white solid (0.194 g., 96% of theory) melting at 165–166° remained. This compound does not give a colored solution when dissolved in concentrated sulfuric acid.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.2; H, 7.94; N, 7.41. Found: C, 76.0; H, 7.75; N, 7.07.

NEW YORK 53, N. Y.

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

Cyclic Diacyl Peroxides. I. Monomeric Phthaloyl Peroxide[1]

BY FREDERICK D. GREENE

RECEIVED OCTOBER 17, 1955

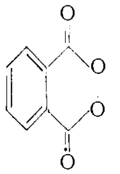
The synthesis and physical properties of monomeric phthaloyl peroxide are reported. From the decomposition of the peroxide in benzene at 80° were isolated carbon dioxide, *o*-phenylbenzoic acid, "polymeric" acid, phthalic acid, benzoic acid, biphenyl and 3,4-benzcoumarin. The mechanism of decomposition in benzene is discussed in terms of induced decomposition *via* a radical chain reaction. The decomposition is accelerated by trichloroacetic acid, leading to phthalic anhydride. The relative rates of decomposition in carbon tetrachloride, benzene and styrene are 1:140:10^5. The decomposition in styrene does not produce polystyrene. The possibility of ring strain, electronic in origin rather than steric, is suggested to account for the unusual reactivity of the peroxide.

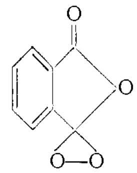
Although a large number of compounds are known which contain the oxygen–oxygen grouping, only a few incorporate this unit in a ring. Of these, the best characterized are the ozonides and the *endo*-peroxides.[2] A few cyclic alkyl peroxides are known: cyclic peroxides from the oxygenation of bicyclohexenyl and 1-phenylcyclohexene,[3] 3,3,5,5-tetramethyl-1,2-dioxacyclopentane and the homologous six-membered ring compound.[4] Cyclic diacyl peroxides were reported in 1894[5] but the compounds to which a cyclic structure was originally assigned were actually polymeric.[6,7] Monomeric cyclic diacyl peroxides have been reported recently by Kleinfeller and Rastadter[8] and by Russell.[9] We have been interested in the study of compounds of this class from two standpoints: the intrinsic interest associated with a new type of structure and interest in the diradicals, which might be produced by the decomposition of such systems. This report will deal with the unusual behavior of phthaloyl peroxide.

Results

Synthesis.—Reaction of phthaloyl chloride with an ethereal solution of hydrogen peroxide and sodium carbonate affords phthaloyl peroxide in good yield. Material containing 99.5% of the theoretical active oxygen content (by iodometric titration) may be obtained by recrystallization. The compound has the following physical properties: m.p. 126–127°, exploding violently at 130°; density, 1.56 g. cm.$^{-3}$; soluble in chloroform, methylene chloride and moderately soluble in hot benzene, carbon tetrachloride and cyclohexane; very sensitive to shock.[10] Cryoscopic determinations of the molecular weight in benzene solution gave values of 167, 170, 173, an average of 3–4% above the calculated value of 164. The presence of a small amount of dimeric (or higher) material may be responsible for this discrepancy.

Structure.—The two structures that warrant consideration are I and II. Although both structures are without close analogy in the literature, a distinction may be made on the basis of spectroscopic evidence. The ultraviolet absorption spectra of phthaloyl peroxide (A), phthalic anhydride (B), ψ-phthaloyl chloride (3,3-dichlorophthalide, C) and phthalide (D) are shown in Fig. 1. The great similarity between the spectra of phthaloyl peroxide and phthalic anhydride is strong evidence for structure I. The infrared absorption spectrum of monomeric phthaloyl peroxide in carbon tetrachloride exhibits a single moderately sharp peak at 1768 cm.$^{-1}$ with a slight shoulder at 1750 cm.$^{-1}$ and two very weak bands at 1719 and 1702 cm.$^{-1}$ (Davison reports the spectral bands for polymeric phthaloyl peroxide at 1805 and 1783 cm.$^{-1}$ in Nujol).[11] Acyclic diacyl peroxides normally possess two well-defined maxima in the carbonyl region, separated by 20 cm.$^{-1}$ (*e.g.*, benzoyl peroxide: 1792 and 1772 cm.$^{-1}$).[12] Although the lactone band of phthalides and 3-substituted phthalides shows strong absorption in the infrared[12] at 1750–1770 cm.$^{-1}$, structure I might be expected to show absorption in this region (at lower wave numbers than the acyclic diacyl peroxides) because of the conjugation of the carbonyl groups through the benzene ring. The presence of a small amount of II is not excluded by the spectral data but structure I is favored as the major, if not sole, component.


