[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE FLORIDA STATE UNIVERSITY]

Iodo Substituents and the Decomposition of Diaroyl Peroxides[1]

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Bis-(*o*-iodobenzoyl) peroxide in chloroform solution at room temperature rearranges rapidly to a cyclic compound containing trivalent iodine. The rearrangement is several thousand times as fast as the decomposition of other *o*-substituted benzoyl peroxides in ordinary solvents. Bis-(*o*-nitrobenzoyl) peroxide in methyl iodide solution decomposes about 300 times as fast as it does in a solution of chloroform and iodine.

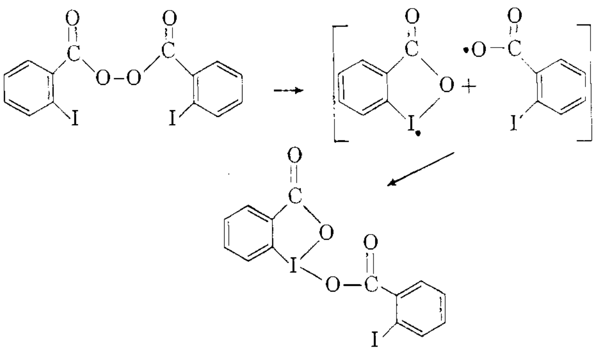
An iodo substituent in the vicinity of a weak bond has a good probability, *a priori*, of producing an effect quite different from that of other substituents of similar steric or electrostatic character. One likely result is the trapping, by a concerted process or otherwise, of the nascent intermediate, an analog of the neighboring group effect in carbonium ions. Another possibility is a special catalytic effect due to the high nuclear charge of iodine, usually referred to as the heavy atom effect.[2]

m- and *p*-iodobenzoyl peroxides are in no way remarkable,[3] but the remoteness of the iodine atom from the peroxide bond would not only prevent any bond formation but would also greatly attenuate any field effects. Benzoyl peroxide decomposes in ethyl iodide as solvent at a rate comparable to its decomposition in other solvents not containing iodine.[4] Free iodine inhibits the chain decomposition of benzoyl peroxide without apparently accelerating the initial cleavage into free radicals.[5] It is believed that the benzoyloxy radicals from the peroxide react with iodine to form benzoyl hypoiodite, but that there is no direct reaction between iodine and the peroxide.

In contrast to the inertness of benzoyl peroxide toward iodine and toward ethyl iodide, bis-(*o*-iodobenzoyl) peroxide decomposes by a mechanism intimately involving the *o*-iodo substituent, and *o*-nitrobenzoyl peroxide reacts directly with methyl iodide. These observations are not, of course, sufficient evidence that the peroxides in question decompose by a non-adiabatic mechanism, or even by an exclusively radical mechanism.

Bis-(*o*-iodobenzoyl) Peroxide.—This substance has not been isolated previously, although Vanino and Uhlfelder[6] found that *o*-iodobenzoyl chloride in acetone reacted with hydrogen peroxide and alkali to form what appeared to be a mixture of the iodo- and iodoso-benzoyl peroxides. Cooper[3] prepared a solution which probably contained the peroxide, and measured the rate at which kinetically free radicals were produced by observing the initiation of the polymerization of styrene.

The peroxide can be isolated as described in the Experimental section, but it is extraordinarily unstable. Heated rapidly, it explodes at 90°; heated slowly it melts at a much higher temperature, somewhat below the melting point of its principal decomposition product, compound A. The solid phase transformation into compound A will also take place at room temperature, being essentially complete in six weeks. Because compound A is an oxidizing agent for iodide the usual analytical method for following peroxide decompositions cannot be employed. The reaction rate, as measured by the shrinking of two infrared absorption bands characteristic of the peroxide and the growth of three bands characteristic of compound A, is given by the first-order rate constant 1.86×10^{-3} sec.$^{-1}$ (chloroform at 22°). Even though compound A is not isolated in 100% yield, it is the major product. The spectrum of an aged solution of the peroxide is identical with that of a fresh solution of pure compound A.



Compound A

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF BIS-(*o*-IODOBENZOYL) PEROXIDE IN CHLOROFORM AT $22^{\circ a}$

Position of band (wave numbers)	Rate constant, sec.$^{-1}$ $\times 10^3$
1290	1.84
1019	2.0
1690	1.89
1785	1.64
985	1.91

[a] The first three bands grow during the decomposition and the last two shrink. There is an isosbestic point between the growing band at 1690 and the shrinking band at 1785.

