m.p. 91°, $[\alpha]^{20}$D +7.02° (c 1.42, water),[9] were prepared by the usual methods.

Kinetic Measurements of the Reactions of II → III, III → IV, IV → III, and I → II.—Sulfuric acid was weighed into 50 g. of acetone in a standard flask which was then placed in a thermostat at the appropriate temperature. To the solution was added about 0.4 g. of the water to keep the water in the solution constant, and then 5 g. of the sugars. (1) Samples (1 ml.) were titrated by Karl Fischer's method.[7] The data are shown in Fig. 1, 2, 3, and 4, and Table I. (2) Samples (1 ml.) were titrated by Bertrand's method.[8] The data are shown in Fig. 4 and Table II.

TABLE II

THE RATE CONSTANTS OF THE REACTION OF I → II

Reaction temp., °C.	Sulfuric acid, mole/l.	Rate constants × 10^{-5}, mole/l. sec.
30	0.71	0.61
40	0.73	3.20

After the reactions were over, the solutions were poured into a saturated solution of sodium carbonate to make the solution alkaline, evaporated to dryness in vacuo, and extracted with acetone. Evaporation of the solvent gave a brown sirup. (1) II, III, and IV were obtained from the sirup prepared from the

(9) T. I. Temnikova and V. V. Sklyarava, Zh. Prikl. Khim., **21**, 1131 (1954); Chem. Abstr., **49**, 2952 (1955).

reaction of II → III, and were detected by gas chromatography (conditions: column, 1.5 m. × 6 mm. silicone 550 on Chromsorb.; temp., 200°; flow rate, hydrogen 100 ml./min.; retention times of the sugars: II, 13.25 min., III, 16.5 min., IV, 20.5 min.). (2) III and IV were obtained from the sirup prepared from the reactions of III → IV and IV → III, and were detected by gas chromatography.

The reaction of 0.1 g. of II, 0.038 g. of sulfuric acid, and 1.86 g. of dioxane was allowed to stand at 30°. The color of the solution changed from colorless to pink (after 30 min.) and then violet (after 1 hr.). After about 30 min., crystals started to form, which then polymerized to a black tarry product. After 1 hr., the reaction mixture was made alkaline, evaporated to dryness in vacuo, and extracted with chloroform. From the extract, II, III, and IV were detected by gas chromatography and, from the residue, I, II, III, and IV were detected by paper chromatography (n-BuOH–AcOH–H₂O, 4:1:5, ascending method). In order to reveal the position of the sugars, the paper was sprayed with 1 N hydrochloric acid, dried at room temperature, sprayed again with benzidine solution,[10] and heated at 90–95° for 5–10 min. The sugars appeared as brown spots. The R_f values were I, 0.25; II, 0.65; III, 0.88; IV, 0.68.

(10) R. H. Horrocks, Nature, **164**, 144 (1949).

Diacyl Peroxide–Olefin Reactions.   Epoxidation of Tetramethylethylene by an Aroyl Peroxide[1]

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Reaction of m,m'-dibromobenzoyl peroxide and tetramethylethylene in benzene at 45° affords tetramethylethylene oxide (72%), m,m'-dibromobenzoic anhydride (75%), m-bromobenzoic acid (13%), and a small amount of allylic m-bromobenzoates. Oxygen-18 labeling experiments show that the tetramethylethylene oxide oxygen is derived exclusively from the peroxygen bond of the peroxide. From kinetic evidence, utilizing the stable free-radical galvinoxyl, it is concluded that the reaction proceeds by direct reaction between olefin and peroxide; contributions from free-radical chain processes are negligible.

Reaction between m,m'-dibromobenzoyl peroxide and p,p'-dimethoxy-trans-stilbene has been shown to afford a mixture of meso- and d,l-dihydroanisoin bis-m-bromobenzoates.[2] The reaction occurs principally via a nonchain, bimolecular reaction between peroxide and olefin. In this paper, evidence is presented for a direct reaction between this diacyl peroxide and a purely aliphatic olefin, tetramethylethylene, in which, in marked contrast to the cited case, the major course of the reaction is single oxygen atom transfer from peroxide to olefin.