I


II

Decomposition in Benzene.—A degassed sample of phthaloyl peroxide in benzene was decomposed at 80° and the products were isolated by initial division into a neutral and acid fraction by extraction with 5% aqueous sodium bicarbonate solution. The following products were obtained: biphenyl (less than 1%), 3,4-benzcoumarin (0.5%), benzoic acid (5%), phthalic acid (7%), *o*-phenylbenzoic acid (50%) and "polymeric" acid (*ca.* 25%). Carbon dioxide, 78% (based on one mole of carbon dioxide per mole of peroxide) was determined separately by absorption on Ascarite. From a product analysis carried out by chromatography on silica gel, the product composition was similar except that phthalic anhydride (2%) replaced half of the phthalic acid. The first five products listed above were identified by comparison of the infrared spectra and melting points with authentic samples. A sample of 3,4-benzcoumarin was

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[1] Presented before the Organic Division of the 128th meeting of the American Chemical Society in Minneapolis, Minnesota, September, 1955.

[2] W. Bergmann and M. J. McLean, *Chem. Revs.*, **28**, 367 (1941).

[3] H. Hock and M. Siebert, *Chem. Ber.*, **87**, 554 (1954). See also A. Mustafa and A. M. Islam, *J. Chem. Soc.*, S81 (1949); J. L. Bolland and H. Hughes, *ibid.*, 492 (1949); G. Wittig and W. Gaub, *Chem. Ber.*, **80**, 367 (1947).

[4] R. Criegee and G. Paulig, *ibid.*, **88**, 712 (1955).

[5] H. v. Pechmann and L. Vanino, *ibid.*, **27**, 1510 (1894).

[6] A. Baeyer and V. Villiger, *ibid.*, **34**, 762 (1901).

[7] H. A. Shah, F. Leonard and A. V. Tobolsky, *J. Polymer Sci.*, **7**, 537 (1951).

[8] H. Kleinfeller and K. Rastadter, *Angew. Chem.*, **65**, 543 (1953).

[9] K. E. Russell, THIS JOURNAL, **77**, 4814 (1955).

[10] Preliminary tests have shown that the peroxide is exploded by the impact from a 2 kg. weight dropped from a height of 2 cm. We are indebted to Dr. Handrick of Arthur D. Little, Inc., for this information.

[11] W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

[12] J. F. Grove and H. A. Willis, *ibid.*, 882 (1951).

prepared by the method of Graebe and Schestakow[13a] and one of *o*-phenylbenzoic acid by the procedure of Graebe and Rateanu.[13b] The "polymeric" acid was obtained as an amorphous solid, softening at 100°. The average molecular weight of the material was 760 (cryoscopic in benzene) and the neutral equivalent was 300, suggesting that the material is largely dimeric in benzene.

Rate of Decomposition.—The complexity of the product mixture formed by decomposition of the peroxide in benzene prompted a preliminary investigation of the kinetics of decomposition. The kinetic picture is incomplete but the following results are pertinent. The rate is dependent on the solvent and on the initial concentration of peroxide, is dependent on the degassing procedure (thorough degassing produces a ten-fold increase in the initial rate of disappearance of peroxide) and is subject to acceleration by decomposition in the presence of trichloroacetic acid. Within a single run, the reaction in benzene is approximately zero order in peroxide; but the zero-order rate constant varies with change in the initial concentration of peroxide, suggesting that the reaction involves an autocatalysis superimposed on a peroxide-dependent process. *o*-Benzoylbenzoic acid, the major product of the decomposition in benzene, has been shown to double the rate of decomposition of phthaloyl peroxide (0.02 *M* in benzene) when present at an initial concentration of 0.2 *M*. The catalytic effect of this acid, when produced by decomposition of phthaloyl peroxide in benzene alone, is not great enough for it to be the only product catalyzing the decomposition. Rates of reaction, expressed as the time required for 50% decomposition, are shown in Table I. The thermal decomposition of phthaloyl peroxide in toluene, xylene, methyl methacrylate and styrene has been investigated by Russell.[9] In these solvents the rate of decomposition is also much greater than in carbon tetrachloride and the kinetics appears to be complex.

