was recrystallized from petroleum ether to yield 0.80 g. of labeled **ethyldimethylacetamide**, m.p. 103–104° (reported[51] m.p. 103–104°).

Plates of varying thickness, spread over a uniform area, were made so that the specific activity could be evaluated for an infinitely thin plate. The amide gave 38.0 c./min./mg. (4380 c./min./mmole) above background of 70 c./min., extrapolated to zero thickness.

The labeled ethyldimethylacetamide, 0.7 g., was rearranged to the carbamate ester using the procedure described for the amide from Vc. In this case the carbamate ester did not crystallize. It was hydrolyzed and decarboxylated as described above to give 0.25 g. (33%) of ***t*-amylamine hydrochloride (VIb)**, m.p. 229–231°, and 0.76 g. (63%) of barium carbonate (yields based on the amide).

Anal. Calcd. for $C_5H_{14}NCl$: C, 48.57; H, 11.42; N, 11.33; Cl, 28.68. Found (unlabeled duplicate sample): C, 48.42; H, 11.57; N, 11.44; Cl, 28.58.[49]

The picrate melted at 180–182° (reported[52] 182–183°).

Anal. Calcd. for $C_{11}H_{16}N_4O_7$: C, 41.77; H, 5.10; N, 17.72. Found (unlabeled duplicate sample): C, 41.76; H, 5.11; N, 17.81.[49]

Both the *t*-amylamine hydrochloride and the barium carbonate were radioactive. Plates of varying thickness were made from portions spread over a uniform area so that the specific activity could be evaluated for an infinitely thin plate. The amine salt gave 23.5 c./min./mg. (2900 c./min./mmole) and the carbonate gave 6.45 c./min./mg. (1270 c./min./mmole) above background of 70 c./min., extrapolated to zero thickness. The results were corrected for the 2.4% *t*-butylamine hydrochloride (*vide infra*), which had all the activity of the ethyl *t*-butyl ketone, and the 2.4% barium carbonate, which had none of the activity of the ethyl *t*-butyl ketone, to give 2870 c./min./mmole for *t*-amylamine hydrochloride and 1300 c./min./mmole for barium carbonate from the methyl *t*-amyl ketone.

Liberation of the labeled *t*-amylamine from its hydrochloride and subjection to vapor-phase chromatography[48] detected the presence of 2.4% *t*-butylamine as a contaminant.

Reference Compounds.—Hexamethylacetone (IVc) was prepared as described earlier.[47] **Methyl *t*-amyl ketone (IIIb)** was prepared in 61% yield by the reaction of ethyldimethylacetyl chloride[53] with dimethylcadmium according to the procedure described above for making pinacolone-carbonyl-C^{14}. The material distilled at 128–130°, n_D^{25} 1.4087 (reported b.p. 131.5–132.5°,[53] n_D^{20} 1.4100[54]); 2,4-dinitrophenylhydrazone, m.p. 111–112° (reported[54] 112°). **Ethyl-*t*-butyl ketone (IVb)** was prepared by the method of Whitmore, Noll and Meunier.[41] The product contained some unsaturated material, as indicated by its infrared spectrum. Treatment with dilute permanganate in acetone solution followed by redistillation gave a sample which was homogeneous as determined by vapor-phase chromatography, b.p. 120°, n_D^{20} 1.4025 (reported[41] b.p. 124.5°, n_D^{20} 1.4049–1.4052); 2,4-dinitrophenylhydrazone, m.p. 144–145° (reported[41] m.p. 143.5–144.5°). Pure samples of ***t*-butylamine and *t*-amylamine** were generated from the hydrochlorides which had been prepared by Hofmann degradation of the corresponding amides. The picrates melted at 196–198° (reported[52] 197–198°) and 178–181° (reported[58] 182–183°), respectively.

Kinetic Measurements.—Solutions of the glycols (0.03–0.1 molar) in aqueous sulfuric acid were prepared and stored at 25.0 ± 0.1°. Five-ml. samples were quenched periodically with 5 g. of ice, and extracted with 1.00 ml. of carbon tetrachloride. The carbon tetrachloride solutions were analyzed for total ketone content by infrared analysis, using the carbonyl absorption peak. Known mixtures could be analyzed in this way with an error of less than 5%. The first-order rate constants were determined graphically.