Results

Products.—Tetramethylethylene and m,m'-dibromobenzoyl peroxide undergo a moderate reaction at 45° in benzene to give tetramethylethylene oxide (72%), m,m'-dibromobenzoic anhydride (75%), m-bromobenzoic acid (13%), and a neutral oil, assigned the composition of a mixture of the allylic esters, 2,3-dimethyl-but-3-ene-2-yl m-bromobenzoate and 2,3-dimethyl-but-2-ene-1-yl m-bromobenzoate on the basis

(1) This work was supported 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.

(2) F. D. Greene, W. Adam, and J. E. Cantrill, J. Am. Chem. Soc., **83**, 3461 (1961).

of the spectroscopic, hydrolytic, and hydrogenolysis data given in the Experimental section.

Kinetics.—Rate studies were conducted in benzene in the absence of oxygen. By use of olefin in excess, the rate of the peroxide–olefin reaction exceeded the rate of unimolecular decomposition of peroxide by more than 100-fold. The kinetic data are summarized in Table I.

TABLE I

REACTION OF m,m'-DIBROMOBENZOYL PEROXIDE (P) WITH TETRAMETHYLETHYLENE (TME) IN BENZENE AT 44.8°

Run no.	Reactants, $M \times 10^2$ P	TME	G^a	$k_2 \times 10^5\ M^{-1}$ sec.$^{-1}$ P^b	$k_1 \times 10^5$ sec.$^{-1}$ $G^{a,c}$
1	1.00	0	0	d	
2	1.00	0	0.095	e	
3	0	100	0.95		23.2
4	5.00	111	0	4.71	
5	5.00	97	0	4.70	
6	5.00	47	0	4.72	
7	5.00	100	0.95	5.13	24.0
8	5.00	112	0.90	4.83	
9	5.00	100	0	1.0^f	
10	5.00	100	0	9.1^g	

^{a} Galvinoxyl, see ref. 2 and 3. ^{b} Titrimetric. ^{c} Spectroscopic. ^{d} k_1 for peroxide decomposition = 1.84×10^{-7} sec.$^{-1}$. ^{e} k_1 = 1.98×10^{-7} sec.$^{-1}$. ^{f} At 30.3°. ^{g} At 54.8°.

Compound	Atom % excess O^{18} per molecule	
	Expt. A	Expt. B
Tetramethylethylene oxide	0.00	0.00
m,m'-Dibromobenzoic anhydride	1.596	1.602
m-Bromobenzamide[a]	0.501	0.537
m-Bromobenzoic acid[a]	1.100	1.069
m-Bromobenzoic acid	0.31[b,c]	
m-Bromobenzoic anhydride	0.47[b,c]	

[a] From ammonolysis of anhydride (ref. 5). [b] From equilibration experiment of unlabeled anhydride with m-bromobenzoic acid of 1.81 atom % excess O^{18}. [c] Ratio of O^{18} between acid and anhydride observed, 0.66; calcd. for complete equilibration, 0.67.