TABLE I

COMPARISON OF RATE OF DECOMPOSITION OF PHTHALOYL PEROXIDE AND BENZOYL PEROXIDE

Solvent[a]	Phthaloyl peroxide Time in hr. for 50% decomposition	°C.	Benzoyl peroxide[b] $t^{1}/_{2}$, hr.	°C.
Carbon tetrachloride	275	80	6.34	80
Benzene	2	80	4.50	80
Styrene	10	0	4.40[c]	80

[a] All initial concentrations, 0.05 *M*. [b] C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5428 (1950). [c] J. T. Clarke, Ph.D. Thesis, Massachusetts Institute of Technology, 1949.

Decomposition of Phthaloyl Peroxide in the Presence of Trichloroacetic Acid.—The rate of decomposition of the peroxide in carbon tetrachloride at 80° is accelerated by a factor of ten by the presence of 0.1 *M* trichloroacetic acid. The major products are phthalic anhydride (71%) and phthalic acid (14%). Analysis for carbon dioxide showed that it was produced to a maximum extent of 57% (see Experimental). The phthalic acid and the anhydride were isolated from a silica gel column, and the phthalic acid may have been derived from hydrolysis of some of the phthalic anhydride. In another experiment phthalic anhydride was isolated directly from the reaction mixture, demonstrating that its formation occurred in the reaction proper and not during the chromatographic separation. The over-all result is that trichloroacetic acid has been oxidized.

This result is contrary to the behavior of acyclic diacyl peroxides under acid conditions, both with respect to rate and to products. Benzoyl peroxide exhibits only a 50% rate acceleration by decomposition in benzene, 0.3 *M* in trichloroacetic acid.[14a] Those compounds that do show pronounced acid catalysis afford products derived from heterolytic cleavage of the oxygen–oxygen bond and subsequent rearrangement (bis-phenylacetyl peroxide[14a] and *p*-nitro-*p*′-methoxybenzoyl peroxide[14b]).

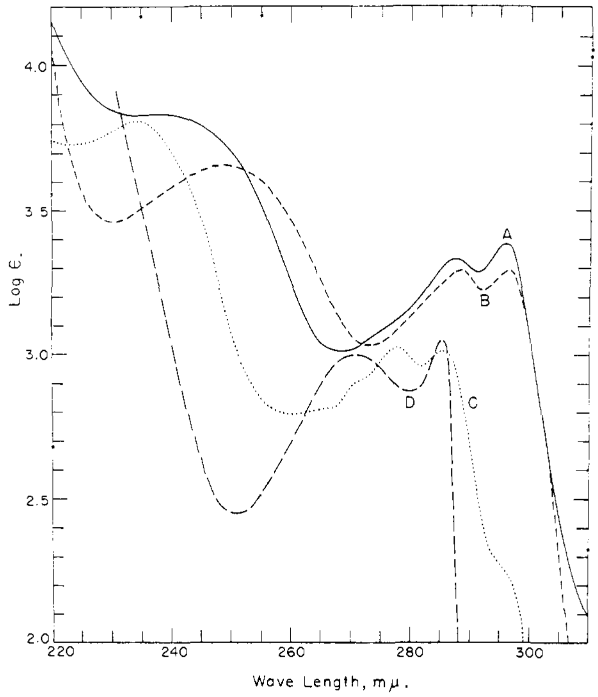

Fig. 1.—Ultraviolet absorption spectra of phthaloyl peroxide (A, ———); phthalic anhydride (B, ---------); ψ-phthaloyl chloride (C, ...) and phthalide (D, — —). A, B and C were taken in ether solution on a Beckman Model DU Spectrophotometer; D (in ethanol) is from M. Ramart-Lucas and M. J. Hock, *Bull. soc. chim. France*, [5], **2**, 337 (1935).

The findings that at least 85% of the product derived from the acid-induced cleavage of phthaloyl peroxide involves no carbon-to-oxygen rearrangement and that acid has been oxidized clearly differentiate the effect of acid on phthalic and on acyclic peroxides. The evidence at hand does not allow a unique mechanism to be drawn. A mechanism consistent with these results involves the intermediate formation of *o*-carboxybenzoyltrichloroacetyl peroxide and its conversion to phthalic anhydride and pertrichloroacetic acid, followed by decomposition of the peracid, in part, to carbon dioxide.

