distilling head. The product was analyzed by gas chromatography without further purification. Yields were generally between 30 and 60%. Table III summarizes the analyses and melting points of the biphenyl products.

Vapor phase chromatographic method. The gas chromatography was carried out with either a Perkin-Elmer Model 154C or a Pye Argon instrument. The Perkin-Elmer was equipped with a 2-m. stainless steel column packed with fire brick C-22 (mesh 40–60) impregnated with Dow Corning Silicone Fluid 550 (10%). The eluent was helium and the column temperature was in the range of 180–200°. The Pye Argon was equipped with a 4.5-foot column packed with Celite (mesh 80–100) impregnated with Dow Corning Silicone Fluid 550 (5%). The eluent was argon and the column temperature was in the range of 150–160°.

Oxidation of biphenyl derivatives. General method. One gram of biphenyl derivative was dissolved in 20 ml. of acetic acid (gl.). Three grams of chromic anhydride was added to a solution of 1 ml. of water in 20 ml. of acetic acid. The two preparations were combined and heated on a steam bath for 2 hr. The reaction mixture was then poured into excess ice water and the precipitate collected and recrystallized from benzene. The benzoic acid product was then identified by mixed melting point with authentic sample or by infrared analysis.

Acknowledgment. The author wishes to thank William D. Ross and James M. Schlater for their excellent work on the gas chromatographic analyses.

DAYTON, OHIO

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

o-Iodo-p'-nitrobenzoyl Peroxide[1]

WOLFGANG HONSBERG AND J. E. LEFFLER

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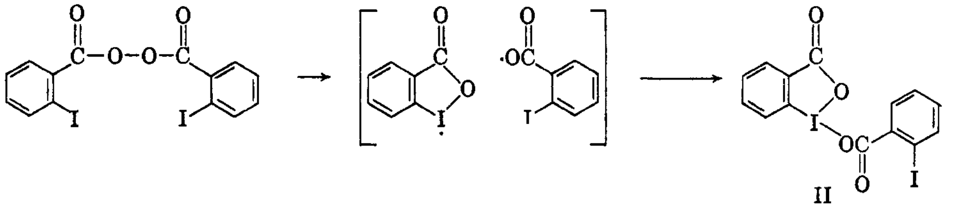
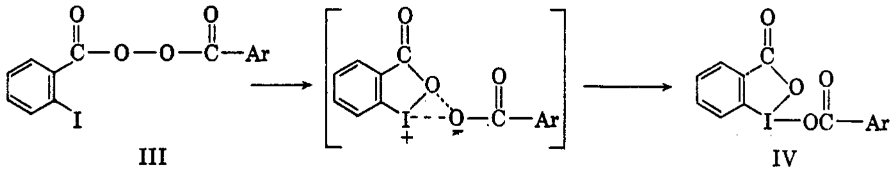
Bis(o-iodobenzoyl) peroxide and o-iodo-p'-nitrobenzoyl peroxide decompose by a concerted free radical mechanism leading to heterocyclic iodo radicals. The change from an o'-iodo to a p'-nitro substituent markedly decelerates the decomposition rather than accelerating it as would be expected for an ionic mechanism. The decomposition of o-iodo-p'-nitrobenzoyl peroxide is not subject to acid catalysis but is accelerated to an unusual extent by polar solvents. Vinyl chain polymerization is initiated by the peroxide even in polar solvents.

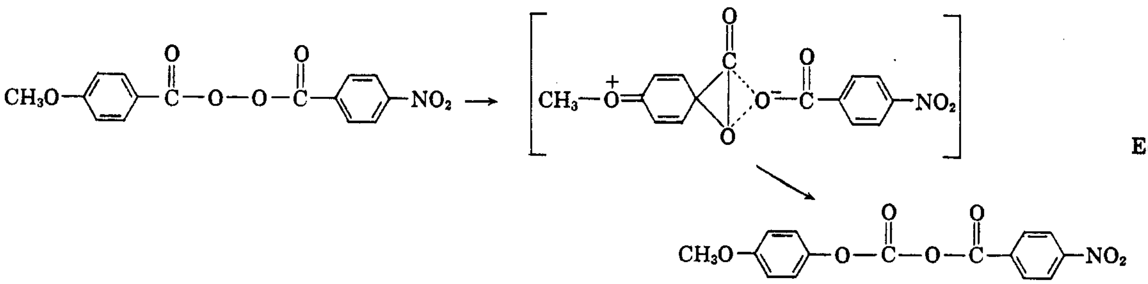
The decomposition of bis(o-iodobenzoyl) peroxide (I) is a fast reaction involving participation of the *ortho* iodo substituent in the cleavage of the peroxide bond.[2] The main product is a cyclic compound (II), presumably arising from the recombination of free radicals. However, the initiation of polymerization by the peroxide (I) is inefficient, probably because of primary recombination of the radicals, but leaving open the possibility of some concurrent, nonradical decomposition. The most likely nonradical reaction path would be decomposition into ion pairs (Equation 2) analogous



