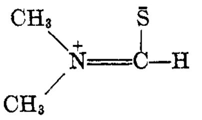


must contribute significantly to the hybrid structure in this compound also. We have obtained the nmr spectrum of *t*-butyl dimethyltrithioperoxycarbamate (XXVI) and found that it exhibited only two sharp singlets at 3.55 and 1.30 ppm. For this compound, resonance structure XXVIc must contribute an important amount to its over-all structure.

Experimental Section[12]

All compounds except XXVI were synthesized by adding N,N-dimethylcarbamoyl chloride to a benzene solution of pyridine and the appropriate alcohol, mercaptan, phenol, or thiophenol.[13] After the reaction mixtures were stirred at room temperature, usually overnight, they were processed by standard procedures.

Compound XXVI, *t*-butyl dimethyltrithioperoxycarbamate,[14] which was available from previous work, had mp 70–72.5°, lit.[15] mp 69–70°.

Anal. Calcd for $C_7H_{15}NS_3$: C, 40.15; H, 7.22; N, 6.69; S, 45.94. Found: C, 40.01; H, 7.08; N, 6.82; S, 45.75.

Acknowledgment.—Grateful acknowledgment is extended to Drs. M. Beroza, P. Sonnet, and N. Wakabayashi of this Division for helpful discussions. In addition, the author wishes to thank two other Division members: Mr. E. Gooden for obtaining the nmr spectra, and Mr. J. Ingangi for his helpful assistance.

---

[12] Mention of a proprietary product or company does not necessarily imply endorsement of the product or the company by the U. S. Department of Agriculture.

[13] The thiocresols were obtained as samples from Pitt-Consol Chemical Co.

[14] This compound was originally donated by Phillips Petroleum Co.

[15] C. M. Himel and L. O. Edmonds (to Phillips Petroleum Co.), U. S. Patent 2,792,394 (May 14, 1957); *Chem. Abstr.*, **52**, P1282*h* (1958).

Benzoyl Hypoiodite and the Radical-Chain Decomposition of Phenyliodine Dibenzoate[1]

J. E. Leffler, W. J. M. Mitchell, and B. C. Menon

The Department of Chemistry, Florida State University, Tallahassee, Florida

Received October 22, 1965

The decomposition of phenyliodine dibenzoate in chlorobenzene gives phenyl benzoate in which the phenyl moiety of the ester comes exclusively from the phenyliodine moiety of the dibenzoate. Benzoic anhydride suppresses a water-induced reaction and causes a fast reaction after a prolonged induction period. The nature of the products during the induction period, the effects of changes in concentration, and the effects of added styrene on the kinetics suggest an initial reaction: $^*C_6H_5I(OCOC_6H_5)_2 \rightarrow {}^*C_6H_5OCOC_6H_5 + C_6H_5COOI$, followed by reaction of the benzoyl hypoiodite with benzoic anhydride to form a chain-transfer agent. In the presence of benzaldehyde there is no induction period and the rate law at 126.8° is $-d[\text{dibenzoate}]/dt = 1.2 \times 10^{-5}[\text{dibenzoate}] + 66 \times 10^{-5}[\text{aldehyde}][\text{dibenzoate}]^{1/2}$. The rate constant 1.2×10^{-5} is the same as that for the disappearance of the dibenzoate during the induction period process in the absence of benzaldehyde. It is suggested that benzoyl radicals are chain carriers in both the reaction with aldehyde and the postinduction period reaction in the absence of aldehyde. The induction period is also eliminated by decomposition products of benzoyl peroxide.

The decomposition of phenyliodine dibenzoate in monosubstituted aromatic solvents gives iodobenzene, biaryls, phenyl benzoate, benzoic acid, and carbon dioxide as the major products.[2-4] The biaryls are unsymmetrical, one moiety originating from the benzoyloxy groups of the phenyliodine dibenzoate and the other from the solvent. *ortho* phenylation predominates, the percentages of the *ortho* isomer being 57.0 ± 0.5 for chlorobenzene[3] and 57.5 for nitrobenzene.[2,4] The corresponding figures for the decomposition of benzoyl peroxide in the same solvents are 62.2[5] and 56%.[4] Despite the similarity of these directive effects, we find on closer study that the decomposition of phenyliodine dibenzoate, although in part a radical reaction, is by no means a simple analog of the decomposition of benzoyl peroxide. The yield of phenyl benzoate is greater and the phenyl moiety comes exclusively from the iodosobenzene moiety of the phenyliodine dibenzoate and not at all from the decarboxylation of benzoyloxy groups.

The Effect of Water.—The presence of small amounts of water in nominally dry chlorobenzene[6] catalyzes a rapid decomposition of phenyliodine dibenzoate, as shown in Figure 1. Both the rate and the amount decomposed in the fast initial reaction vary from run to run, depending on how much the solvent has been exposed to atmospheric moisture. Runs that have slowed after expending their adventitious water can be made to resume their high rate by new injections of water.[7] The effect of water on the products can be judged by comparing the yields (Table I, reaction conditions IV and V) from experiments with high initial dibenzoate concentrations with those from experiments with low initial dibenzoate concentrations and hence higher water/dibenzoate ratios. The yields of biphenyls and ester are decreased.

---

[1] The authors wish to acknowledge the generous assistance of the National Science Foundation in this investigation.

[2] B. M. Lynch and K. H. Pausacker, *Australian J. Chem.*, **10**, 329 (1957).

[3] See Table I.

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

[5] (a) D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 44 (1953); (b) D. R. Augood, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *ibid.*, 3412 (1953); (c) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

[6] (a) Distilled from P_2O_5. (b) Water has a solubility of about 0.03 *M* in chlorobenzene at room temperature and is monomeric: E. Högfeldt and B. Bolander, *Arkiv Kemi*, **21**, 161 (1963).