Although the principal products of the reaction—epoxide and anhydride—are suggestive of a direct reaction rather than a chain reaction, it was desired to ascertain whether chain reaction was of any importance here. In the case of m,m'-dibromobenzoyl peroxide and p,p'-dimethoxy-*trans*-stilbene, experiments employing the hindered phenoxyl radical galvinoxyl[2,3] indicated that the major course of that peroxide–olefin reaction proceeded by direct reaction, on which was superimposed a radical chain reaction of short chain length. The suitability of galvinoxyl for that study originated in the inertness of galvinoxyl towards the reactants, a condition that does not extend to tetramethylethylene. In spite of the concomitant reaction of galvinoxyl with tetramethylethylene,[4] the kinetic data for this peroxide–olefin reaction in the presence of galvinoxyl are informative on the nature of the reaction. In the presence of all three components (peroxide, olefin in large excess, and galvinoxyl), galvinoxyl exerts only a small effect (a small increase, see Table II of ref. 2) on the rate of disappearance of peroxide; the rate of disappearance of galvinoxyl in the presence of both tetramethylethylene and the peroxide is essentially the same as in the presence of olefin alone. (For runs 7 and 3, in 30 min. the extent of consumption of galvinoxyl was 35.4% and 35.5%, respectively. The extent of destruction of peroxide in run 7 in 30 min. was 8.84%; the extent of unimolecular decomposition of peroxide in 30 min. under the conditions of run 7 is calculated to be 0.034%.) Thus, in the presence of excess olefin, the galvinoxyl–olefin and peroxide–olefin reactions appear to proceed independently of each other. Since ample galvinoxyl was present in the reaction mixture, one concludes that the reaction of the peroxide with tetramethylethylene does not provide scavengeable radicals, thereby excluding radical chain mechanisms from consideration for the peroxide–olefin reaction. Further refinement of mechanism was sought in studies employing oxygen-18. Oxygen-18 data for the reaction of m,m'-dibromobenzoyl peroxide-*carbonyl*-O^{18} with tetramethyl ethylene (Table II) show that the oxygen in the tetramethylethylene oxide is derived exclusively from oxygen of the peroxygen bridge of the peroxide. The distribution of

oxygen-18 in anhydride was determined by cleavage to amide and acid under conditions that have been shown not to effect equilibration of the oxygen atoms during the ammonolysis.[5] The ratio of oxygen-18 in acid to amide is 2.2, 2.0, close to the value calculated for complete equilibration (O^{18}-acid/O^{18}-amide: 2.0). Such equilibration might occur under the conditions of the experiment by interchange of anhydride with the small amount of m-bromobenzoic acid produced by the peroxide–olefin reaction. In a control experiment (Table II, last two entries) complete equilibration *did* occur between acid labeled with oxygen-18 and the anhydride in 30 min. at 80° in benzene. (The acid was not sufficiently soluble to duplicate the actual peroxide–olefin reaction conditions of 45°, 6 hr.)

Discussion

It is of interest to compare the results of this system with those in several closely related reactions of peroxygen compounds from the following standpoints: (1) product composition, (2) point of attack of the nucleophile on diacyl peroxides, and (3) relative reactivity.

Product Composition.—With the aliphatic olefin, tetramethylethylene, the major products from reaction with the acyclic peroxide (m,m'-dibromobenzoyl peroxide) are derived from single oxygen transfer leading to epoxide and anhydride. Involvement of allylic hydrogens (formation of unsaturated ester plus acid) occurs but is of minor importance. In the reaction of the cyclic peroxide (phthaloyl peroxide) over-all involvement of allylic hydrogens is of major importance; the principal products are allylic monoesters of phthalic acid.[6] Towards diarylethylenes both the acyclic peroxide (m,m'-dibromobenzoyl peroxide) and the cyclic peroxide (phthaloyl peroxide) behave similarly in that the major products are 1:1 adducts. The acyclic peroxide affords a 2:1 mixture of d,l- and *meso*-dihydroanisoin bis-m-bromobenzoate[2]; phthaloyl peroxide affords a mixture of diester and lactone ortho ester of dihydroanisoin.[7] (In the reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene the stereochemistry was shown to be that of *cis* addition.[8])

The principal example of single oxygen transfer in other types of peroxygen compounds is the reaction of peracids with olefins. This type of process also has been observed as a minor pathway in the reaction of phthaloyl peroxide with olefins.[6a]

Point of Nucleophilic Attack.—For the diacyl peroxide–tetramethylethylene reaction of this study, the oxygen-18 data establish that the oxygen transferred originates from the peroxygen link. Whether the oxygen transfer occurs by a cyclic process (eq. 1), analogous to that suggested for the epoxidation of olefins by peracids,[9] or by ion-pair paths[10] cannot be said, since the facile interchange between anhydride and

(3) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

(4) From a product study of the galvinoxyl–tetramethylethylene reaction, hydrogalvinoxyl was isolated in low yield. No other discrete product was obtained from the residual tar.