Eq. 1



Eq. 2



Eq. 3

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[1] This investigation was supported by a grant from the National Science Foundation.

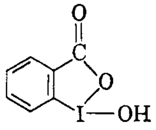
[2] J. E. Leffler, R. D. Faulkner, and C. C. Petropoulos *J. Am. Chem. Soc.*, 80, 5435 (1958).

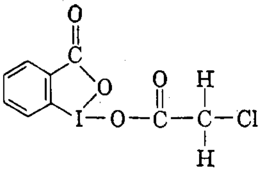
to the polar decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide (Equation 3).[3]

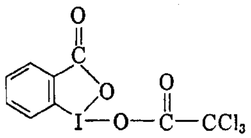
The reaction represented by Equation 2, like that of Equation 3, should be accelerated by a *p*-nitro group in the presumed anionic moiety of the peroxide and it should also be accelerated by polar solvents and subject to acid catalysis. Compound (III) (Ar = *p*-nitrophenyl) decomposes about ten times as fast in nitrobenzene as in benzene, thus fulfilling one of the expectations for the ionic mechanism, but not the others. The new peroxide is not sensitive to acids, the structural change *o*-I → $p-NO_2$ decelerates the decomposition by about a factor of ten instead of accelerating it,[4] and even in nitrobenzene solution the new peroxide initiates the polymerization of acrylonitrile.

The rate constants for the decomposition of *o*-iodobenzoyl-*p*′-nitrobenzoyl peroxide are given in Tables I and II. The rates were measured spectrophotometrically using the infrared band at 990 cm.$^{-1}$ Except when solvent absorption interfered, the band at 1770 cm.$^{-1}$ was found to give the same rate constants.

The main product is the cyclic compound IV (Ar = *p*-nitrophenyl), and at higher temperatures its noncyclic polymeric analog. Compound IV does not itself decompose into free radicals or initiate vinyl polymerization under the reaction conditions used in the decomposition of the peroxide. Compound IV is converted into the noncyclic polymeric form on heating. In acetone the only readily isolable product is the iodoso acid (V). In the presence of chloroacetic and trichloroacetic acids the compounds VI and VII are formed, but apparently not in the rate-determining step.


V


VI


VII

We conclude that neither bis(*o*-iodobenzoyl)-peroxide nor *o*-iodobenzoyl-*p*′-nitrobenzoyl peroxide decomposes by the ion-pair mechanism. The unusual response of the rate of the radical decomposition of the later peroxide to an increase in polarity of the solvent implies a highly polar transition state. The effect of the nitro substituent implies that the polarization is not in the same direction as in the case of peroxides decomposing by the ionic mechanism. A more precise description of the transition state may be possible when the effect of further substituents is known.

TABLE I

RATES OF DECOMPOSITION OF *o*-IODO-*p*′-NITROBENZOYL PEROXIDE AT 25°

Solvent	k (sec.$^{-1}$)
Benzene	5.7×10^{-5}
Carbon tetrachloride	3.4×10^{-5}
Chloroform[a]	28×10^{-5}
Acetone	30×10^{-5b}
Acetonitrile	21×10^{-5}
Nitrobenzene	62×10^{-5b}

[a] Contains ethanol as stabilizer. The rate constant for the decomposition of bis-*o*-iodobenzoyl peroxide in chloroform is about 200 × 10^{-5}. [b] Not thermostated, temperature approximately 25°.