[7] The water-catalyzed reaction was investigated only briefly. It appears to be approximately second order with respect to total oxidizing titer. At 100°, 0.01 *M* benzoic acid reduces the rate by an order of magnitude, but at 127° the initial reduction in rate is followed by a pronounced acceleration, probably related to the effect of benzoic anhydride to be described later.

TABLE I

PRODUCTS OF THE DECOMPOSITION OF PHENYLIODINE DIBENZOATE IN CHLOROBENZENE[a] AT 126.8°

	Reaction conditions		Yields, moles/mole of dibenzoate						
			Chlorobiphenyls						
No.	C_0[b]	A_0[c]	o	m and p	o/(m and p)	Phenyl[d] benzoate	Benzoic acid	Iodo-benzene	CO_2
I	0.042	0.0083	0.46	0.35	1.31	0.12[e]	0.90	0.99	
II	0.01	0.01	0.40	0.30	1.33	0.135	1.4 ± 0.1[f]		0.64
III	0.01	0.005					1.6 ± 0.2[f]		
IV	0.04	0	0.32	0.24	1.39	0.25, 0.25[g]	0.71, 0.75[g]	0.99[g]	
V	0.01	0	0.17	0.13	1.30	0.10			
VI	0.01 Benzoic acid = 0.01 M Water = 0.03 M	0	0.155	0.12	1.29	0.08			

[a] Distilled from P_2O_5, but exposed briefly to the atmosphere before the reaction vessel was sealed and degassed. [b] Initial molarity of phenyliodine dibenzoate. [c] Initial molarity of benzoic anhydride. [d] No chlorophenyl benzoates were found. [e] p-Fluorophenyliodine dibenzoate, C_0 = 0.035, A_0 = 0.01, gave p-fluorophenyl benzoate as the only ester. [f] Estimated by infrared. Includes any acid formed by reaction of the anhydride with traces of water. [g] p-Tolyiodine dibenzoate under similar conditions gave 0.01 p-tolyl benzoate, no phenyl benzoate, 0.9 p-iodotoluene, 0.09 iodobenzene, and 1.20 benzoic acid.

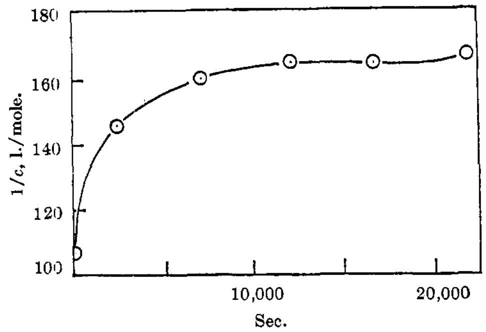


Figure 1.—Phenyliodine dibenzoate, 0.00977 M, at 126.8° in C_6H_5Cl freshly distilled from P_2O_5.

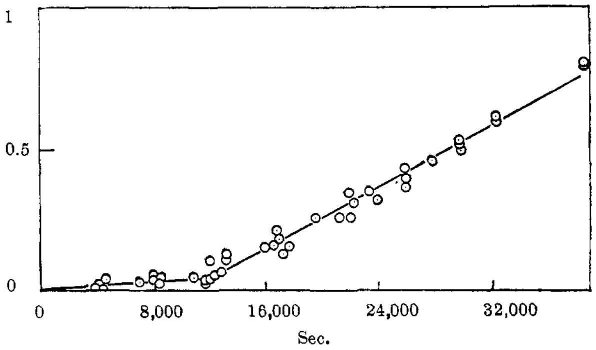


Figure 3.—Decomposition of 0.00488 M phenyliodine dibenzoate in 0.01 M benzoic anhydride in chlorobenzene at 126.8°.

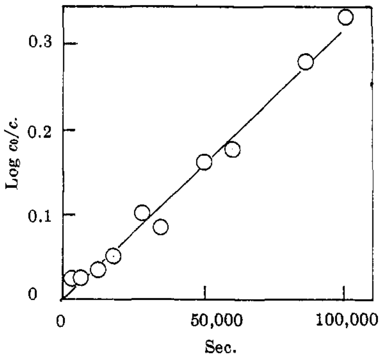


Figure 2.—Decomposition of phenyliodine dibenzoate, 0.01 M, in chlorobenzene at 126.8°. The ampoules were prepared by vacuum-line procedure.

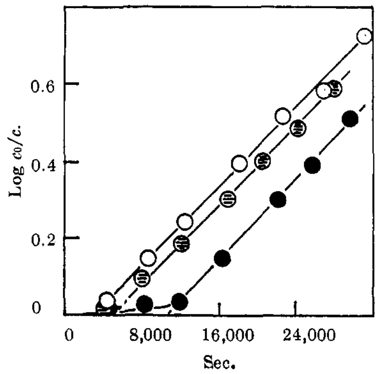


Figure 4.—Decreasing induction periods with increasing initial concentrations 0.00489, 0.00977, and 0.0195 M.

Kinetics and Products in the Absence of Water or Other Catalysts.—To avoid the complications caused by adventitious water the ampoules containing the dry phenyliodine dibenzoate were attached to a vacuum manifold and the chlorobenzene distilled in directly from a bulb containing a large excess of P_2O_5, with which the solvent had been in contact for at least 40 min. The ampoules were then degassed and sealed without any exposure to the atmosphere. Figure 2 shows a first-order plot of the combined titrimetric data from two such runs. The rate constant at 126.8° is 0.74×10^{-5} sec^{-1}; corrected for the formation of free iodine, it is 1.2×10^{-5} sec^{-1}. The other products and their yields can be judged from Table I, reaction condition IV. Table I also contains the results of experiments with p-tolyliodine and p-fluoroiodine dibenzoates, showing that the aryl moiety of the ester comes from the aryliodine moiety of the aryliodine dibenzoate.