(5) (a) M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Am. Chem. Soc.*, **78**, 2563 (1956); (b) D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957); **79**, 3701 (1957).

(6) (a) F. D. Greene and W. W. Rees, *ibid.*, **80**, 3432 (1958); (b) **82**, 890 (1960).
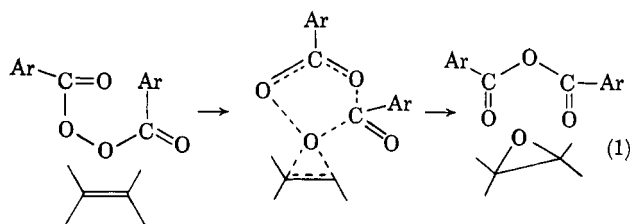
(7) Unpublished results of these laboratories.

(8) F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2250 (1956).

(9) P. D. Bartlett, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.). **11**, 47 (1950).

(10) M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Am. Chem. Soc.*, **78**, 2563 (1956).

$$Ar-C=O \quad Ar \quad \longrightarrow \quad \cdots \quad \longrightarrow \quad \cdots \quad (1)$$

acid (which is formed as a side product) effaces the oxygen-18 distinction between oxygen atom transfer by these two paths.

The preferential attack of a nucleophile on a peroxygen atom of a diacyl peroxide, demonstrated in this work for the peroxide–olefin reaction, previously has been established for the reaction of aroyl peroxides with triphenylphosphine[10] (forming anhydride and triphenylphosphine oxide) and with tributylphosphine,[5b,11] for the reaction of benzoyl peroxide with the α-ethoxyethyl radical[12] (forming α-ethoxyethyl benzoate), with the triphenylmethyl radical[13] (forming triphenylmethyl benzoate), and with dibenzylamine[14] (forming N,N-dibenzylhydroxylamine benzoate). This pattern may also obtain in the reaction of sodio acetoacetate with benzoyl peroxide.[15]

Relative Reactivity.—A number of comparisons on the effect of variation in olefin structure on rate of reaction with peroxygen compounds in the series, perbenzoic acid, phthaloyl peroxide, and m,m'-dibromobenzoyl peroxide[16] are summarized in Table III. Towards all three of these peroxygen compounds, electron-donating groups on the olefin enhance the rate of reaction.[17] Two features of note in this table are (1) the enhanced reactivity of peracid towards the aliphatic olefins, and (2) the enhanced reactivity of phthaloyl peroxide and m,m'-dibromobenzoyl peroxide towards *trans-p,p'*-dimethoxystilbene (associated in part, with a greater sensitivity to electron-donating

TABLE III

RELATIVE REACTIVITY OF PEROXYGEN COMPOUNDS TOWARD OLEFINS IN BENZENE AT 30° ($k_2 \times 10^3$, M^{-1} SEC.$^{-1}$)

Olefin	Perbenzoic acid	Phthaloyl peroxide	m,m'-Dibromobenzoyl peroxide
Tetramethylethylene	3000[a]	20[b]	0.01[c]
Cyclohexene	31[d]	0.2[b]	<0.0001[c]
trans-4,4'-Dimethoxystilbene	12.8[e]	1700[f]	0.23[g]
trans-4-Methoxystilbene	3.14[e]	30[b]	0.007[g]
trans-Stilbene	0.66[e]	0.6[b]	

[a] Estimated from the data cited in ref. 17. [b] Estimated from the data of ref. 6a. [c] An upper limit for k_2. The rate constant for unimolecular decomposition of peroxide under these conditions is estimated to be 4×10^{-8} sec.$^{-1}$ These data indicate little enhancement by cyclohexene on the rate of decomposition of this peroxide. [d] Ref. 17. [e] Ref. 18. [f] Ref. 7. [g] Estimated from the data of ref. 2.

(11) The reaction of this phosphine with *t*-butyl perbenzoate also has been studied: D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Am. Chem. Soc.*, **82**, 1726 (1961).

