run, and several runs at intermediate peroxide concentrations have been omitted.

seen from Figures 2 and 3 the induced decomposition of the dianisate is very sensitive to the first increments of added peroxide, but subsequent increments (above about 0.0005 *M*) have a much smaller effect. The induced decomposition rate at that point is about 2.5×10^{-8} *M* sec^{-1}, or comparable to that observed in runs *without* peroxide but *with* decomposition products corresponding to 0.01 *M* peroxide. At higher peroxide concentrations the rates of the two decomposition reactions appear to be linearly related.

Figure 3 also shows that the effects of bis(*p*-bromobenzoyl) peroxide ($k_{1p} = 2.01 \times 10^{-5}$, point 1) and dianisoyl ($k_{1p} = 10 \times 10^{-5}$, points 5 and 6) are similar to that of benzoyl peroxide ($k_{1p} = 2.9 \times 10^{-5}$) if they are compared at equal decomposition rates rather than at equal concentrations.

Phenyliodine dibenzoate (points labeled 2 in Figure 3) decomposes at very nearly the same rate as the dianisate.

The effect of changing the initial concentration of dianisate (**1b**) at constant initial benzoyl peroxide concentration (0.01 *M*) can be seen by comparing points 3 (0.005 *M* dianisate) and 4 (0.015 *M* dianisate) and the line (0.010 *M* dianisate). Although the reproducibility of the maximum dianisate decomposition rates is only fair, they can be described roughly as a linear function of the product of the benzoyl peroxide and dianisate initial concentrations. The intercept of this function is nonzero and appears to be the same as the intercept of the straight-line portion of Figure 3. Both intercepts are close to the rates observed in solutions of benzoyl peroxide decomposition products, with no peroxide remaining at the beginning of the run.

In summary, the rate of decomposition of the phenyliodine dicarboxylate seems to have a constant contribution characteristic of a certain minimum amount of peroxide or peroxide decomposition products, and a variable contribution proportional to the dicarboxylate concentration and the rate of homolysis of the peroxide.

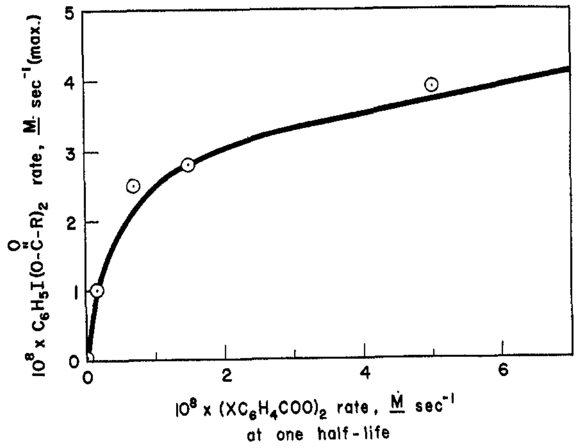
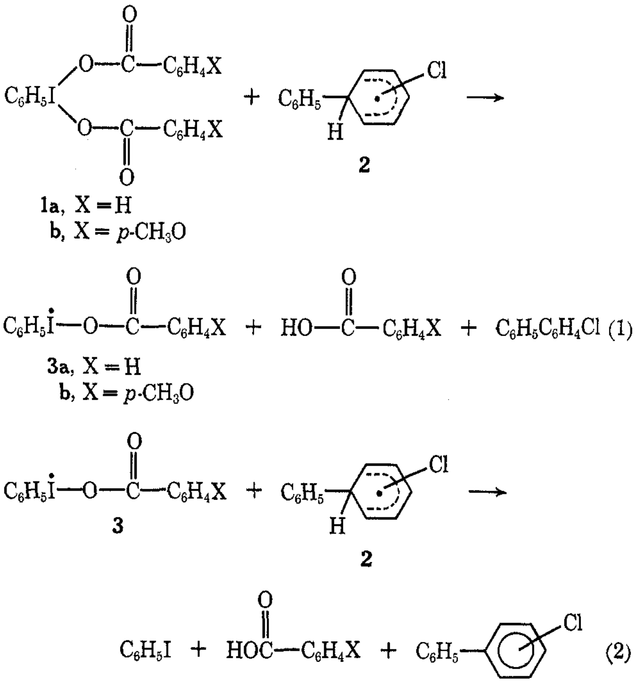


Figure 2.—The maximum rate of disappearance of phenyliodine dianisate, intially 0.01 *M*, in C_6H_5Cl at 78°, as a function of the rate of disappearance of benzoyl peroxide initiator. The latter rates were arbitrarily taken at the end of the first half-life and represent different initial peroxide concentrations.