Catalysis and Diversion of Intermediates by Benzoic Anhydride.—Interference from water can be most easily prevented by adding benzoic anhydride to the reaction mixture, in which case brief exposure of the solution before degassing the ampoules has no effect.[8] The initial titrimetric rate in the presence of benzoic anhydride is the same as that for runs without anhydride in which the solvent is transferred on the vacuum manifold. However, later in the runs there is an abrupt increase in the first-order rate constant as shown in Figures 3 and 4. The duration of the normal slow reaction, which we will call the "induction period," is inversely proportional to the initial dibenzoate concentration and independent of the benzoic anhydride

---

[8] The anhydride acts by benzoylating partly hydrolyzed material rather than by scavenging water. The direct reaction between the anhydride and water in chlorobenzene is extremely slow, even at much higher concentrations of water.

concentration, provided that the latter is at least 0.005 *M*. Below 0.005 *M* anhydride the results tend to be erratic.

The titrimetric rate constant[9] for the reaction following the induction period, $(6.07 \pm 0.3) \times 10^{-5}$ sec^{-1} at 126.8°, is independent of both the anhydride concentration (0.005–0.015 *M*) and the initial concentration of phenyliodine dibenzoate (0.00489–0.0195 *M*).

Substituent Effects on the Reaction in the Presence of Anhydride.—The decomposition of phenyliodine diacetate in chlorobenzene is not accelerated by the corresponding anhydride and its rate constant is about the same as that of the induction period of the dibenzoate decomposition.[10]

p-Tolyliodine dibenzoate, initial concentration 0.00489 *M*, with 0.01 *M* benzoic anhydride in chlorobenzene at 126.8°, gave an initial first-order rate constant of about 3×10^{-5} sec^{-1}, decreasing after about 35% reaction to 1×10^{-5} sec^{-1}. Our tentative explanation of this is that the *p*-tolyliodine dibenzoate–benzoic anhydride combination scavenges water more slowly than does the phenyliodine dibenzoate–benzoic anhydride combination. The rate constant in the latter part of the run was about the same as that for a typical dry phenyliodine dibenzoate run in the absence of anhydride. The last point at 44,000 sec and 58% decomposition showed somewhat more reaction than might be expected and may indicate the onset of a postinduction-period acceleration.

p-Fluorophenyliodine dibenzoate, initial concentration 0.01 *M*, with 0.01 *M* benzoic anhydride, in chlorobenzene at 126.8°, had an induction period during which the first-order rate constant was only 0.3×10^{-5} sec^{-1}. The induction period lasted for at least 43,000 sec but was too variable to permit a precise evaluation of the postinduction-period rate constant. The most probable value is about 5×10^{-5} sec^{-1}.

Reaction Products in the Presence of Benzoic Anhydride.—The products of the decomposition of phenyliodine dibenzoate in the presence of benzoic anhydride are summarized in Table I (reaction conditions I, II, and III).

About 10% of the phenyl moieties in the iodobenzene come from the benzoyloxy groups. The phenyl moiety in the ester comes exclusively from the phenyliodine moiety of the dibenzoate. At *high* initial dibenzoate concentrations addition of benzoic anhydride significantly decreases the yield of ester. Under these conditions the induction period is very short and the bulk of the reaction products must be products of the chain reaction. Hence it is probable that the ester is *not* a product of the benzoic anhydride induced chain reactions but only of the induction-period reaction. This conclusion is supported by the changes in the infrared absorption in the carbonyl region during and after the induction period, although there are serious interferences from peaks due to benzoic acid and benzoic anhydride. In the presence of added benzoic anhydride, the absorption peak of carbon dioxide appears suddenly at the end of the induction period.

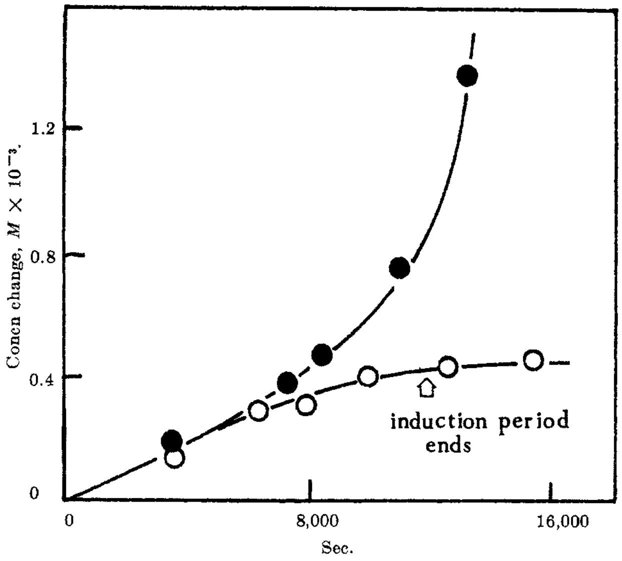


Figure 5.—Rate of disappearance of phenyliodine dibenzoate (filled circles) and rate of appearance of iodine atoms (open circles). Initial concentration of phenyliodine dibenzoate, 0.005 *M*; benzoic anhydride, 0.01 *M*, in chlorobenzene at 126.8°.

The rate of formation of iodine during the induction period, calculated as iodine atoms, is very nearly equal to the rate of disappearance of dibenzoate during the same period. At the end of the induction period the iodine concentration levels off and parts company with the decrease in dibenzoate concentration as shown in Figure 5.