Acknowledgment.—The advice and coöperation of Professor W. W. Meinke in the radiochemical work is gratefully acknowledged.

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[51] A. Haller and E. Bauer, *Ann. chim.*, [9] **1**, 5 (1914).

[52] R. Brown and W. E. Jones, *J. Chem. Soc.*, 781 (1946).

[53] A. Wischnegradsky, *Ann.*, **178**, 103 (1875).

[54] F. C. Whitmore and C. E. Lewis, THIS JOURNAL, **64**, 2964 (1942).

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Diacyl Peroxides. IV.[1,2] Phthaloyl Peroxide-*carbonyl*-O^{18}

BY FREDERICK D. GREENE

RECEIVED OCTOBER 2, 1958

Reaction of phthaloyl peroxide-*carbonyl*-O^{18} with *trans*-stilbene in carbon tetrachloride affords cyclic phthalate of *dl*-1,2-diphenylethanediol (I) in which 11% of the excess oxygen-18 is located at alkyl oxygen. The same distribution of oxygen-18 in cyclic phthalate is obtained from phthaloyl peroxide that has been subjected to 80° in carbon tetrachloride for four days prior to reaction with olefin. From these results it is concluded that equilibria between phthaloyl peroxide and any species in which a carbonyl oxygen atom becomes symmetrically located with respect to an oxygen of the oxygen–oxygen link are unimportant. The bearing of the oxygen-18 results on the stability of phthaloyl peroxide and the relationship of the results to the reaction of phthaloyl peroxide with olefins are discussed.

Previous papers in this series[3,4] have focused attention on some of the marked differences between the behavior of the cyclic peroxide, phthaloyl peroxide and acyclic analogs such as benzoyl peroxide. These differences lie in three areas: in thermal stability, in sensitivity of rate to nature of the solvent, and in reactivity toward carbon–carbon unsaturation. This paper reports the results of some experiments utilizing phthaloyl peroxide labeled with oxygen-18 which aid in delineation of the above differences.

Results

Phthaloyl peroxide containing excess oxygen-18 in the carbonyl oxygen atoms was prepared from labeled phthaloyl chloride. Subjection of phthaloyl chloride to water enriched in oxygen-18 (1.4 atom per cent. enrichment) for an extended reflux period afforded phthalic acid of approximately 1.2 atom per cent. oxygen-18 at each oxygen atom.[5] The phthalic acid-O^{18} was converted to phthaloyl chloride-O^{18}, which was con-

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[1] Part III, F. D. Greene and W. W. Rees, THIS JOURNAL, **80**, 3432 (1958).

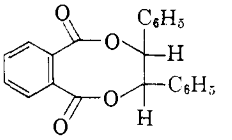
[2] (a) This work was supported in part by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the United States Government. (b) Presented before the Organic Division at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

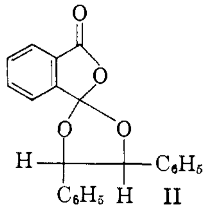
[3] Part II, F. D. Greene, *ibid.*, **78**, 2250 (1956).

[4] Part I, F. D. Greene, *ibid.*, **78**, 2246 (1956).

[5] See M. L. Bender, R. R. Stone and R. S. Dewey, *ibid.*, **78**, 319 (1956), and D. B. Denney, *ibid.*, **78**, 590 (1956), for evidence on the slowness of the equilibration of carboxyl oxygen with water oxygen-18.

verted to phthaloyl peroxide-*carbonyl*-O^{18} by hydrogen peroxide *via* the method developed previously.[4] The labeled phthaloyl peroxide was employed in two experiments. In the first (referred to as "direct reaction") equimolar amounts of the peroxide and *trans*-stilbene were heated at reflux in carbon tetrachloride for 16 hours. It has been shown previously that this reaction affords two products which are stable under the conditions of the experiment, a cyclic phthalate I in 25% yield and a lactonic *ortho*-ester II in 75% yield[3] both of which are converted in high yield to *dl*-stilbenediol (1,2-diphenylethanediol) and phthalic acid by alkaline hydrolysis. The cyclic phthalate I was isolated and a portion of this ester was hydrolyzed to the diol.