TABLE II

DECOMPOSITION OF *o*-IODO-*p*′-NITROBENZOYL PEROXIDE IN BENZENE PLUS ADDED ACID AT 25°

Acid	k (sec.$^{-1}$)	Reaction Product
None	5.7×10^{-5}	IV
CH_3COOH, 0.175*N*	5.4×10^{-5}	V
$ClCH_2COOH$, 0.099*N*	10^{-4a}	VI
Cl_3CCOOH, 0.056*N*	10^{-4a}	VII

[a] Approximate due to interference from absorption by the acid.

EXPERIMENTAL

o-Iodo-p′-nitrobenzoyl peroxide. To a cold, freshly prepared solution of 15 g. of sodium *p*-nitroperbenzoate in 300 cc. of 5% sodium carbonate was added 7 g. *o*-iodobenzoyl chloride in three times its volume of ether. The mixture is stirred for 3 hr. at 0° and allowed to stand in a refrigerator for 12 hr. The slightly yellow precipitate which forms was washed with sodium bicarbonate solution, water, and methanol. It was purified by solution in chloroform at room temperature and immediate precipitation by ice cold methanol; yield 3 g.

Anal. Calcd. for $C_{14}H_8O_6NI$: C, 40.70; H, 1.95; N, 3.39; active oxygen, 3.87. Found: C, 40.78; H, 2.14; N, 3.50; active oxygen, 3.86.

Infrared bands: 1770s, 1525s, 1235s, 1220s, 1040m, 990s, 870m, 862m, 775m, 732s, 710s cm.$^{-1}$ (in Nujol mull). Melting point: heated slowly it sintered below 200°, melted with decomposition at 214°, exploded when heated suddenly to 120°.

Decomposition of the peroxide in benzene and in nitrobenzene. A solution of 0.600 g. of the peroxide in 30 cc. of benzene was allowed to stand at room temperature in the dark for 60 hr. Compound IV (Ar = *p*-nitrophenyl) precipitated; yield 0.450 g. exclusive of that remaining in solution. In nitrobenzene at room temperature the decomposi-

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[3] J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950); J. E. Leffler and C. C. Petropoulos, *J. Am. Chem. Soc.*, **79**, 3068 (1957).

[4] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951) report that *o,o*′-substituted benzoyl peroxides decompose faster than the related *p,p*′-substituted peroxides, but usually by less than a factor of ten. The steric deceleration caused by the removal of just one ortho substituent should be small.

tion of the peroxide gave *o*-iodosobenzoic acid, *p*-nitrobenzoic acid, and an estimated 60% yield of compound IV. Decomposition of the peroxide in benzene at 50° or heating compound IV gave a highly insoluble substance (VIII) believed to be the noncyclic polymer of IV.

Compounds IV *and* VIII. To 8 g. of *o*-iodobenzoic acid dichloride suspended in methylene chloride was added 15.2 g. of silver *p*-nitrobenzoate and the mixture was then extracted with hot methylene chloride. The filtrate was concentrated to dryness and extracted with ether to remove *p*-nitrobenzoic acid. The residue was essentially pure IV, but could be recrystallized from methylene chloride if necessary. Compound IV showed some signs of decomposition at 200° and melted with decomposition at 204–205°. The infrared spectra in Nujol of the synthetic material and the material from the decomposition of the peroxide were nearly identical and had the following bands: 1715s, 1630s, 1330s, 1270s, 1240s, 1120s, 842m, 742s, 723s cm.$^{-1}$. The spectrum of the closely related compound (II) from the decomposition of bis(*o*-iodobenzoyl) peroxide was very similar and had the following bands: 1695s, 1610s, 1320s, 1270s, 1230s, 1110s, 738s cm.$^{-1}$. Both spectra closely resembled that of the cyclic acetyl derivative of *o*-iodosobenzoic acid.

Anal. of Compound IV: Calcd.: Active oxygen, 3.87. Found: Active oxygen, 3.90.

Hydrolysis of compound IV in water at 60° for 3 hr. gave an equimolar mixture of *o*-iodosobenzoic acid and *p*-nitrobenzoic acid. Reduction of compound IV gave *o*-iodobenzoic acid and *p*-nitrobenzoic acids in equimolar amounts.