The Effect of Miscellaneous Substances on the Reaction in the Presence of Anhydride.—In the experiments with wet solvents benzoic acid appeared to exert a delayed accelerating effect on the decomposition similar to that of benzoic anhydride in the dry reaction mixtures. However, when benzoic acid was added to a dry reaction medium, 0.01 *M* in benzoic anhydride, no additional effect of the benzoic acid over that of the anhydride was observed. It is significant that the effect of the anhydride itself levels off at concentrations above 0.005 *M*.

Iodosobenzene, iodobenzene, iodine, and benzil also had no effect on the kinetics in the presence of benzoic anhydride, and hence can be eliminated as intermediates, traps for intermediates, or chain-transfer agents. Oxygen, air, and benzoquinone each caused an initial fast reaction, but points later in the run were not reproducible.

Styrene in low concentrations lengthens the induction period and makes the transition to the postinduction-period rate less sharp. At higher concentrations the normal postinduction-period rate may never be attained. For example, in a run with 0.005 *M* phenyliodine dibenzoate, 0.01 *M* benzoic anhydride, and 0.01 *M* styrene the extent of decomposition had reached only about 20% in 34,000 sec. The most straightforward interpretation is that styrene competes successfully with benzoic anhydride for an intermediate.

Retardations similar to that caused by styrene were obtained by interrupting reactions in the presence of benzoic anhydride and adding fresh phenyliodine dibenzoate.[11] The restarted runs not only still required a second induction period, but actually required a *longer* induction period. The results were somewhat variable, depending on whether the addition of fresh

---

(9) No correction for free I_2 is needed in this part of the run, and the rate constant derived from the rate of fading of the infrared band at 1625 cm^{-1} agrees well with the titrimetric rate constant.

(10) L. J. Story, this laboratory.

(11) The interruptions were timed to be well after the induction period would normally have ended, but before the end of the reaction.

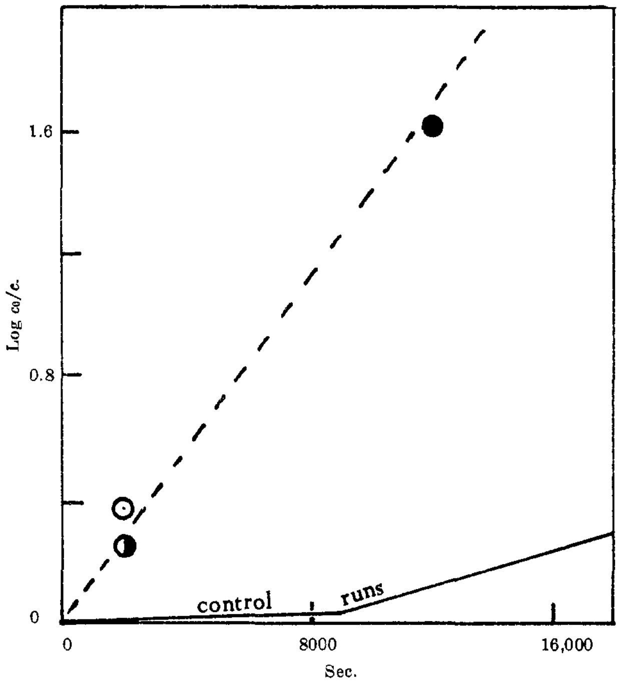


Figure 6.—Effect of peroxide decomposition products. (●) Triple ampoule experiment: phenyliodine dibenzoate, 0.0054 *M*; benzoic anhydride, 0.01 *M*; benzoyl peroxide, 0.01 *M*. (○) Double ampoule experiment: phenyliodine dibenzoate, 0.0055 *M*; benzoic anhydride, 0.01 *M*; benzoyl peroxide, 0.024 *M*. (◑) Double ampoule experiment: phenyliodine dibenzoate, 0.0067 *M*; benzoic anhydride, 0.01 *M*; benzoyl peroxide, 0.025 *M*.

phenyliodine dibenzoate to the ampoule was made using ordinary drybox techniques or by a more rigorous ampoule-within-an-ampoule technique. A run 0.005 *M* in dibenzoate and 0.01 *M* in anhydride was interrupted merely by cooling the sealed ampoule to room temperature for 1 hr after about 80% of the normal induction period was calculated to have elapsed. When this run was continued in the normal way only 66% decomposition was observed at an elapsed heating time that should have given 75% decomposition. A similar run in which the ampoule was carefully shielded from light during the cooling period gave 65% decomposition.

If the radicals from the decomposition of phenyliodine dibenzoate at 126.8° behave like those from the decomposition of benzoyl peroxide at 80°, then the peroxide decomposition products should have the same effect on the decomposition of phenyliodine dibenzoate as its own decomposition products. Instead, *there is a very large initial acceleration* when the phenyliodine dibenzoate–benzoic anhydride reaction is carried out in the presence of the decomposition products of benzoyl peroxide (Figure 6).

Solutions of a mixture of phenyliodine dibenzoate, benzoic anhydride, and benzoyl peroxide decomposition products were prepared without exposure of the decomposition products to air by means of multiple ampoule techniques. In the double ampoule technique, phenyliodine dibenzoate sufficient for a 0.005 *M* solution was preserved as solid in a sealed and evacuated inner ampoule while a degassed solution of 0.01 *M* benzoyl peroxide and 0.01 *M* benzoic anhydride was decomposed for 5000 sec at 126.8° in the outer ampoule. At this temperature, 5000 sec should be considerably more than 50 half-lives of benzoyl peroxide. The inner ampoule was then broken to bring about solution and the run was started. In the triple ampoule technique, the phenyliodine dibenzoate and the benzoic anhydride were kept isolated in separate inner ampoules during the decomposition of the peroxide dissolved in chlorobenzene in the outer ampoule. In both cases, whether the peroxide was isolated merely from the dibenzoate, or from the anhydride as well, the decomposition of the peroxide generated a very effective catalyst.