Decomposition in Styrene.—The action of the cyclic peroxide, phthaloyl peroxide, on styrene stands in striking contrast to the decomposition of acyclic peroxides in this medium. The decomposition of phthaloyl peroxide in styrene at 0° is only slightly slower than in benzene at 80° (see Table I), and the decomposition in styrene does not produce polystyrene. This lack of polymerization of styrene has also been noted by Russell.[9] The extent of polymerization of styrene by phthaloyl peroxide, 0.5% after heating at 80° for one hour, is within experimental error of the thermal polymerization value at 80° for pure styrene alone, 0.42%.[15] Reaction of phthaloyl peroxide with olefins appears to be a general reaction. The nature and the products of this reaction will be reported in Part II of this series.[16]

Discussion

Any mechanism of the decomposition of the peroxide must take into account the hundred forty-fold difference in the rate of decomposition in benzene and in carbon tetrachloride and the large inhibitory effect of oxygen. These two facts are strongly suggestive of the operation of a chain mechanism. Two distinct types of chain mechanism warrant consideration: (a) direct radical attack on phthaloyl peroxide and (b) removal by a

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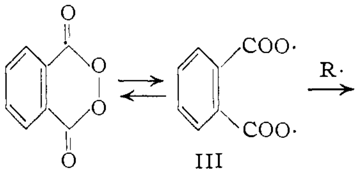
[13] (a) C. Graebe and P. Schestakow, *Ann.*, **284**, 317 (1895); (b) C. Graebe and A. Sc. Rateanu, *ibid.*, **279**, 260 (1894).

[14] (a) P. D. Bartlett and J. E. Leffler, THIS JOURNAL, **72**, 3030 (1950); (b) J. E. Leffler, *ibid.*, **72**, 67 (1950).

[15] G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B34**, 187 (1936).

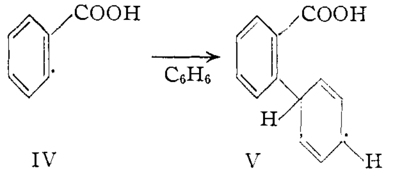
[16] F. D. Greene, THIS JOURNAL, **78**, 2250 (1956).

radical of the diradical III, produced by reversible cleavage of the oxygen–oxygen bond of phthaloyl peroxide. A possible chain mechanism involves the *o*-carboxyphenyl radical IV as the chain carrier.

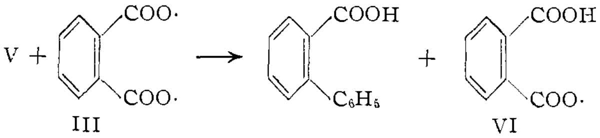


(1)

As a phenyl radical, this radical would have a strong tendency to attack benzene by addition,[17] producing radical V. Hydrogen transfer from radical V to radical III (or to phthaloyl peroxide) forms

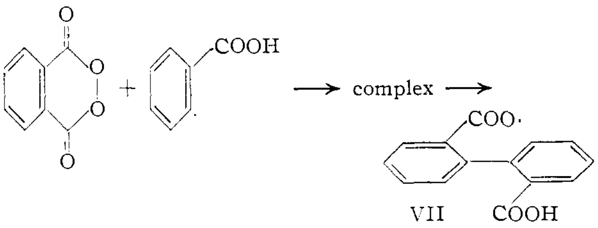


o-phenylbenzoic acid and generates the *o*-carboxybenzoyloxy radical VI, which may be decarboxylated during this transfer reaction or, subsequently,



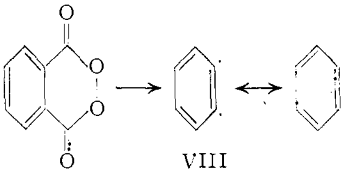
regenerating the *o*-carboxyphenyl radical IV. Benzoic acid and phthalic acid may arise by hydrogen atom transfer to radicals IV and VI, respectively. The formation of the small amounts of biphenyl and of 3,4-benzcoumarin is possible by a variety of routes. The latter compound may arise from attack by the decarboxylated form of radical III on benzene, yielding a dihydrobenzocoumarin, subsequently dehydrogenated to 3,4-benzcoumarin.

The formation of the "polymeric" acid raises the question of the selectivity of radical IV. The following argument is based on two lines of evidence. First, it has been shown that the affinity of methyl radicals for various substrates varies greatly,[18] with great affinity for quinones[19] and moderate affinity for aromatic nuclei containing electron-withdrawing substituents. Secondly, the available evidence strongly suggests that the selectivity of methyl radicals and phenyl radicals toward various substrates is similar.[17,18] The *o*-carboxyphenyl radical IV may complex preferentially with phthaloyl peroxide (because of the quinonoid-like character of the peroxide this preference may be considerable), followed by breakdown of the complex with the ejection of carbon dioxide and the formation of a new carboxylate radical VII.[20] Decarboxylation of VII and addition to benzene (or to more peroxide) leads to "polymeric" acid. Oxygen may inhibit the decomposition in benzene by converting radicals IV and V to inactive forms.