Heating compound IV in benzene at 50° for 2 hr. converted it in about 50% yield to the polymeric material compound VIII. Melting point (dependent on rate of heating) was varied from 214–216° to 219–221°. Compound VIII was remarkably stable against hydrolysis in water, but was quantitatively reduced by a mixture of sodium iodide and sodium sulfite in methanol, acidified with hydrochloric acid, to an equimolar mixture of *o*-iodobenzoic acid and *p*-nitrobenzoic acid. Compound VIII dissolved readily in warm acetic acid giving a precipitate of *o*-iodosobenzoic acid on addition of petroleum ether.

Anal. Calcd. for ($C_{14}H_8O_6NI$): C, 40.70; H, 1.95; N, 3.39; active oxygen 3.87. Found: C, 40.52; H, 1.68; N, 3.25; active oxygen 3.86.

The infrared spectrum of compound VIII in Nujol differed somewhat from that of compound IV and had the following bands: 1690s, 1660s, 1525s, 1270s, 1240s, 1120s, 1110s, 842m, 765s, 723s cm.$^{-1}$.

Decomposition of the peroxide in acetone. Heating 0.150 g. of the peroxide in 10 cc. of acetone for 2 hr. at 50° gave a precipitate of 0.060 g. of *o*-iodosobenzoic acid.

Decomposition of the peroxide in thionyl chloride. The peroxide was reduced by this reagent to a mixture of *o*-iodobenzoyl chloride and *p*-nitrobenzoyl chloride. In contrast to *p*-methoxy-*p*'-nitrobenzoyl peroxide[3] it did not appear to give the carboxy inversion reaction.

Decomposition of the peroxide in the presence of acids. In benzene containing acetic acid a precipitate of *o*-iodosobenzoic acid was formed. In benzene containing chloroacetic or trichloroacetic acid precipitates were also formed. These substances have been tentatively identified as the chloroacetyl and trichloroacetyl derivatives of *o*-iodosobenzoic acid. Their infrared spectra in Nujol resembled that of the acetyl derivative of *o*-iodosobenzoic acid.

Polymerization experiments. A solution of 0.050 g. of the peroxide in 5 cc. of acrylonitrile at room temperature quickly became opaque and began to deposit solid polymer within 2 min., followed shortly by a rapid exothermic reaction converting almost all of the acrylonitrile to solid polymer. Solutions of 0.09 g. of the peroxide in 4 cc. portions of mixed nitrobenzene and acrylonitrile (1:2, 1:1, and 2:1 proportions by volume) became warm and appeared to give complete polymerization within 15 min. Nitrobenzene retarded the initiation of polymerization by benzoyl peroxide. Compound IV did not initiate the polymerization of pure acrylonitrile at room temperature.

Decomposition in the solid state. The solid peroxide on standing at room temperature showed no significant change in its infrared spectrum in Nujol in 24 hr., but appeared to be about half decomposed in 2 weeks.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STEVENS INSTITUTE OF TECHNOLOGY]

Application of the Hammett Equation to Acetylenic Systems[1a,b,c]

MARVIN CHARTON

Received February 15, 1960

Ionization constants of 3-substituted propiolic acids, rates of alkaline hydrolysis of 3-substituted ethyl propiolates, and dipole moments of substituted acetylenes, 1-hexynes, 1-heptynes, and cyanides are correlated with the Hammett equation using the σ_p substituent constants. Transmission of substituent effects through the *trans*-vinylene, acetylene, and *p*-phenylene groups is in the order *p*-phenylene≪acetylene < *trans*-vinylene.

The Hammett equation, Equation 1, has been widely applied to the correlation of rate and equilibrium data, and of certain physical properties, for *meta*- and *para*-substituted benzene reaction series.[2,3] The Hammett equation has also been applied to heterocyclic systems including furan, thiophene and pyridine.[2,4,5] Recently it has been shown that the Hammett equation is directly applicable to olefins, using the σ_p constants.[6–9]

$$\log \frac{K_X}{K_H} = \rho\sigma_X \qquad (1)$$

[1a] Presented at the 136th Meeting, ACS, Atlantic City, September 1959.

[1b] Abstracted from part of the doctoral dissertation of M. Charton, Stevens Institute of Technology, Hoboken, N. J.

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(2) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, pp. 118–123.

(3) H. H. Jaffé, *Chem. Revs.* **53**, 191 (1953).

(4) E. Imoto and Y. Otsuji, *Bull. Univ. Osaka Prefect.*, Ser. **A, 6**, 115 (1958).

(5) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).