Discussion

The formation of iodobenzene and anisic acid as the major products of the induced decomposition suggests eq 1 and 2 as probable components of the mechanism. These reactions are closely analogous to induced decomposition and chain-breaking steps that have been proposed for the decomposition of benzoyl peroxide in benzene.[5] The fact that the induced decomposition of the peroxide is suppressed and the yield of monochlorobiphenyls is raised by the presence of the iodine compound is also explained by reactions **1** and 2, since these reactions divert phenylchlorocyclohexadienyl radicals from attacking the peroxide and decrease the dimerization to the corresponding tetrahydroquaterphenyls. The lower proportion of *o*-chlorobiphenyls in this reaction than in the decomposition of benzoyl peroxide by itself is not unexpected in view of the fact that the trivalent iodine compound



1a, X = H
b, X = *p*-CH_3O

2

(1)

3a, X = H
b, X = *p*-CH_3O

3

2

(2)

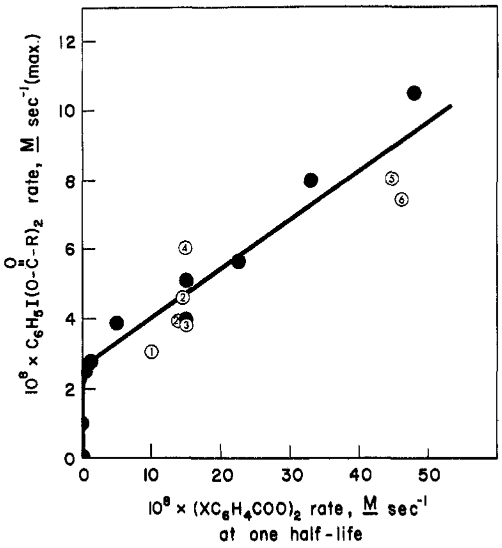


Figure 3.—The ordinate is the maximum rate of disappearance of the phenyliodine dianisate or dibenzoate. The abscissa is the rate of peroxide decomposition at the end of the first peroxide half-life. The solid circles represent 0.01 *M* dianisate with various concentrations of benzoyl peroxide. The open circles with numbers represent the following: (1) 0.01 *M* (p-$BrC_6H_4COO)_2$ and 0.01 *M* dianisate; (2) 0.01 *M* benzoyl peroxide and 0.01 *M* dibenzoate; (3) 0.01 *M* benzoyl peroxide and 0.005 *M* dianisate; (4) 0.015 *M* dianisate and 0.01 *M* benzoyl peroxide; (5) 0.01 *M* anisoyl peroxide and 0.01 *M* dibenzoate; (6) 0.01 *M* anisoyl peroxide and 0.01 *M* dianisate.

and the iodine radical (**3**) are more hindered than benzoyl peroxide and benzoyloxy radicals.

Since chlorine-substituted *p*-methoxybiphenyls are formed in only 4–7% yield, the dissociation of **3b** into iodobenzene and anisoyloxy radicals is not an important process, a conclusion that is also supported by the rate of decomposition of the benzoyl peroxide, which should be increased if extra aroyloxy radicals are formed.

However, even if eq 1 and 2 are accepted as contributors, the entire mechanism is far from being elucidated. The yield of anisic acid from **1b** requires more hydrogen atoms than can be balanced by the yield of biphenyls. One possible source is reaction with phenylchlorocyclohexadienyl dimers. These would be oxidized to a large number of involatile quaterphenyl isomers which would not appear in our isolated products.

A second problem is the nature of the chain-transfer agent that seems to be required by the kinetics. We suggest that this substance is formed by the decomposition of benzoyl peroxide by itself and to a lesser extent by the decomposition of benzoyl peroxide in the presence of phenyliodine dicarboxylates. An obvious candidate is the mixture of substituted tetrahydroquaterphenyls. A test of this hypothesis was attempted by means of model compounds. First it was ascertained that the chloro substituents are not essential by showing that the product mixture from the decomposition of benzoyl peroxide in *benzene* also accelerates the reaction. Then experiments were conducted with 1,3-cyclohexadiene and 1,4-dihydrobiphenyl. Cyclohexadiene appeared to accelerate the reaction, but the interpretation of this result is uncertain because of interference with the iodometric analysis for **1b**. The effect of 1,4-dihydrobiphenyl was to *inhibit* the reaction, *i.e.*, to protect the iodine compound from the peroxide. On the other hand, a considerably enhanced acceleration was observed when the product mixture from benzoyl peroxide, previously decomposed in the presence of 1,4-dihydrobiphenyl, was added. That product mixture should contain an enhanced proportion of tetrahydroquaterphenyls, and the observed acceleration supports the hypothesis that compounds of this type act as chain-transfer agents.