I


II

In the second experiment (referred to as "delayed reaction"), a sample of labeled phthaloyl peroxide was heated at 80° in carbon tetrachloride for 96 hours in a sealed tube. Titration of an aliquot of the solution after the 4-day period indicated only a 13% drop in peroxide titer. An equivalent of *trans*-stilbene was added to the filtered solution which was heated at reflux for an additional 16 hours. The cyclic phthalate was isolated as before and a portion was hydrolyzed to the diol. The results of the oxygen-18 analyses on ester and on diol are summarized in Table I. The same source of phthaloyl peroxide was used for both series of experiments. Consequently similar oxygen-18 excesses are expected for the two samples of cyclic phthalate. (The oxygen-18 content of cyclic phthalate might be expected to be slightly greater from the "delayed" reaction than from the direct reaction if the oxygen-18 exerts an isotope effect on the decomposition step of the peroxide.) The ratios of oxygen-18 excess in diol to oxygen-18 excess in cyclic phthalate for the "direct" and the "delayed" reactions are 0.111 and 0.107, respectively.

TABLE I

OXYGEN-18 DISTRIBUTION FROM REACTION OF PHTHALOYL PEROXIDE-*carbonyl*-O^{18} AND *trans*-STILBENE IN CARBON TETRACHLORIDE

Sample	Exptl. conditions	Atom % excess O^{18}[a]
Cyclic phthalate (I)	"Direct"[b]	1.96[c]
dl-Stilbenediol		0.218
Cyclic phthalate (I)	"Delayed"[b]	2.20
dl-Stilbenediol		0.236

[a] Excess over the normal abundance of 0.204 atom % oxygen-18. [b] Defined in previous paragraph. [c] 0.98 atom % excess oxygen-18 per carboxylate group.

Calculation Concerning the Structure of Phthaloyl Peroxide.—In view of the established preference of hydrogen peroxide for the conformation in which the dihedral angle is approximately 95°[6,7] (presumably the conformation with minimal repulsive interaction between the orbitals of the lone pair electrons on the adjacent oxygen atoms), some calculations have been made on two possible conformations of phthaloyl peroxide. A model of phthaloyl peroxide constructed on the basis of the following assumptions (aryl carbon-to-aryl carbon distance, 1.39 Å.[8a]; aryl carbon-to-carbonyl carbon distance, 1.47 Å.[8b,9]; carbonyl carbon-to-oxygen of the oxygen–oxygen bridge, 1.37Å.[8c]; all internal angles, 120°) leads to a calculated length for the oxygen–oxygen link of 1.49 Å. The observed oxygen–oxygen bond length in hydrogen peroxide is 1.46–1.49 Å.[6,7] This completely planar structure for phthaloyl peroxide may possess two elements of strain: the carbon-to-carbon-to-alkyl oxygen angle of an ester is preferably less than 120°[8c]; the planar structure of phthaloyl peroxide embodies complete eclipsing of the lone pair orbitals on the adjacent oxygen atoms. Although accurate data on the height of the barrier to rotation of the oxygen–oxygen bond in hydrogen peroxide are not available, the energy barrier may be several kcal.[10] A calculation was made to determine the maximum dihedral angle that could be accommodated by phthaloyl peroxide assuming an aryl carbon-to-aryl carbon-to-carbonyl carbon angle of 120° and an aryl carbon-to-carbonyl carbon-to-peroxygen angle of 112° and utilizing the bond distances indicated above. The model used in the calculation is depicted in Fig. 1 from which equations 1, 2 and 3 may be derived.

$$\mathrm{CE} = 1.43 - \mathrm{AD} \tag{1}$$

$$\mathrm{AD} = 1.37 \cos\psi \cos(120° - \phi)$$

$$\cos\phi = \cos 68°/\cos\psi$$

$$\mathrm{CE} = 0.73 \sin\sigma \tag{2}$$

$$\cos\sigma = 1.37 \sin\psi/0.73$$

$$\tan\gamma = \tan\psi \operatorname{cosec}(120° - \phi) \tag{3}$$

Solution of equations (1) and (2) for ψ leads to a value of 15° 24′ for this angle. Solution of equation (3) for γ leads to a value of 19° 3′ for this angle, and consequently a dihedral angle (2γ) of 38° 6′. The calculated carbonyl carbon-to-peroxygen-to peroxygen angle ($\angle$AOE) is 111° 51′. The extent to which the dihedral angle may differ from the value of 38° 6′ will be dependent on the balance between internal angle strains and any possible strain resulting from repulsion between the lone pair electron orbitals on the adjacent oxygen atoms.