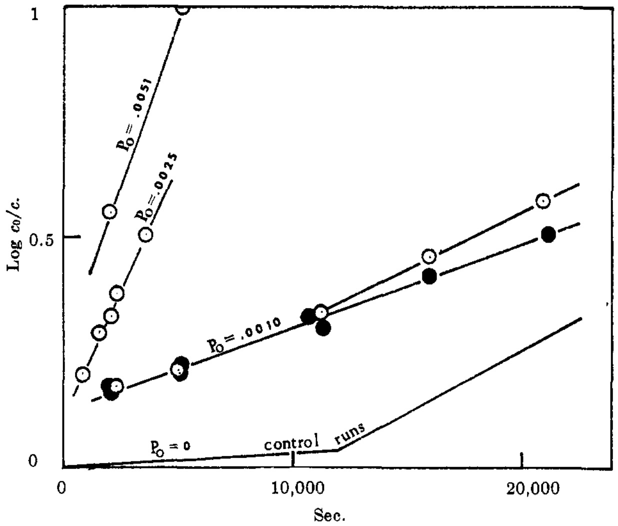


Figure 7.—Effect of peroxide. Initial phenyliodine dibenzoate concentration, C_0, is 0.0050 *M*; initial benzoyl peroxide concentration is given by P_0. Benzoic anhydride concentration is 0.01 *M* (open circles) or zero (filled circles).

The remarkable difference between the effect of the products from phenyliodine dibenzoate and the effect of those from benzoyl peroxide must be due to minor unidentified products, since iodobenzene has no effect and the other *major* products of the two reactions are identical.

When benzoyl peroxide is simply allowed to decompose in the presence of phenyliodine dibenzoate in chlorobenzene at 126.8° instead of temporarily isolating the dibenzoate in an inner ampoule, there is again a large acceleration of the initial part of the decomposition of the dibenzoate. The peroxide is essentially all gone by the time the first kinetic point is taken at 800–2000 sec (at least 8–20 half-lives), and the titrimetric run is therefore exclusively a phenyliodine dibenzoate decomposition from then on. Although extrapolation back to zero time is uncertain, it does not appear that the peroxide destroys much of the dibenzoate during the lifetime of the peroxide but rather that the runs (Figure 7) are very much accelerated during the next few thousand seconds. Later the first-order constant may decrease, but not much below the constant for the post-induction-period parts of runs without peroxide.

Figure 7 also shows that the presence of benzoic anhydride has no effect on the *early* part of a phenyliodine dibenzoate–benzoyl peroxide run.[12] When the induction period of a control run would normally be ending there is a slight acceleration in the run with both peroxide and anhydride but not in the run with the peroxide alone.

Although the amount of acceleration produced by the peroxide decreases steadily as the concentration of

---

[12] Mr. H. Gibson, Jr., of this laboratory has shown benzoic anhydride to be without effect on the decomposition of benzoyl peroxide in benzene at 80°.

peroxide added to the 0.005 M phenyliodine dibenzoate–0.01 M benzoic anhydride system is decreased from 0.005 to 0.001 M, a further decrease to less than 10^{-5} M does not bring about a reproducible further decrease in acceleration. In one run with less than 10^{-5} M peroxide the increase in first-order rate constant over that for the induction period of the control runs was still a factor of 16 although the amount of peroxide relative to dibenzoate was less than 0.5%.

The Effect of Benzaldehyde on the Reaction in the Presence of Anhydride.—Some of the more plausible mechanisms for the chain decomposition of phenyliodine dibenzoate in the presence of benzoic anhydride involve benzoyl radicals, which can be generated readily by attack of various radicals on benzaldehyde. Benzoyl radicals tend to attack various substrates at oxygen atoms. For example, benzoic anhydride is formed by attack on benzoyl peroxide, presumably with displacement of a benzoyloxy radical.[13]

Table II shows the marked acceleration caused by added benzaldehyde (freshly purified by crystallization of the sodium bisulfite adduct) on the decomposition of phenyliodine dibenzoate with 0.01 M benzoic anhydride in degassed chlorobenzene at 126.8°. The initial titrimetric first-order rate constants for disappearance of the dibenzoate are correlated with the concentrations of aldehyde and dibenzoate by eq 1, which also accounts for the moderate deviations from first-order kinetics within the runs. The first term in (1) is the

$$k = 1.2 \times 10^{-5} + 66 \times 10^{-5}[\text{aldehyde}]/[\text{dibenzoate}]^{1/2}\ \text{sec}^{-1} \tag{1}$$

first-order rate constant for the induction period reaction in the absence of aldehyde. The fit of the initial first-order rate constants to (1) is shown in Figure 8. A run using day-old benzaldehyde but otherwise like run 32 gave three times the expected acceleration, presumably because of autoxidation to peroxide. Several chain mechanisms predict rate laws compatible with (1), and the probable mechanism is considered in the Discussion section.

Table II

Run	Phenyliodine dibenzoate, M	Benzaldehyde, M	$10^5 \times$ initial rate constant, sec^{-1}
Controls	0.005	0	1.2
20	0.00500	0.0188	18.7
28	0.00506	0.0099	11.9
30	0.0100	0.0099	7.5
31	0.0150	0.0099	5.8
32	0.00506	0.00495	6.1
33	0.00250	0.00743	10.1

Discussion

The induction period before the accelerating effect of benzoic anhydride manifests itself can not be due to the exhaustion of an adventitious impurity, since different experimenters working with different materials get the same results. We have also shown that it is not changed by added glass and that the phenyliodine dibenzoate is not converted to an equivalent quantity of some other oxidizing species during the induction period.[14] The only remaining possibility is degenerate branching,[15,16] *i.e.*, some *intermediate* must react with benzoic anhydride to produce a moderately stable chain-transfer agent which slowly accumulates during the induction period until there is enough to sustain a chain reaction.