(12) D. B. Denney and G. Feig. *ibid.*, **81**, 5322 (1959); J. C. Martin and E. H. Drew, *Chem. Ind.* (London), 929 (1959).

(13) W. von E. Doering. K. Okamoto, and H. Krauch, *J. Am. Chem. Soc.*, **82**, 3579 (1960).

(14) D. B. Denney and D. Z. Denney, *ibid.*, **82**, 1389 (1960); also see R. Huisgen and F. Bayerlein, *Ann.*, **630**, 138 (1960).

(15) S. O. Lawesson and C. Berglund, *Acta Chem. Scand.*, **13**, 1716 (1959).

(16) For leading references, see ref. 2 and 6a.

(17) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

substituents for the reaction of the stilbenes with these peroxygen compounds *vs.* reaction with the peracid).

For peracid epoxidations, from the known dependence of rate on olefin and on peracid structure,[17,18] one may estimate the rate of epoxidation of tetramethylethylene by m-bromoperbenzoic acid in benzene at 30° to have a k_2 of 11 M^{-1} sec.$^{-1}$. Thus, although both m,m'-dibromobenzoyl peroxide and m-bromoperbenzoic acid hand over a single oxygen atom to tetramethylethylene the latter is a million times more effective than the former.

Experimental

Oxygen-18 analyses were performed by Dr. Josef Nemeth, University of Illinois. The oxygen-18 data are summarized in Table II and were calculated by the equations of Miller and Anderson.[19]

m,m'-**Dibromobenzoic anhydride** was prepared by the action of water on the acid chloride in pyridine. Several recrystallizations from hexane afforded material of m.p. 98–99°.

Anal. Calcd. for $C_{14}H_8Br_2O_3$: C, 43.80; H, 2.10; Br, 41.62. Found: C, 43.99; H, 2.19; Br, 41.86.

Tetramethylethylene oxide was prepared by the action of ethereal perbenzoic acid on tetramethylethylene (b.p. 73°) and collected from a g.l.p.c. 550 silicone column, b.p. 93° (lit. b.p. 93°); infrared in carbon tetrachloride, 3000 (s), 2980 (s), 1468 (m), 1372 (s), 1202 (s), 1168 (s), 1137 (s), 895 (w), 840 (s) cm.$^{-1}$; n.m.r. in deuteriochloroform, single band at 8.78 τ.

m,m'-**Dibromobenzoyl Peroxide-***carbonyl***-O^{18}.**—To a solution of sodium peroxide in 38 ml. of water, cooled to 0°, was added a solution of 6.55 g. (0.03 mole) of m-bromobenzoyl chloride-O^{18} (prepared from the acid by the action of thionyl chloride) in 10 ml. of cyclohexane within 10 min., keeping the temperature of the reaction mixture below 5°. After 30 min. of additional stirring, the reaction mixture was filtered on a sintered glass funnel and washed well with water. The peroxide was dissolved in chloroform and precipitated by addition of several volumes of methanol. Repeated crystallization afforded 4.18 g. (0.0105 mole), m.p. 125.5–126°, of m,m'-dibromobenzoyl peroxide-*carbonyl*-O^{18} better than 99% pure, by iodometric titration.

Reaction of m,m'-Dibromobenzoyl Peroxide with Tetramethylethylene.—To a dry, constricted test tube was added 2.0 g. (0.005 mole) of m,m'-dibromobenzoyl peroxide and 5 ml. of tetramethylethylene. The tube was degassed on the vacuum line and sealed under reduced pressure. It was heated at 80° for 10 min. to dissolve the peroxide and then placed in a constant temperature bath at 44.8° for 6 hr. After removal from the bath the tube was centrifuged. The supernatant liquid was removed from the white precipitate by means of a dropper. To the solid, 2 ml. of tetramethylethylene was added, and the test tube was centrifuged again. The tetramethylethylene and the liquid reaction product were combined.