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[6] W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corporation, New York, New York, 1955, Ch. VI.

[7] X-Ray diffraction data indicate a dihedral angle of the same magnitude for a series of crystalline diacyl peroxides and a probable oxygen-oxygen distance of 1.44 Å.; L. S. Silbert, L. P. Witnauer, D. Swern and C. Ricciuti, Abstracts of the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958, p. 32-S.

[8] (a) Average value in large number of aryl compounds; (b) salicylic acid, nicotinic acid, isatin; (c) methyl formate, methyl acetate; G. W. Wheland, "Resonance in Crganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, Appendix on Interatomic Distances and Bond Angles in Organic Molecules.

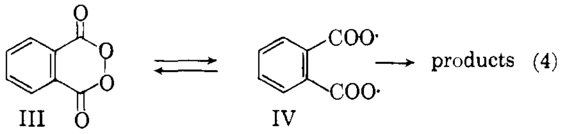
[9] The best value for the distance between two singly-bound carbon atoms, when both are in sp^2 hybridized state appears to be 1.47 Å.; M. J. S. Dewar, Conference on Hyperconjugation, Indiana University, Bloomington, Ind., June 2–4, 1958.

[10] See ref. 6, pp. 323–325.

Discussion

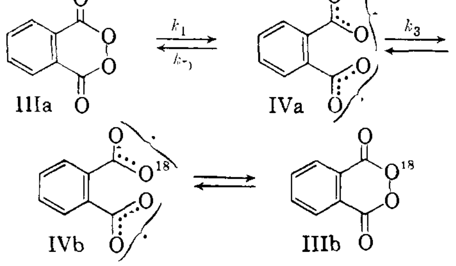
The data of Table I afford two principal results: (1) only a small amount of oxygen-18 originally located in a carbonyl group of phthaloyl peroxide becomes bonded to a carbon atom of the olefin; (2) the amount of oxygen-18 ultimately attached to carbon of the olefin is essentially independent of the time that phthaloyl peroxide itself has been subjected to 80° in carbon tetrachloride. The main conclusion drawn from these results is that equilibria between phthaloyl peroxide and any species in which a carbonyl oxygen atom becomes symmetrically located with respect to an oxygen atom of the oxygen–oxygen link are unimportant.

Bearing of the Oxygen-18 Results on the Stability of Phthaloyl Peroxide.—One of the unique features of phthaloyl peroxide is its enhanced stability in carbon tetrachloride compared with benzoyl peroxide, a 57-fold difference in rate of decomposition. (For both cases the rate of decomposition in carbon tetrachloride is first order in peroxide and essentially free of contribution from induced decomposition processes.) This stability, *a priori*, may be inherent in the cyclic diacyl ring system, or may be the result of an equilibrium between phthaloyl peroxide and the diradical formed by homolytic fission of the oxygen–oxygen bond.



(4)

Diradical IV represents a species with the option for a built-in cage reaction, and return to III might be expected to be faster than competing processes such as decarboxylation or attack on solvent. The equilibrium as written implies the equilibration of carbonyl oxygen and oxygen of the peroxidic link. In terms of a labeled oxygen atom such equilibration can be achieved only by rotation of the carbonyl-carbon to ring-carbon bond. The observation that the amount of oxygen-18 attached to carbon of olefin in the cyclic phthalate is independent of the length of time that phthaloyl peroxide is subjected to 80° in carbon tetrachloride makes it clear that conversion of IIIa and IIIb, by any mechanism, is unimportant under the experimental conditions. With regard to the question of diradical formation (IIIa to IVa), it is clear from the calculations of the structure of phthaloyl peroxide that thermal homolytic fission of the oxygen–oxygen bond could only be achieved by considerable twisting of the carbonyl carbon-to-ring carbon bonds. The condition imposed by the oxygen-18 results is that k_{-1} be much greater than k_3. The exclusion of k_3 of importance relative to k_{-1}, even from the necessarily twisted configuration of IVa, places a major restriction on the lifetime of a diradical IV, and, in our opinion, effectively excludes this fragment from serious consideration as an intermediate in the reactions of phthaloyl peroxide. The basis for the greater stability of phthaloyl peroxide over the acyclic analogs well may lie in the fact that oxygen–oxygen fission in an acyclic peroxide may be achieved by a simple stretching of the oxygen–oxygen bond whereas the related rupture in phthaloyl peroxide could be achieved only by twisting of the carbonyl carbon to ring carbon bonds.[11]