Alternative chain mechanisms for the decomposition of phthaloyl peroxide in benzene are possible (*e.g.*, with chain propagation by the phenyl radical) but are considered less likely than the proposed mechanism because of the necessity of a chain-carrying step involving abstraction by a carboxylate radical of a hydrogen atom from a benzene ring, a process that has been shown to be unlikely.[17]

A possible diradical theoretically capable of formation from phthaloyl peroxide is the phenylene diradical (of paired spins) VIII, benzyne.[21] These experiments do not shed light on this species.[22]



The most notable feature of phthaloyl peroxide is the great difference in its behavior from that of the acyclic diacyl peroxides. The induced decomposition in benzene and the "acid-catalyzed" decomposition are prominent to a far greater degree than obtains with benzoyl peroxide, and the rapid reaction with olefins is without parallel in the acyclic analogs. These points are to be contrasted with the stability of phthaloyl peroxide in pure carbon tetrachloride. Three factors deserve consideration. First, there is considerable evidence for repulsion between adjacent non-bonded electron pairs of peroxy-oxygen atoms. The structure of hydrogen peroxide contains a preferred dihydral angle of 95°,[23] and a calculated barrier of upwards of 10 kcal. to rotation about the oxygen–oxygen bond.[24,25] Such repulsion if operative in phthaloyl peroxide would introduce an element of strain that would be minimized by a conformation that places one peroxygen atom above the plane of the ring and the other one below. Secondly, the –COO–OOC– grouping of phthaloyl peroxide is more exposed and consequently more subject to attack than is the corresponding grouping in the acyclic analogs. Thirdly, phthaloyl peroxide is a system potentially

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[17] D. H. Hey and G. H. Williams, *Disc. Faraday Soc.*, **14**, 216 (1953). See also D. H. Hey, A. Nechvatal and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951).

[18] M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

[19] A. Rembaum and M. Szwarc, *ibid.*, **77**, 4469 (1955).

[20] The insensitivity of rate of decomposition of acetyl peroxide to large changes in radical concentration[18] suggests that induced decomposition, often observed with aromatic diacyl peroxides, may arise in part from addition of the inducing radical to the aromatic ring. However, induced decomposition of benzoyl peroxide in ether appears to involve attack at the peroxide group, W. E. Cass, *ibid.*, **69**, 500 (1947).

[21] J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, *ibid.*, **75**, 3290 (1953).

[22] Experiments directed toward the production of diradical VIII by the irradiation of phthaloyl peroxide are in progress.

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

[24] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

[25] E. N. Lassettre and L. B. Dean, Jr., *ibid.*, **17**, 325 (1949).

capable of resonance stabilization. In the completely flat representation, it possesses 14 p electrons (of parallel orbitals) to be distributed over 12 nuclei. Since delocalization of the peroxygen electrons would result in making both these atoms positively charged, stabilization of this kind may be small or perhaps absent. The stability of the peroxide in carbon tetrachloride is not necessarily evidence in support of such delocalization. If homolytic cleavage of the oxygen–oxygen bond is followed by recyclization (eq. 1), then the over-all rate of disappearance of peroxide is not a direct measure of the stability of this diacyl ring. The reason for the stability in carbon tetrachloride may lie in the absence in this reaction of species capable of removing diradical III, or capable of inducing the decomposition of the peroxide. The olefin reaction, the "acid-catalyzed" reaction and the induced decomposition in benzene of phthaloyl peroxide are measures of the reactivity of the peroxide toward a variety of substrates. Destruction of peroxide either by direct reaction with these substrates or by opening to diradical III (and its removal by substrate attack) indicates that the diacyl ring is opened without difficulty. An explanation of the ease of ring opening may be the relief of strain afforded by this process, the origin of the strain in the diacyl ring being ascribed to the repulsion between the non-bonded electron pairs of the peroxy-oxygen atoms.