A. Tetramethylethylene Oxide.—The combined tetramethylethylene wash and liquid reaction products were distilled at aspirator pressure, trapping the volatile reaction products in a Dry Ice–acetone-cooled container. The volatile reaction products, 4.55 g., were analyzed on a 550 silicon oil column at 60.5°. In addition to unchanged tetramethylethylene, a new peak was present in the chromatogram. The compound was collected and identified as tetramethylethylene oxide by identity of the infrared spectrum and retention time on the column with the authentic substance. Quantitative study by means of v.p.c. showed that the solution was 7.9% tetramethylethylene oxide (72% yield based on initial moles of benzoyl peroxide).

B. m-Bromobenzoic Acid.—The solid reaction product obtained from the centrifugation of the reaction mixture and the residue from the distillation experiment were dissolved in ether and separately extracted with 5% aqueous sodium bicarbonate. The basic extracts were neutralized with hydrochloric acid, extracted with methylene chloride, and dried over anhydrous magnesium sulfate. After filtration and removal of the solvent at reduced pressure, a total of 0.259 g. (13% yield based on initial moles of peroxide), m.p. 156–157°, of m-bromobenzoic acid was

(18) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(19) W. G. Miller and L. Anderson, *Anal. Chem.*, **31**, 1668 (1959).

isolated. The identity of the acid was shown by mixture melting points with the authentic m-bromobenzoic acid.

C. m,m'-Dibromobenzoic Anhydride.—The neutral ether solution, from which the m-bromobenzoic acid was extracted was dried over anhydrous magnesium sulfate. After filtration, and removal of the solvent at reduced pressure, 1.8 g. of a white residue was obtained. Fractional recrystallization from n-hexane afforded 1.35 g. (70% yield based on initial moles of peroxide), m.p. 90–94°, of a crystalline precipitate. An infrared spectrum in carbon tetrachloride was virtually identical with m,m'-dibromobenzoic anhydride. The anhydride was purified by recrystallization from n-h xane, m.p. 98–99°, m.m.p. 98–99°.

The solvent was evaporated from the mother liquor and the residue was recrystallized until the final mother liquor showed no anhydride absorption (1790 and 1720 cm.$^{-1}$) in the infrared spectrum. In this manner, another 0.1 g. (5% yield based on the initial moles of peroxide), m.p. 89–96°, of m,m'-dibromobenzoic anhydride was obtained. The total anhydride yield thus was 75%.

D. Characterization of the Residual Oil.—The mother liquor, after removal of all m-bromobenzoic anhydride and evaporation of the solvent consisted of a yellowish, sweet-smelling oil. An infrared spectrum of this oil in carbon tetrachloride showed ester absorption at 1720 (s), gem-dimethyl group absorption at 1380 and 1365 (m), and terminal methylene absorption at 900 cm.$^{-1}$ (m).

1. Saponification of the Residual Oil with Potassium Hydroxide.—To a solution of 10 ml. of 10% aqueous potassium hydroxide was added 0.200 g. of the residual oil. Under a nitrogen atmosphere, the reaction mixture was heated at reflux for 10 hr. The reaction mixture was cooled and extracted with methylene chloride. The methylene chloride solution was dried over anhydrous magnesium sulfate. An infrared spectrum of the neutral extract in chloroform indicated that all the ester was saponified (no absorption at 1720 cm.$^{-1}$). No well defined material could be isolated from the neutral extract.

The basic aqueous solution was acidified, and the precipitate was collected and dried over phosphorus pentoxide at high vacuum to yield 0.120 g. of m-bromobenzoic acid, m.p. 156–158°.

2. Hydrogenation of the Residual Oil.—To a solution of 0.179 g. of the residual oil in 3 ml. of freshly distilled tetrahydrofuran was added 0.018 g. of platinum oxide. A total of 20 ml. (STP) of hydrogen was taken up. The reaction mixture was filtered and the solvent removed at reduced pressure. The residue was dissolved in ether and extracted with 5% aqueous sodium bicarbonate. The basic aqueous extract was acidified and filtered. The precipitate, after drying over phosphorus pentoxide at high vacuum, was 0.035 g. of m-bromobenzoic acid, m.p. 154–157°, m·m.p. 154–156°. The neutral ether solution was dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, an infrared spectrum in carbon tetrachloride of the residue indicated ester absorption at 1720 (s) and gem-dimethyl group absorption at 1380 and 1365 cm.$^{-1}$ (m).