Attempts were made to fit[8] the concentration–time curves with detailed mechanisms of the type suggested above, but none of these mechanisms was satisfactory for all three reaction conditions, pure solvent, peroxide decomposition products present, and peroxide present.[9]

Experimental Section

Chlorobenzene (Eastman Organic Chemical or Matheson Coleman and Bell) was purified by stirring vigorously with sulfuric acid until the acid layer was no longer colored. It was distilled over phosphorus pentoxide through a 35-in. column packed with glass helices after washing with water and sodium bicarbonate solution and successive 24-hr periods of drying with calcium chloride and phosphorus pentoxide. The middle fraction (bp 131.5°) was collected, kept in a ground-stoppered round-bottom flask, and sealed with Parafilm.

Benzoyl peroxide (Fisher Scientific Co.) was purified twice by dissolving it in a minimum amount of chloroform and then precipitated by dropwise addition of two volumes of methanol at room temperature. The white crystalline precipitate was collected on a fritted-glass filter, air-dried, and ground to powder with a glass spatula before further drying over calcium chloride or Drierite under vacuum. It had a purity of about 99% by iodometric titration.

***p*-Bromobenzoyl peroxide** and ***p*-anisoyl peroxide** were prepared by the reactions of the corresponding benzoyl chlorides (prepared from acids and thionyl chloride) with lithium peroxide[10] (Alfa Inorganics, Inc.). Both compounds could be purified either by crystallization from hot dry toluene (80°) or by the chloroform–methanol procedure described above for the purification of benzoyl peroxide.

p-Bromobenzoyl peroxide[10] [mp (explodes) 144°] had a purity of 99.4% (iodometric titration).

p-Anisoyl peroxide [mp (explodes) 123–124°, lit.[10] 126–127°] had a purity of 99.6% (iodometric titration).

Phenyliodine diacetate was prepared by the reaction of iodobenzene with peractic acid.[11]

Phenyliodine dianisate was prepared by the exchange reaction of phenyliodine diacetate with anisic acid. Finely powdered phenyliodine diacetate (4.0 g, 0.0124 mol) was stirred in a solution of anisic acid (4.5 g, 0.0296 mol) in anhydrous ether (500 ml). (This is close to the solubility of anisic acid in ether.) The reaction mixture became homogeneous in about 15 min,[12] after which phenyliodine dianisate gradually separated from the clear solution during about 2 min. Stirring was continued for 5 hr. The yield of the crude product was 54% (3.8 g).

About 2.0 g of phenyliodine dianisate (mp 180–181°) was obtained after two recrystallizations from chloroform–*n*-pentane following the procedure described above for the purification of benzoyl peroxide. It had a purity of 98–99% (iodometric titration).

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[8] Using REMECH; *cf.* D. F. DeTar and C. E. DeTar, *J. Phys. Chem.* **70**, 3842 (1966).

[9] A spontaneous initiation rate adequate to fit the results under the latter two conditions predicts excessively rapid decomposition in the pure solvent. It may be that an intermediate such as the dimer of radical **3** accumulates and extends the duration of the rapid induced decomposition. It was not considered worthwhile to devote additional computer time to testing this hypothesis, however.

[10] "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y. 1955, p 649.

[11] H. Saltzman and J. G. Sharefkin, *Org. Syn.*, **43**, 60 (1963).

[12] Phenyliodine diacetate is only slightly soluble in ether. An ether-soluble intermediate was presumably formed at this stage.

Phenyliodine dibenzoate[13] was prepared by the reaction of phenyliodine oxide (prepared from phenyliodine diacetate and sodium hydroxide)[11] with benzoic acid in chloroform.[14] The crude product was crystallized twice from chloroform–*n*-pentane, mp 160–161°, purity 101.2% (iodometric titration).

Kinetic Procedure.—The ampoules were cleaned and dried as described previously.[2] For runs requiring 20-ml aliquots, the ampoules consisted of 25-ml round-bottom flasks with 18 × 250 ml necks terminating in 19/38 ground-glass joints. A tube containing P_2O_5 was connected to a vacuum manifold and to a side arm fitted with a joint for attachment of the kinetic ampule. Both necks of this apparatus were plugged with glass wool to prevent any accidental transfer of P_2O_5 while the solvent was distilled onto the P_2O_5 for drying, and then returned to the kinetic ampoule. It was found that the P_2O_5 could be used for three runs without reloading, if it was kept evacuated after the kinetic tube had been sealed off.