Experimental[26]

Phthaloyl Peroxide.—To a mixture of 16 g. of anhydrous sodium carbonate and 350 ml. of dry ether at 0° was added 130 ml. of a 1.12 *M* solution of hydrogen peroxide (0.145 mole, a 5% excess) in ether prepared by the addition of a sample of 90% hydrogen peroxide to anhydrous ether. A sample of redistilled Eastman Kodak white label phthaloyl chloride (20 ml., 0.138 mole, b.p. 86–88° at 0.1 mm.) was added to the cold mixture with stirring (nichrome wire stirrer). After completion of addition (20 min.), the mixture was stirred for 72 hours at 0°. The mixture was filtered and the residue was washed with 250 ml. of cold water. The remaining water-insoluble residue amounted to 8.0 g. The ethereal filtrate was washed twice with saturated ammonium sulfate solution, with water, twice with 10% sodium bicarbonate solution, with water, with saturated sodium chloride solution and then was dried over anhydrous magnesium sulfate. Filtration and removal of the solvent under reduced pressure afforded 7.0 g. of colorless, crystalline material. The combined residues, 15 g. (about 92% phthaloyl peroxide), were recrystallized two times from methylene chloride (5 ml. of methylene chloride per gram of peroxide) affording 6.4 g. (28% yield) of phthaloyl peroxide of 98% purity (determined by iodometric titration). Material of 99.5% purity may be obtained by a third recrystallization. Successive recrystallizations of the material from the filtrates yielded an additional 5.0 g. of peroxide of 98.5% purity, corresponding to an over-all yield of 11 g. of 98% purity (50% yield). The pure material melts with slight decomposition at 126–127° and explodes at 130°; density 1.56 g. cm.$^{-3}$. The compound is very sensitive to shock. (This preparation has been carried out several times on twice the scale described here without any explosions. However, the material has an active oxygen content of 10% and should be treated with great care.)

Anal. Calcd. for $C_8H_4O_4$: C, 58.56; H, 2.46; mol. wt., 164.1. Found: C, 58.36; H, 2.70; mol. wt., 167, 170, 173 (cryoscopic in benzene).

Phthaloyl peroxide is soluble in cold chloroform and methylene chloride is moderately soluble in hot cyclohexane, benzene and carbon tetrachloride. The compound dissolves instantly in concentrated sulfuric acid to give a colorless solution. The compound dissolves slowly in water with concomitant hydrolysis to monoperphthalic acid. The infrared absorption spectrum of phthaloyl peroxide exhibits a strong band in the carbonyl region with the maximum at 1768 cm.$^{-1}$ and strong bands at 1285, 1092, 1040 and 690 cm.$^{-1}$ (in carbon tetrachloride). The ultraviolet absorption spectrum of this compound in chloroform exhibits a twin-peaked band with maxima at 289 mμ (log ϵ 3.40) and at 298 mμ (log ϵ 3.45) and a minimum at 270 mμ (log ϵ 3.00).

***o*-Phenylbenzoic Acid.**—A sample of this acid was prepared by the action of concentrated potassium hydroxide on fluorenone according to the procedure of Graebe and Rateanu.[13b] Three recrystallizations from hexane yielded material of m.p. 112–113° (reported m.p. 112–113°).

3,4-Benzcoumarin.—The procedure of Graebe and Schestakow,[13a] involving the reaction of phenol with the diazonium bisulfate of anthranilic acid, was used. Two recrystallizations of the lactone from hexane gave needles, m.p. 93–94° (reported m.p. 92.5°).

Rate of the Decomposition of Phthaloyl Peroxide.—A sample of the peroxide was dissolved in a solvent and approximately 5-ml. portions were introduced into Pyrex test-tubes. The tubes were degassed by three cycles of freezing, evacuating, thawing and shaking and then sealed under vacuum. Omission of the degassing operation results in a much slower rate of disappearance of peroxide. The tubes were placed in a bath at 80°. Samples were withdrawn and 2-ml. portions were added to oxygen-free acetic acid containing 1 ml. of freshly prepared, saturated potassium iodide solution. The liberated iodine was titrated with a standard solution of thiosulfate.

Decomposition of Phthaloyl Peroxide in Benzene.—A solution of 4.0 g. (0.0244 mole) of phthaloyl peroxide of 99.5% purity and 150 ml. of reagent benzene in a flask with a constricted neck was degassed in the above manner and the flask was sealed under vacuum. The flask was placed in a bath at 80° for 2 days, opened and the solution was reduced to a small volume. The solution was diluted with ether and extracted three times with 5% aqueous sodium bicarbonate solution. The aqueous extracts were combined, acidified and extracted separately first with ether and then with ethyl acetate. Drying of the ethyl acetate extract and removal of solvent left 0.28 g., which on sublimation yielded 0.15 g. of phthalic anhydride, m.p. 127–129°, mixed m.p. with an authentic sample 128–130°. The ether extract, dried over anhydrous magnesium sulfate, yielded after solvent removal 3.4 g. of an acid mixture. Refluxing the mixture with 90 ml. of hexane effected the solution of 2.0 g. of material, which solidified upon removal of the hexane. Sublimation of a powdered 0.246-g. sample of this material at 80° (15 mm.) yielded 19 mg. of benzoic acid, m.p. 116–118°, mixed m.p. with an authentic sample 118–120°, neut. equiv. 123. The residue from the sublimation was almost pure *o*-phenylbenzoic acid, m.p. 106–110°. Recrystallization of a portion of the initial 2.0-g. sample yielded material of m.p. 111.5–113°. The compound was shown to be *o*-phenylbenzoic acid by mixed m.p. determination, 111–113°, with an authentic sample and by conversion to fluorenone, m.p. and mixed m.p. 81–83°.