Reaction of m,m'-Dibromobenzoic Anhydride-O^{18} with Ammonia.—The m,m'-dibromobenzoic anhydride was obtained by allowing m,m'-dibromobenzoyl peroxide-carbonyl-O^{18} to react with tetramethylethylene under the conditions of the previous product study. The anhydride was rigorously purified by

fractional crystallization from n-hexane until a melting point of 98–99° was obtained. A 96-mg. sample of the m,m'-dibromobenzoic anhydride-O^{18} was ammonolyzed in 20 ml. of ammonia at −33° and the acid and amide were worked up by the published procedure.[5] The m-bromobenzamide was recrystallized from an ether–pentane mixture affording 28 mg., m.p. 153–155°. Recrystallization of the amide from methanol–water afforded 23 mg., m.p. 153–155°.

The basic aqueous solution was acidified with hydrochloric acid and the precipitate collected. Recrystallization from n-hexane gave 0.046 g., m.p. 154–156°, of m-bromobenzoic acid. Repeated crystallization from n-hexane raised the melting point to 155–157°. Recrystallization from a methanol–water mixture afforded 0.028 g., m.p. 155–157°, of acid. The m-bromobenzamide and m-bromobenzoic acid were dried over phosphorus pentoxide at high vacuum for 3 days prior to analysis for oxygen-18. (A mixture melting point of amide and acid was 120–130°.)

Exchange Reaction of m-Bromobenzoic Acid-O^{18} with m,m'-Dibromobenzoic Anhydride.—The m,m'-dibromobenzoic anhydride (0.72 g. or 1.88 mmoles) and m-bromobenzoic acid (0.13 g. or 0.65 mmole) were added to 2.5 ml. tetramethylethylene (concentration at which the reaction of labeled m,m'-dibromobenzoyl peroxide with tetramethylethylene was studied). After degassing the tube was sealed and heated at 80° for 45 min. On cooling, a precipitate formed; 15 ml. of ether was added and the resulting solution was extracted with cold aqueous sodium bicarbonate solution (a control experiment established that washing with cold aqueous sodium bicarbonate does not effect the hydrolysis of m,m'-dibromobenzoic anhydride in ether). The basic extracts were washed with ether and then neutralized with hydrochloric acid. Several recrystallizations from hexane and a mixture of methanol–water afforded acid of m.p. 155–156°.

Galvinoxyl was prepared and purified by the method described previously.[2]

Kinetics.—The procedure described previously[2] was employed. A representative run is reported in Table IV.

TABLE IV

REACTION OF m,m'-DIBROMOBENZOYL PEROXIDE[a] WITH TETRAMETHYLETHYLENE[b] IN THE PRESENCE OF GALVINOXYL[c] AT 44.8° IN BENZENE

Time (sec. × 10^{-3})	S$_2$O$_3^{-2}$,[d] ml.	O.D.$_t$ (λ, 434 mμ)	k_1 × 10^5 sec.$^{-1e}$
0.0	10.43	0.236	
1.8	9.45	0.186	5.38
3.6	8.65	0.142	5.18
5.4	7.84	0.102	5.30
7.2	7.07	0.076	5.40
9.0	6.45	0.076	5.35
10.8	5.85	0.044	5.35
14.4	4.75	0.035	5.45
18.0	4.00	0.033	5.31
21.6	3.25	0.032	5.40

[a] 0.05 M initial concentration. [b] 1.12 M initial concentration. [c] 0.00190 M initial concentration. [d] Corrected for galvinoxyl titer. [e] $k_1 = 5.35 \pm 0.0535 \times 10^{-5}$ sec.$^{-1}$, $k_1 = 4.78 \times 10^{-5}$ M^{-1} sec.$^{-1}$, % average deviation = 1.00%.