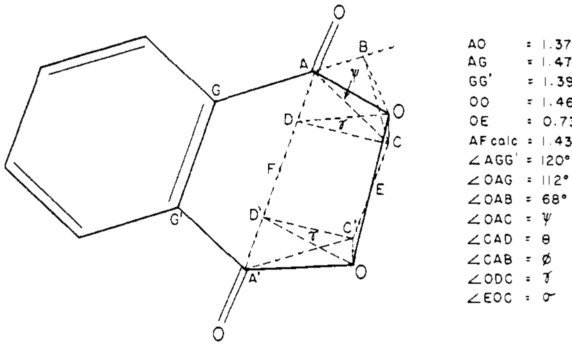
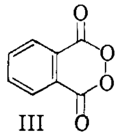
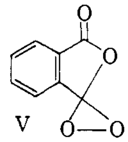


Fig. 1.—Model for calculation of dihedral angle (2γ) in phthaloyl peroxide.

The oxygen-18 results also eliminate from consideration equilibrium between III and V, and obviously exclude V from consideration as the structure of phthaloyl peroxide. Structure V was initially rejected on the basis of the close correspondence in ultraviolet absorption spectra of phthaloyl peroxide and phthalic anhydride.[12]


III


V

Relationship of the Oxygen-18 Results to the Reaction of Phthaloyl Peroxide with Olefins.—The exclusion of thermal processes for the equilibration of carbonyl oxygen with oxygen of the oxygen–oxygen link still leaves several possibilities for oxygen-18 incorporation into alkyl oxygen of the ester: (1) oxygen-18 shuffling in the process of formation of phthaloyl peroxide (from phthaloyl chloride and hydrogen peroxide in ether in the presence of sodium carbonate); (2) isomerization of lactonic *ortho*-ester II to cyclic phthalate I; (3) isomerization of cyclic phthalate—*carbonyl*-O^{18} to cyclic phthalate-*alkyl*-O^{18}; (4) oxygen-18 shuf-

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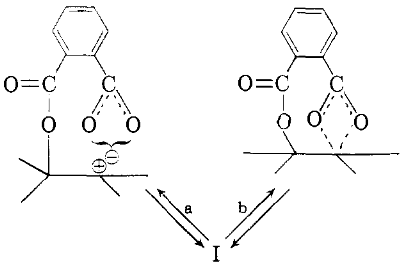
[11] For a detailed picture of the relation of structure and reactivity in a number of oxygen–oxygen cleavage reactions of peresters see P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

[12] The elegant work of W. D. Emmons, THIS JOURNAL, **79**, 5739 (1957), on the oxaziranes (structures containing nitrogen, oxygen and carbon in a three-membered ring) should substantially reduce any prejudice against the possible occurrence of an oxygen–oxygen link in a three-membered ring.

fling in the process by which cyclic phthalate is formed from peroxide and olefin. We see no plausible path for isotopic shuffling in the process of formation of peroxide and exclude the first possibility on this basis. Earlier work[3] has shown that the lactonic *ortho*-ester II and cyclic phthalate I have high thermal stability and are *not* interconverted, excluding the second possibility. The third possibility represents an interconversion that might take place by way of an ion-pair process (a) or a molecular SNi process (b). Although neither of these possibilities is excluded by the evidence at hand, the resistance of simple esters to this type of interconversion[13] and the slowness of isomerization of tosylates under conditions that are far more conducive to ionization[14] do not lend encouragement to the acceptance of alternatives a or b as the mechanism of oxygen transposition.[15] On the other hand, isotopic shuffling in the olefin reaction itself is consistent with kinetic and product evidence.[1] This matter will be discussed in detail in a forthcoming publication in conjunction with additional information bearing on the mechanism of the reaction of phthaloyl peroxide with carbon–carbon unsaturation.



Experimental

Phthaloyl Chloride-O^{18}.—A mixture of 11 g. of phthaloyl chloride (Eastman Kodak Co. white label, redistilled, b.p. 86–88° at 0.1 mm.) and 100 ml. of water containing 1.4 atom % oxygen-18 (Stuart Oxygen Co.) was heated at reflux overnight. From the cooled mixture 9.4 g. of phthalic acid was obtained, dec. p. 207–208°. This material was converted to phthaloyl chloride-O^{18} by means of phosphorus pentachloride.