All ampoules were degassed to better than 5×10^{-6} mm and the solvent was carefully dried by means of the P_2O_5 tube unless otherwise stated. Normally, one of the eight tubes used in each run was used to determine the inital concentration. Other tubes were quenched in ice–water as soon as they were removed from the thermostat.

Effect of Peroxide Decomposition Products.—Ampoules containing degassed chlorobenzene (or in one case, benzene) solutions of 0.01 *M* benzoyl peroxide were heated for at least 15 half-lives of the peroxide, either at 80 or 127°. The ampoule containing the solution of peroxide decomposition products was put into a larger ampoule contining the phenyliodine dianisate, or a solution of the dianisate, and the outer ampoule was degassed and sealed. The inner ampule was then broken open by shaking and the resulting solution used to obtain one point of a kinetic run.

Method of Following the Decomposition. Procedure A.—(1) Add two pieces of Dry Ice to 10 ml of phenyliodine dianisate–benzoyl peroxide solution in a 125-ml erlenmeyer flask; (2) add 20 ml of carbonated glacial acetic acid; (3) add 30 ml of carbonated, deionized water and swirl for 1–2 min; and (4) add 2 ml of saturated potassium iodide solution in carbonated water, swirl for 3–5 min, and titrate the liberated iodine with thiosulfate. Benzoyl peroxide is not reduced by iodide ion under these conditions. Benzoyl peroxide can be determined from the difference between the total oxidant titer (procedure B) and the trivalent iodine compound titer (procedure A).

Procedure B consists of steps 1 and 2 of procedure A; then add 3 ml of saturated potassium iodide and swirl for 15–20 min; add 30 ml of water and titrate. Dry Ice was added from time to time throughout the titration.

The rate of the first-order decomposition of benzoyl peroxide determined by following the peak height of the ir absorption at 998 cm^{-1} agrees with the titrimetric rate only during the first 5 hr.

Usually, 20.5 or 10.5 ml of solution was placed in the tube before degassing so that two exactly equal aliquots (10.0 or 5.0 ml) could be removed by pipet. Precisely measured amounts of solution were placed in the tube when only one component was to be titrated, in which case the tube was rinsed with carbonated acetic acid.

The concentration of sodium thiosulfate solution used in the present work was 0.01 ± 0.00030 *N*. The carbonated water and glacial acetic acid showed a negative blank test.

Product Analysis.—The decrease of ir absorptions of both phenyliodine dianisate [1610.0 ($\nu_{>C=O}$), 1250.5 and 1170.0 cm^{-1} (ν_{-OCO-})] and benzoyl peroxide [1775.0 ($\nu_{>C=O}$) and 998.0 cm^{-1} (ν_{-OCO-})] was observed during the course of reaction. There was no uv absorption in the wavelength region near 500 mμ, indicating that no iodine was formed.

The last tube of a kinetic run after a long period of time was used for product analysis. The content was first treated with a small amount of ethereal diazomethane to convert acid products to methyl esters, and was then subjected to gas chromatography, using an F & M Model 700, a flame ionization detector, and either column A (10% SE-30 on Chromosorb W, $^1/_8$ in. × 6 ft) or column B [5% poly(*m*-phenyl ether) (5-ring) on silanized Chromosorb W, $^1/_8$ in. × 8 ft].

Iodobenaene and methyl benzoate were determined on column A at 100° (internal standard, *p*-iodoanisole) and on column B at 70° (internal standard, *m*-bromochlorobenzene). Biphenyl, methyl anisate, and *o*-chlorobiphenyl were determined on column A at 130° and on column B at 135° (internal standard, *p*-iodoanisole). The yields of *m*- and *p*-chlorobiphenyls were determined by measuring the ratio of the integration counts of the area of the unresolvable peaks to that of *o*-chlorobiphenyl.

After the solvent had been removed under high vacuum, the residue was dissolved in a small amount of acetone and used for determination of the high-boiling products, phenyl benzoate, 1-chloro-4′-methoxybiphenyl, and phenyl anisate on column A at 150° (internal standard, *p*-iodophenyl benzoate). Gas and low-boiling products were not determined quantitatively.

Registry No.—**1a**, 6597-18-8; **1b**, 28237-96-9; benzoyl peroxide, 94-36-0; anisoyl peroxide, 849-83-2.

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[13] The convenient procedure for the preparation of phenyliodine dianisate described above is not a satisfactory method of the preparation of phenyliodine dibenzoate.

[14] D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1475 (1956).