The magnitude of the effect of the *o*-iodo substituent on the rate at which the peroxide decomposes can be appreciated from the fact that other

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[1] This investigation was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] (a) An electron moving in the neighborhood of a heavy nucleus experiences a magnetic field. The field will enhance the probability of any process involving a change in electronic multiplicity: for example, Kasha found that ethyl iodide as solvent strengthens the otherwise weak and forbidden singlet–triplet absorption band of α-chloronaphthalene. The heavy atom effect is similar in principle to the catalytic effects of paramagnetic ions reported by Yuster and Weissman and by Gelles and Pitzer. (b) M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952); (c) P. Yuster and S. I. Weissman, *ibid.*, **17**, 1182 (1949); (d) E. Gelles and K. S. Pitzer, THIS JOURNAL, **77**, 1974 (1955).

[3] W. Cooper, *J. Chem. Soc.*, 3106 (1951).

[4] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[5] G. S. Hammond, *ibid.*, **72**, 3737 (1950).

[6] L. Vanino and E. Uhlfelder, *Ber.*, **33**, 1049 (1900).

o-substituted benzoyl peroxides,[7] in ordinary solvents, have half-lives measured in weeks rather than in minutes at 22°. The ratio between the observed rate constant and that which would be expected by analogy with other peroxides is of the order of five or ten thousand.

Fig. 1.—Infrared spectra in $CHCl_3$. As the reaction proceeds a band at 1800 cm.$^{-1}$ (due to the peroxide) is replaced by one at 1700 cm.$^{-1}$ (due to compound A).

Cooper[3] noted that the rate at which bis-(*o*-benzoyl) peroxide produced free radicals in styrene at 0° was about 10^3 times that of the *p*-iodo peroxide. The rate of radical production, as measured by Cooper, is apparently very much less than the rate of disappearance of the bis-(*o*-iodobenzoyl) peroxide, since we have found the yield of polystyrene to be very low. Another indication of a mechanism unproductive of kinetically free radicals is the failure of such radical traps as iodine, benzoquinone or triphenylmethane to prevent the formation of compound A. On the other hand, the fact that some polymer is produced and the fact that the peroxide bleaches diphenylpicrylhydrazyl make a caged radical mechanism for the production of compound A an economical alternative to a simple polar rearrangement.

Attempts to synthesize compound A from *o*-iodosobenzoic acid and *o*-iodobenzoyl chloride were unsuccessful, but its infrared spectrum (Fig. 2) is nearly identical with that of the analogously constituted acetyl derivative, compound B. The spectrum of the peroxide, in a Nujol mull, resembles that of benzoyl peroxide.

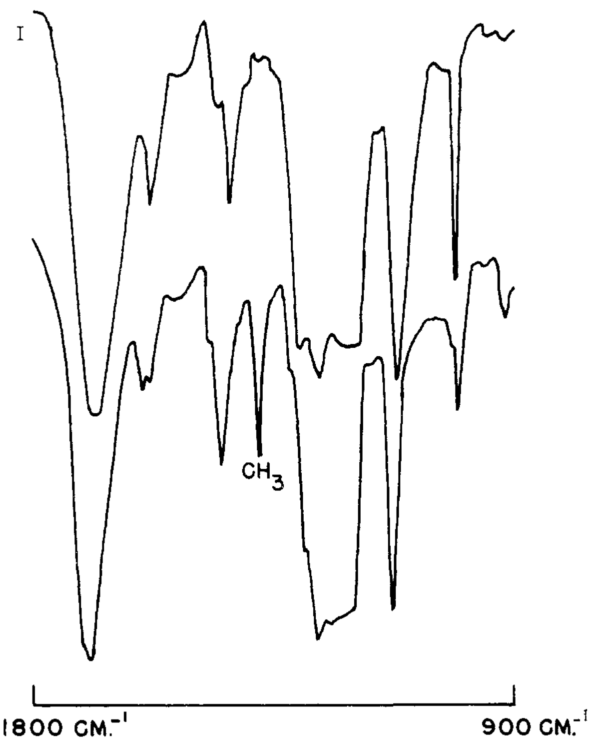
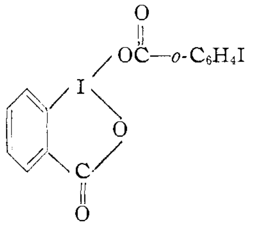
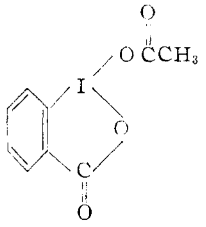


Fig. 2.—Infrared spectra in chloroform: upper curve Compound A, lower curve Compound B.