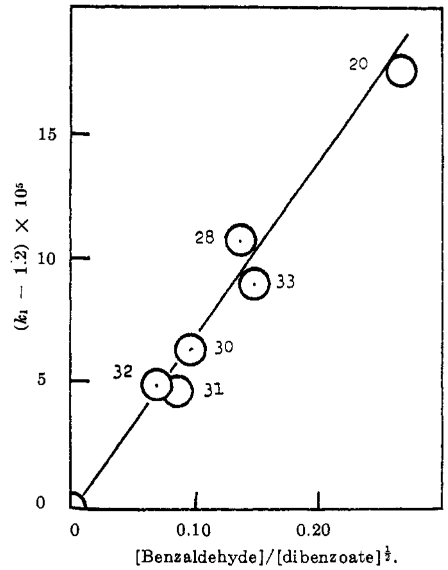


Figure 8.—Test of eq 1. The run numbers are from Table II.

Our adding various substances to the reaction mixture with benzoic anhydride was an attempt to find plausible structures for the hypothetical intermediate trapped by the benzoic anhydride, and for the chain-transfer agent and chain-carrying species. Although the chain-transfer agent has to be a great deal more stable than benzoyloxy or phenyl radicals, it does not need to be isolable. In the present case it does not survive short interruptions of the reaction well enough to eliminate the need for a new induction period on restarting the reaction, and it is probably never present in very high concentration.

The fact that further amounts of benzoic anhydride cease to have any additional effect on the length of the induction period after a certain concentration has been reached means that the chain-transfer agent is formed from some intermediate that is trapped *quantitatively* by the anhydride. The stoichiometry during the induction period corresponds, as far as we can tell, to the formation of one molecule of phenyl benzoate and almost one atom of iodine and *no* appreciable amount of CO_2. This stoichiometry and the result of our labeling experiment suggests eq 2 and 3, an intermediate such as X_1 providing the iodine in a later step. The fact that styrene prolongs the induction period also fits, since styrene could be expected to compete with the anhydride in the reaction with the benzoyl hypoiodite intermediate.[17]

---

[13] C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).

[14] There is no large change in the infrared, and extraction of the solution with water failed to generate the iodine or iodine plus periodate [S.-J. Yeh and R. M. Noyes, *J. Org. Chem.*, **27**, 2978 (1962)] to be expected if the dibenzoate were converted into benzoyl hypoiodite or iodine tribenzoate.

[15] Although any chain reaction can have an induction period, a delay of several thousand seconds is out of the question if the only intermediates involved in the chain carrying are species such as phenyl or benzoyloxy radicals with half-lives less than 1 μsec.

[16] A typical example is the oxidation of cyclopropane with molecular oxygen, in which the rate constant increases sharply to its maximum value only after a long delay during which time a critical concentration of formaldehyde is building up: A. C. McEwan and C. F. H. Tipper, *Proc. Roy. Soc.* (London), **A220**, 266 (1953).

[17] When iodine is present in the reaction medium for the decomposition of benzoyl peroxide, decarboxylation is prevented, and if an alkene is also present, the major reaction product corresponds to addition of benzoyl hypoiodite across the double bond: A. Perret and A. Perrot, *Helv. Chim. Acta*, **28**, 558 (1945); G. S. Hammond, *J. Am. Chem. Soc.*, **72**, 3737 (1950).

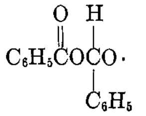
TABLE III[a]

$$C_6H_5I(OB)_2 \xrightarrow{1} C_6H_5I + 2BO\cdot$$
$$C_6H_5I(OB)_2 \xrightarrow{2} C_6H_5OB + BOI$$
$$BOI + BOB \xrightarrow{3} X_1$$
$$X_1 \xrightarrow{4} X + C_6H_5I + 2CO_2$$
$$X + X_1 \xrightarrow{5} 2BOB + C_6H_5S + HI$$
$$(HI + X_1 \xrightarrow{\text{fast}} I_2 + BOH + BOB)$$
$$BO\cdot \xrightarrow{6} C_6H_5\cdot + CO_2$$
$$C_6H_5\cdot + X_1 \xrightarrow{7} BOB + R_1$$
$$R_1 + X \xrightarrow{8} C_6H_5I + BOH + C_6H_5S + B\cdot$$
$$B\cdot + C_6H_5I(OB)_2 \xrightarrow{9} R_1 + BOB$$
$$BO\cdot + B\cdot \xrightarrow{10} BOB$$

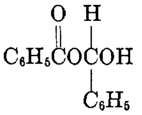
[a] B, benzoyl; S, C_6H_4Cl.