The remaining 1.4-g. acid fraction, after removal of the 2.0-g. fraction, was dissolved in chloroform and added dropwise and with stirring to an excess of hexane, leading to the precipitation of 0.84 g. of an orange-yellow, amorphous solid, m.p. 90–150°. Attempted recrystallizations were without avail.

Anal. Found: C, 71.53; H, 4.64; mol. wt., 760 (cryoscopic in benzene); neut equiv., 300.

A 0.18-g. sample of this material was refluxed for 8 hours in 20% sodium hydroxide solution. The solution was acidified and extracted with ethyl acetate. Sublimation of the oil obtained by removal of the ethyl acetate yielded 30 mg. of phthalic anhydride (no trace of salicylic acid), and the residue failed to sublime even at 300° (0.1 mm.).

The chloroform–hexane filtrate obtained after separation of the "polymeric" acid was evaporated to dryness, leaving 0.57 g. of solid. Recrystallization from hexane yielded 0.47 g. of *o*-phenylbenzoic acid, m.p. 109–111°, mixed m.p. 110–112°. The infrared spectrum of the residual 0.1 g. indicated that it was largely *o*-phenylbenzoic acid.

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[26] We are indebted to Dr. S. M. Nagy and his associates for analyses and infrared spectra, which were recorded with a Baird double beam infrared recording spectrophotometer equipped with a sodium chloride prism.

The original ether extract, containing the neutral products of the decomposition reaction, was dried and the solvent removed. The 0.8 g. of residual oil was chromatographed on 100 g. of a mixture of anhydrous magnesium sulfate–Celite (5:1). Fractional sublimation of the first few fractions yielded as a first sublimate a semi-solid, purified by chromatography on alumina, 28 mg., m.p. and mixed m.p. with biphenyl, 69–70°. The second sublimate was an oil. Recrystallizations from hexane yielded 22 mg. of needles, m.p. 93–94°, identified as 3,4-benzcoumarin by the superimposability of the infrared spectra and by mixed m.p. 93–94°.

The other fractions from the chromatography of the neutral fraction were unsublimable oils that resisted crystallization.

Analysis for carbon dioxide in the products of decomposition of the peroxide was carried out in a separate run. A solution of 0.4034 g. (2.46 mmoles) of phthaloyl peroxide in 30 ml. of freshly distilled benzene was placed in a flask having an inlet and an outlet tube provided with break-off joints. The solution was degassed by the standard procedure and sealed under vacuum. The flask was placed in a bath at 80° for 48 hours, then cooled, and the carbon dioxide content was measured by sweeping the flask with nitrogen and collecting the gas in an absorption tube containing Ascarite; weight of carbon dioxide, 0.0836 g. (1.90 mmoles). A duplicate determination with 0.3012 g. (1.83 mmoles) of peroxide gave 0.0635 g. (1.44 mmoles) of carbon dioxide.

Decomposition of Phthaloyl Peroxide in Carbon Tetrachloride in the Presence of Trichloroacetic Acid.—A solution of 3.0 g. of the peroxide and 15 g. of trichloroacetic acid in 200 ml. of carbon tetrachloride was degassed, sealed under vacuum and placed in a bath at 80° for 30 days. The flask was cooled and opened. A 10-ml. portion was evaporated to dryness. Petroleum ether was added to dissolve the trichloroacetic acid. The solid residue of phthalic anhydride melted at 126–127°. Recrystallization from benzene–petroleum ether yielded material of m.p. 128–129°; mixed m.p. with phthalic anhydride, 129–130°.

The bulk of the carbon tetrachloride solution was chromatographed on 200 g. of silica gel. Elution with carbon tetrachloride-ether (9:1) yielded a 14.50-g. fraction. Trituration with cold water effected the removal of trichloroacetic acid. The residue of 0.50 g. was crude phthalic anhydride, m.p. 120–125°. Recrystallization yielded material of m.p. 129–130°, mixed m.p. with phthalic anhydride 130–131°. Further elution of the column with 20–30% ether in carbon tetrachloride yielded 1.41 g. of phthalic anhydride, m.p. 124–126°. Sublimation of a 0.20-g. portion afforded 0.185 g. of material of m.p. 130–131°. Total yield of phthalic anhydride was 1.91 g., corresponding to a 71% yield from the peroxide. Elution of the column with 50% ether in carbon tetrachloride gave 0.42 g. of phthalic acid, m.p. 195–200° dec., a yield of 14%.