Phthaloyl peroxide-*carbonyl*-O^{18} was prepared from the above acid chloride by the procedure described previously.[3]

Reaction of Phthaloyl Peroxide-*carbonyl*-O^{18} with *trans*-Stilbene.—This reaction was carried out under two sets of conditions. The oxygen-18 analyses are reported in Table I.

By Direct Reaction.—Peroxide and olefin were heated at reflux in carbon tetrachloride for 16 hr. and worked up as described previously.[3] The cyclic phthalate melted at 206–207° after recrystallization from carbon tetrachloride (reported[3] m.p. 206–207°).

Alkaline hydrolysis of the cyclic phthalate[3] afforded *dl*-1,2-diphenylethanediol of m.p. 119.5–120° after recrystallization from hexane.

After Prior Heating of Phthaloyl Peroxide.—A solution of 1.00 g. of phthaloyl peroxide-*carbonyl*-O^{18} in 100 ml. of carbon tetrachloride was sealed in a flask under nitrogen and heated at 80° for 96 hr. Iodometric analysis of a 5-ml. aliquot indicated only 13% destruction of peroxide in this time period. To the remainder of the phthaloyl peroxide solution was added an equimolar amount of *trans*-stilbene, and the solution was heated at reflux for 18 hr. A 3-ml. portion was evaporated to dryness for spectral analysis. The infrared absorption spectrum of this sample in chloroform was the same as that obtained previously from direct reaction of the peroxide and *trans*-stilbene.[3] The cyclic phthalate was isolated as before, m.p. 206–207°.

Alkaline hydrolysis of the cyclic phthalate afforded *dl*-1,2-diphenylethanediol, m.p. 119.5–120° after recrystallization from hexane.

Acknowledgment.—We are indebted to Professor Myron L. Bender for the oxygen-18 analyses and for his encouragement in this problem.

CAMBRIDGE 39, MASSACHUSETTS

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[13] K. B. Wiberg, T. W. Shryne and R. R. Kintner, THIS JOURNAL, **79**, 3160 (1957).

[14] D. B. Denney and B. Goldstein, *ibid.*, **79**, 4948 (1957).

[15] Although processes of the type a and b are considered unlikely under the experimental conditions employed here, these processes may occur under other circumstances.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Thermal Decomposition of Substituted *t*-Butyl N-Phenylperoxycarbamates[1-3]

BY EUGENE L. O'BRIEN, F. MARSHALL BERINGER AND ROBERT B. MESROBIAN[4]

RECEIVED JULY 30, 1958

Addition of *t*-butyl hydroperoxide to substituted phenyl isocyanates gave substituted *t*-butyl N-phenylperoxycarbamates. Their ultraviolet and infrared absorption spectra and their rates of decomposition in toluene over a 30° range of temperatures were measured. First-order rate constants increased with the electron-releasing power of the substituents; a Hammett plot with H. C. Brown's σ^+-values had a slope of −2.2. This may explain the observation that peroxycarbamates bearing *p*-methyl or *p*-methoxyl groups could not be isolated.

In a previous paper[3] the first-order thermal decompositions of *t*-butyl and cumyl N-phenylperoxycarbamates and *t*-butyl N-α-naphthylperoxycarbamate and their efficiencies as initiators of vinyl polymerization were reported. While *t*-butyl N-α-naphthylperoxycarbamate decomposed more rapidly than the N-phenyl analog, the induced decomposition of the former made an exact comparison difficult. In the present work the effect of substituents in the aromatic rings of *t*-butyl N-phenylperoxycarbamates on their thermal decompositions in toluene has been studied over a 30° range.

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[1] Part of this work was supported by the Office of Naval Research under Contract N6onr-26309. Reproduction in whole or in part is permitted for any purpose by the U. S. Government.

[2] This paper is taken from the doctoral dissertation by Eugene L. O'Brien, 1959.

[3] Preceding paper, E. L. O'Brien, F. M. Beringer and R. B. Mesrobian, THIS JOURNAL, **79**, 6238 (1957).

[4] To whom inquiries concerning this paper should be sent: Central Research and Engineering Division, Continental Can Co., Inc., 7622 South Racine Ave., Chicago 20, Ill.