TABLE IV

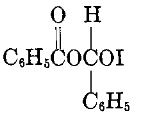
$$C_6H_5I(OB)_2 \xrightarrow{1} C_6H_5I + 2BO\cdot$$
$$C_6H_5I(OB)_2 \xrightarrow{2} C_6H_5OB + BOI$$
$$BO\cdot + BH \xrightarrow{3} BOBH\cdot$$
$$BOBH\cdot + BH \xrightarrow{4} BOBH_2 + B\cdot$$
$$(BOBH_2 \xrightarrow{\text{fast}} BOH + BH)$$
$$B\cdot + C_6H_5I(OB)_2 \xrightarrow{5} BOB + R_1$$
$$(R_1 \xrightarrow{\text{fast}} C_6H_5I + BO\cdot)$$
$$BOI + BH \xrightarrow{6} BOBHI$$
$$BOBHI \xrightarrow{7} 0.5I_2 + BOBH\cdot$$
$$2BOBH\cdot \xrightarrow{8} BOB + BOBH_2$$



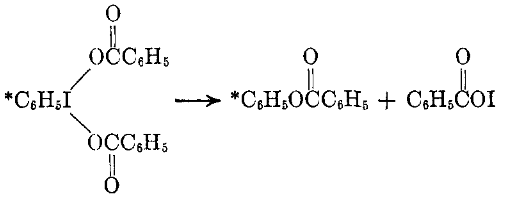
BOBH·



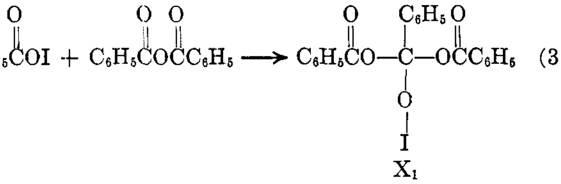
BOBH₂



BOBHI



(2)



$$C_6H_5\overset{O}{\overset{\|}{C}}OI + C_6H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}O-\underset{X_1}{\underset{|}{\underset{I}{\underset{|}{\underset{O}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}}}}}-O\overset{O}{\overset{\|}{C}}C_6H_5 \quad (3)$$

The mechanism beyond eq 3 is even more speculative, although the kinetics of the postinduction-period reaction considerably constrain the range of possibilities. Since the induced part of the reaction is *first order* with respect to phenyliodine dibenzoate and *zero order* with respect to benzoic anhydride, it is necessary to postulate at least three intermediates besides the chain-transfer agent X and the intermediates which lead to its formation. It is likely that there is also a fourth additional intermediate to satisfy the additional constraints on the possible mechanisms imposed by the nature and times of appearance of various products. There are no doubt several mechanisms of this degree of complexity capable of fitting our data. The scheme in Table III can be regarded as an illustration of the kind and number of steps that an adequate mechanism would be required to have. The available evidence does not suggest specific structures for the intermediates X and R_1 of Table III, although at least one structure consistent with the evidence can be written for each of them. In Table III, steady-state assumptions for BOI, X_1 (but not X), BO·, $C_6H_5\cdot$, R_1, and B· lead to the rate expression

$$-d[C_6H_5I(OB)_2]/dt = (k_1 + k_2)[C_6H_5I(OB)_2] + k_9(k_6/k_{10})[C_6H_5I(OB)_2]$$

The reaction of phenyliodine dibenzoate with benzaldehyde, in the presence of benzoic anhydride to suppress the water-induced reactions, obeys a kinetic equation of the form (4). A steady-state analysis of the reaction scheme outlined in Table IV predicts eq 4.

$$-d[C_6H_5I(OB)_2]/dt = (k_1 + k_2)[C_6H_5I(OB)_2] + k_4\left(\frac{2k_1 + k_2}{2k_8}\right)^{1/2}[BH][C_6H_5I(OB)_2]^{1/2} \quad (4)$$

The constants are rate constants for the correspondingly numbered steps in the table. Steps 1 and 2, which contribute the first term to eq 4, are the same as the first two steps of the mechanism in Table III and the value of $(k_1 + k_2)$ is the same as the rate constant for the induction-period reaction of phenyliodine dibenzoate in the presence of benzoic anhydride, or for the decomposition of the dibenzoate in strictly anhydrous chlorobenzene. Step 5 of Table IV was constrained to be identical with step 9 of Table III.

Several other mechanisms will also fit the kinetics of the reaction with aldehyde, but only if certain unlikely constraints are placed on the magnitude of the rate constants, for example, that $2k_1 > k_2$.

Experimental Section

Phenyliodine dibenzoate was prepared by the method of Hey, Stirling, and Williams[4] from iodosobenzene and benzoic acid; mp 160–161.5° after recrystallization from chloroform–petroleum ether (bp 30–60°).

Anal. Calcd for $C_{20}H_{15}IO_4$: C, 53.83; H, 3.38; I, 28.44. Found: C, 53.72; H, 3.37; I, 28.36.

***p*-Tolyliodine Dibenzoate.**—The diacetate was prepared by a modification of the method used by Pausacker[18] for phenyliodine diacetate. Acetic anhydride (305 ml) and 30% H_2O_2 (70 ml) were stirred together for 4 hr at 40°. *p*-Iodotoluene (53.4 g) was then added (exothermic reaction) and the mixture was allowed to stand overnight. Solvent was then stripped off *in vacuo* to a volume of 75 ml. (Caution: some iodobenzene diacetates have exploded under these conditions.) Ether (250 ml) was added and the white solid product was removed by filtra-

---

[18] K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

tion, washed with ether, and dried over NaOH. The yield was 53.6 g (crude, mp 103–108°) after recrystallization from chloroform–petroleum ether. To a solution of benzoic acid (75 g) in anhydrous ether (600 ml) was added 29.5 g of the *p*-tolyliodine diacetate, and the mixture was stirred for 4 hr. The fine white precipitate was then recrystallized from chloroform–petroleum ether giving 21.5 g, mp 148.5–150.5°. The melting point after a second recrystallization was 149–151°.

Anal. Calcd for $C_{21}H_{17}IO_4$: C, 54.80; H, 3.72; I, 27.58; equiv wt, 230.1. Found: C, 55.00; H, 3.86; I, 27.49; equiv wt, 230.5, 229.3.