In a separate run, a solution of 0.3988 g. (2.43 mmoles) of peroxide and 2.0 g. of trichloroacetic acid in 30 ml. of carbon tetrachloride was degassed, sealed under vacuum and heated at 80° for 30 days. Carbon dioxide analysis was carried out as described above. A gain in weight of 0.0617 g. for the Ascarite tube was observed, corresponding to 1.40 mmoles of carbon dioxide. The possibility exists that part of this gain in weight is attributable to hydrogen chloride.

Decomposition of Phthaloyl Peroxide in Styrene.—Five-ml. portions of a solution of 0.415 g. of phthaloyl peroxide in 50 ml. of freshly distilled styrene were placed in test-tubes. The tubes were degassed, sealed under vacuum and stored at 0°. After 18 hours a 2-ml. portion of a tube contained 4.8 mg. of peroxide (71% destruction of the peroxide). (A 16-mg. sample of the peroxide dissolved in 2 ml. of styrene and poured directly into 10 ml. of acetic acid gave a titer corresponding to 15.8 mg. of peroxide.) A second tube (no. 2) was kept at room temperature for a day to ensure complete decomposition of the peroxide. A 2-ml. portion was poured into methanol, giving 10 mg. of a precipitate melting over a wide range, 110–160°. This material shows strong absorption in the infrared at 1710, 1275 and 1120 cm.$^{-1}$, suggestive of a phthalate group.[16] A 25-ml. portion of pure styrene, heated at 80° for 1 hr. and poured into methanol, gave 96 mg. of polystyrene, softening above 200° (0.42% polymerization). A 0.192-g. portion of phthaloyl peroxide in 25 ml. of styrene at 80° for 1.0 hour yielded 238 mg. of precipitate insoluble in methanol; estimated weight of products based on tube no. 2 above, 125 mg.; weight of polystyrene, 113 mg. (0.50% polymerization). A solution of 0.094 g. of 91% benzoyl peroxide in 25 ml. of styrene (0.014 *M*) was heated for 1.0 hour at 80° giving 2.70 g. of polystyrene (11.9% polymerization).

ψ-Phthaloyl Chloride.—A sample of this compound was prepared by the method of Ott.[27] The ultraviolet absorption spectrum was taken on a sample of m.p. 86–89°, dissolved in ether. The spectrum is reported in Fig. 1.

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(27) E. Ott, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., p. 528.

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

Cyclic Diacyl Peroxides. II. Reaction of Phthaloyl Peroxide with *cis*- and *trans*-Stilbene

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Phthaloyl peroxide and *trans*-stilbene undergo a quantitative and stereospecific reaction in refluxing carbon tetrachloride to yield the cyclic phthalate of *dl*-1,2-diphenylethanediol (A) and the 3,3-disubstituted phthalide, *dl*-*trans*-7-keto-2,3-diphenyl-8:9-benz-1,4,6-trioxaspirononane (B). Reaction of the peroxide with *cis*-stilbene affords the cyclic phthalate of *meso*-1,2-diphenylethanediol (D) and the 3,3-disubstituted phthalide (C). The products are stable under the conditions of formation. The reactions are first order in peroxide and first order in olefin. Two mechanisms of product formation are considered.

In part I of this series[1] we reported that the cyclic diacyl peroxide, phthaloyl peroxide, reacted extremely rapidly with styrene without producing polystyrene and suggested that reaction of the peroxide with olefins was general. In this paper we wish to report on the unusual nature of the reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene.

Results

Reaction of phthaloyl peroxide with *trans*-stilbene in refluxing carbon tetrachloride yields two isomeric compounds, A, m.p. 206–207°, and B, m.p. 125–126°, which were isolated by fractional recrystallization. Both compounds gave analyses corresponding to the addition of one mole of phthaloyl peroxide to one mole of *trans*-stilbene. The molecular weights determined cryoscopically in benzene were the same and indicated a molecular formula of $C_{22}H_{16}O_4$.

Examination of the infrared absorption spectra of the compounds revealed the following informa-

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(1) F. D. Greene, THIS JOURNAL, **78**, 2246 (1956).