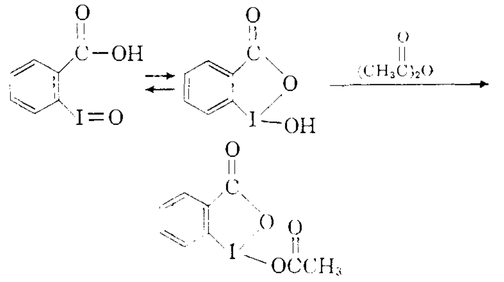


A



B

Bis-(*o*-nitrobenzoyl) Peroxide in Methyl Iodide.—The unusual effect of iodine as an *o*-substituent in benzoyl peroxide made it of interest to re-examine the effect of iodine as a substituent in the molecules of the solvent in which a peroxide is decomposed. Benzoyl peroxide is stable in methyl iodide, and bis-(*o*-chlorobenzoyl) peroxide decomposes in methyl iodide at 25° at a rate ($k_1 = 7 \times 10^{-7}$ sec.$^{-1}$) which is within a factor of five of that predicted by an Arrhenius extrapolation of the rate constants obtained by Blomquist and Buselli[7] in acetophenone.



On the other hand, bis-(*o*-nitrobenzoyl) peroxide decomposes much faster in methyl iodide than in

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(7) A. T. Blomquist and A. J. Buselli, THIS JOURNAL, **73**, 3883 (1951).

other solvents. The reaction appears to be first order, although the low solubility of the peroxide restricts the concentration range to values below 0.01 *N*. The reaction produces free iodine and it is necessary to determine this separately and subtract it from the total for peroxide plus iodine. The yield of iodine depends on whether or not the solution has been de-gassed, and how thoroughly.

Because the rate of decomposition of bis-(*o*-nitrobenzoyl) peroxide in methyl iodide will be compared with other rates, it is necessary to come to some conclusion regarding the importance of chains of radical-induced decomposition. We believe that there is some chain decomposition, but not enough to increase the rate by as much as a factor of two. For one thing, *o*-nitrobenzoic acid is unlikely as the product of a radical-induced decomposition step and the amount in which it is formed limits the contribution of such reactions to a very small part of the over-all rate. The potential inhibitors 1,3,5-trinitrobenzene, 3,4-dichlorostyrene and styrene decrease the rate in methyl iodide either not at all or by an amount not much larger than the probable error. Iodine in small amounts (formed from the methyl iodide) does not appear to affect the rate very much; when present in an initial concentration equal to that of the peroxide it may reduce the rate by about 25%. Table II gives the rate constants for the decomposition of bis-(*o*-nitrobenzoyl) peroxide under various conditions. It will be noted that the rate in methyl iodide at 25° is about 300 times that in chloroform inhibited with iodine, a difference very much greater than that usually found for an ordinary solvent change in such reactions. As compared with the rates obtained by Blomquist and Buselli[7] in acetophenone, the acceleration is due to a lowered activation enthalpy which is not quite counterbalanced by a much more negative entropy of activation.

TABLE II

DECOMPOSITION OF BIS-(*o*-NITROBENZOYL) PEROXIDE

At 24.95°		At 45.05°	
Conditions[a]	k, sec.$^{-1}$	Conditions[a]	k, sec.$^{-1}$
Air present	1.73×10^{-5}	....	1.52×10^{-4}
Air present	1.66×10^{-5}	....	1.54×10^{-4}
Air present, light excluded	1.66×10^{-5}	....	1.44×10^{-4}
....	1.69×10^{-5}	Mean[b]	1.50×10^{-4}
....	1.89×10^{-5}		
....	2.04×10^{-5}	3,4-Dichlorostyrene	1.55×10^{-4}
		added, 0.01 *M*	1.25×10^{-4}
Mean[b]	1.78×10^{-5}	I_2 added, 0.01 *N*	1.12×10^{-4}
In $CHCl_3 + I_2$	6×10^{-8}	TNB added, 0.2 *M*	1.37×10^{-4}
In CH_3I + TNB	1.57×10^{-5}	Styrene added, 0.5 *M*	1.50×10^{-4}

[a] Unless otherwise stated the solvent is CH_3I, the initial concentration is about 0.01 *N*, and the solution has been partially degassed. [b] The activation parameters calculated from these mean rate constants are $\Delta H^{\ddagger} = 19.4$ kcal./mole, $\Delta S^{\ddagger} = -15.3$ cal./° mole.