Kinetics.—Ampoules were washed with chromic acid, rinsed five times with water, soaked in alkaline phosphate solution, rinsed six times with water and twice with methanol, then dried in an oven. After constricting for sealing they were returned to the oven for storage. Chlorobenzene was shaken with H_2SO_4, then four times with water, twice with aqueous bicarbonate, and again with water. After drying with $MgSO_4$ and $CaCl_2$ it was freshly distilled from P_2O_5 through a column before use. Phenyliodine dibenzoate (stored in a desiccator) and any other solutes required by the run were weighed out and washed into a 100-ml volumetric flask with chlorobenzene. Ampoules were removed from the oven, cooled, and flushed in a stream of N_2, then filled with a 10-ml aliquot by means of an automatic pipet. After an additional flushing with N_2 they were subjected to two or more degassing cycles (freezing, pumping, thawing, freezing) before sealing under vacuum. All of the ampoules of a single run were put in the thermostated bath, and the first, or t = 0, ampoule was removed after a 3–5-min warm-up period. The contents of the ampoule was added to 10 ml of acetic acid containing a pellet of CO_2, then 1 ml of saturated KI solution was added, and the flask was lightly stoppered for a few minutes. Finally 10–20 ml of carbonated water was added and the iodine was titrated with sodium thiosulfate.

In some experiments the solid solutes were weighed into each ampoule individually, connected to the vacuum manifold, and filled with solvent by distillation from a bulb containing a large excess of P_2O_5.

Product Analysis.—Free iodine was determined spectrophotometrically. Benzoic acid was determined spectrophotometrically and by isolation. Iodobenzene, chlorobiphenyls, and phenyl benzoate were separated and determined by vapor–liquid partition chromatography over silicone on firebrick, using infrared spectra and the retention times of authentic samples.

Conversion of Equatorial Mesyl Esters of Carbohydrates to Ethers with Retention of Configuration by Reaction with Alkoxides in Dimethyl Sulfoxide[1]

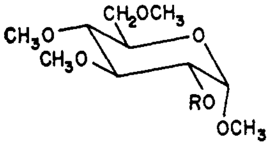
E. D. M. Eades,[2] D. H. Ball, and L. Long, Jr.

Pioneering Research Division, U. S. Army Natick Laboratories, Natick, Massachusetts

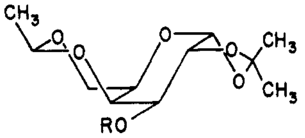
Received October 27, 1965

Mesyl esters of equatorial secondary hydroxyl groups in pyranose rings and of a secondary hydroxyl group in a furanose ring reacted readily with sodium methoxide or ethoxide in dry dimethyl sulfoxide. In each case, the products were the corresponding alkyl ether and hydroxy compound, both of which retained the original configuration. Experiments with ^{18}O-labeled sodium methoxide indicated that the alkoxide oxygen was not incorporated into the alkyl ether. The probable reaction mechanism involves an initial slow nucleophilic attack by the alkoxide ion on sulfur in the mesyl ester followed by a rapid competition between the liberated carbohydrate oxide anion and the excess alkoxide for the alkyl mesylate produced.

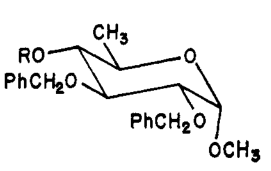
The remarkable effects of dipolar aprotic solvents on the rate or course of base-catalyzed reactions[3] and our interest in the chemistry of sulfonyl esters of carbohydrates led us to a study of the reactions of some mesyl esters with alkoxides in dimethyl sulfoxide (DMSO). In the present work, the esters were chosen such that the mesyl group was "isolated"; *i.e.*, the other hydroxyl functions were blocked by unreactive and nonparticipating groups.[4] In addition, the mesyl groups in the six-membered ring compounds were in equatorial conformations.



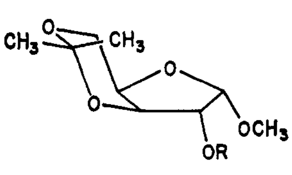
1, R = SO_2CH_3
2, R = CH_3
3, R = H



4, R = SO_2CH_3
5, R = CH_3
6, R = H
7, R = $CH_2 \cdot CH_3$



8, R = SO_2CH_3
9, R = H
10, R = CH_3



11, R = SO_2CH_3
12, R = H
13, R = CH_3

Treatment of methyl 2-*O*-mesyl-3,4,6-tri-*O*-methyl-α-D-glucoside (**1**) with a tenfold excess of sodium methoxide in anhydrous DMSO for 1 hr at 70° gave a mixture of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside (**2**) and methyl 3,4,6-tri-*O*-methyl-α-D-glucoside (**3**). The products were isolated and identified by comparison of physical properties with those of authentic samples and these structures were confirmed by hydrolysis of the methyl tetra-*O*-methylglycoside to crystalline 2,3,4,6-tetra-*O*-methyl-D-glucose and by remesylation of the methyl tri-*O*-methylglycoside to give **1**. Under similar conditions, 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-mesyl-D-galactose (**4**)[5] gave a mixture of 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-methyl-D-galactose (**5**) and 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose (**6**). The products were isolated and identified by comparison with authentic compounds and confirmation of the structure of the ether (a syrup) was afforded by mild acid hydrolysis to give crystalline 3-*O*-

---

(1) Preliminary communication, D. H. Ball, E. D. M. Eades, and L. Long, Jr., *J. Am. Chem. Soc.*, **86**, 3579 (1964).

(2) National Academy of Sciences–National Research Council Visiting Scientist, Resident Research Associate.

(3) (a) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); (b) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

(4) R. S. Tipson, *Advan. Carbohydrate Chem.*, **8**, 107 (1953).

(5) D. H. Ball, *J. Org. Chem.*, **31**, 220 (1966).