The negative entropy of activation is consistent with a mechanism in which a molecule of methyl iodide and the nitrophenyl group are constrained to occupy definite positions and definite orientations in the transition state of the rate-determining step.[8] We believe that the acceleration by methyl iodide is due to concerted bond formation rather than to a heavy atom effect, in view of the lack of catalysis by molecular iodine in chloroform. The relative inertness of *o*-chlorobenzoyl peroxide and benzoyl peroxide in methyl iodide probably is explained by their lower reduction potentials.

Experimental Part

Preparation of Bis-(*o*-iodobenzoyl) Peroxide.—To 5.2 g. of *o*-iodobenzoyl chloride in 5 cc. of toluene at 0° is added 0.9 g. of sodium peroxide in 12 cc. of ice-water, and the mixture stirred for one hour at 0°. The solid product (it does not remain dissolved in the toluene) is washed with water, methanol, sodium bicarbonate and again with water and with methanol. It is then washed repeatedly with chloroform at room temperature and the peroxide is precipitated by adding cold methanol to each chloroform washing. If the addition of the methanol is delayed, no peroxide is obtained. The precipitated peroxide is allowed to stand in an ice-bath only until the mother liquor is clear; it is then removed and dried. The chloroform–methanol recrystallization is repeated once, yielding 1.16 g. of colorless and odorless crystals, m.p. (detonates) *ca.* 90°. *Anal.* Found: C, 34.20; H, 1.70; I, 48.03, peroxide (O–O), 6.58. Calcd.: C, 34.03; H, 1.63; I, 51.2; peroxide (O–O), 6.48.

The infrared spectrum in a mineral oil mull or in a *fresh* chloroform solution resembles that of benzoyl peroxide. The isomeric *o*-iodoso-*o*′-iodobenzoic anhydride is absent from the peroxide since the product is colorless and odorless.

The peroxide is quantitatively reduced to *o*-iodobenzoic acid by sodium iodide in acetone. With hydrochloric acid in acetone, the peroxide gives products largely soluble in aqueous bicarbonate, apparently crude *o*-iodobenzoic acid. In thionyl chloride the decomposition product is an oil, soluble in methanol.

Compound A.—Bis-(*o*-iodobenzoyl) peroxide on standing as a crystalline solid at room temperature for about six weeks gives a substance markedly less soluble in chloroform than the peroxide. This substance is compound A and its infrared spectrum is identical with that of the corresponding acetate B except for the absence of the infrared band due to the methyl group. The spectrum of an aged solution of the peroxide in chloroform is identical to that of a solution of pure compound A. Compound A precipitates from chloroform solutions of the peroxide.

Compound A is purified by recrystallization from benzene–hexane, m.p. 184–185.5° dec. (after several crystallizations). *Anal.* Found: C, 34.02; H, 1.67. Calcd. for $C_{14}H_8I_2O_4$: C, 34.03; H, 1.63.

The Model Compound B.—The known compound B was made from *o*-iodosobenzoic acid and acetic anhydride as described in the literature.[9] Attempts at the synthesis of A from *o*-iodosobenzoic acid and *o*-iodobenzoyl chloride gave only *o*-iodobenzoic anhydride.

Kinetics of the Decomposition of Bis-(*o*-nitrobenzoyl) Peroxide[7] in Methyl Iodide.—The solution, except when otherwise indicated, is degassed by freezing, pumping and thawing cycles using Dry Ice–acetone or liquid nitrogen. The number of cycles is from one to six. The yield of free iodine in runs not degassed at all is in the neighborhood of 50% (based on peroxide decomposed) while with thorough degassing it is reduced to about 25%. The total oxidizing power of the solution is determined by adding excess potassium iodide and a 5-cc. aliquot to 20 cc. of acetic acid, previously saturated with CO_2 by means of a Dry Ice pellet. After 20 minutes another Dry Ice pellet and 50 cc. of carbonated water are added to the mixture and it is titrated with 0.005 *N* thiosulfate to an electrical end-point.[10] The free iodine is determined separately using aqueous potassium iodide without acetic acid; the iodine as determined by the titration agrees with values obtained photometrically.

Products of the Decomposition of Bis-(*o*-nitrobenzoyl) Peroxide in Methyl Iodide.—Besides iodine, which is removed with thiosulfate, the major product is *o*-nitrobenzoic acid, isolated in the usual way in yields of about 85%. The neutral fractions after removal of methyl iodide do not contain anything isolatable by crystallization or chromatography, but have a fruity odor. The methyl iodide from a non-degassed run apparently contains some formic acid, detected by vapor phase chromatography.

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(8) P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

(9) P. Askenasy and V. Meyer, *Ber.*, **26**, 1364 (1893).

(10) E. W. Abrahamson and H. Linschitz, *Anal. Chem.*, **24**, 1355 (1952).