Anal. Calcd. for $C_8Cl_2F_{16}$: F, 64.5; Cl, 15.1; mol. wt., 471. Found: F, 64.5; Cl, 14.6; mol. wt., 437, 458.

II. **Preparation of Perfluoro-(2-allyl-3-methyloxetane).**—Perfluoro-2-(3-fluoroformylpropyl)-3-methyloxetane (11.16 g.) was mixed with 60 ml. of water, and a solution of 4 g. of sodium hydroxide in 25 ml. of water was added until the solution was just alkaline as indicated by phenolphthalein. The solution was then evaporated to dryness on the steam bath, and the resulting salt was dried at 95° in a vacuum oven.

The dried salt was placed in a flask connected through an acetone–solid carbon dioxide cooled trap to a water pump. The system was evacuated, and the flask was heated at 220–265° for several hours. Upon distillation of the trap contents (7.96 g., 86%), there was obtained 6.19 g. (66%) of perfluoro-(2-allyl-3-methyloxetane) distilling at 79–82°.

Anal. Calcd. for $C_7F_{12}O$: C, 25.6; F, 69.5. Found: C, 26.3; F, 69.5.

Purification of Products.—The products, the infrared spectrum of which revealed the presence of small amounts of carbonyl-containing impurities, were shaken with methanolic potassium hydroxide, then with water, dried over anhydrous magnesium sulfate and redistilled.

Many of the products were analyzed by gas chromatography. The details of these analyses are given in Table IV. Preparative scale separations of isomers, such as obtained in the aldehyde-olefin and acyl fluoride-olefin reactions, were carried out in the usual way, generally with 6' × 3/4" columns packed with the same materials as used in the analytical column.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Anchimerically Accelerated Bond Homolysis. II.[1] Neighboring Iodide and Sulfide Groups in *t*-Butyl Perester Decompositions

BY W. G. BENTRUDE AND J. C. MARTIN[2]

RECEIVED OCTOBER 14, 1961

Very large accelerations of the first-order thermal decompositions of *o*-substituted *t*-butyl perbenzoates are provided by certain substituents. Relative rates of decomposition in chlorobenzene at 60° vary with *o*-substituent in the order: C_6H_5S– 2.45×10^4; CH_3S–, 1.41×10^4; I–, 54.1; $(CH_3)_3C$–, 3.8; H–, 1.0. The tremendous rate enhancements observed with the first two of these peresters and the lesser effects accompanying the decomposition of the *o*-iodoperbenzoate are ascribed to neighboring-group participation in a homolytic bond cleavage, the O–O bond cleavage being accompanied by simultaneous O–S (or O–I) bond formation, probably involving an expansion of the sulfur (or iodine) valence octet. The free-radical nature of these decompositions is attested to by product composition and by the results of radical scavenging studies using stable free radicals as scavengers.

The effects of substituents upon rates of the thermal first-order decompositions of substituted benzoyl peroxides and of *t*-butyl perbenzoates have received considerable attention. The influence of *meta* or *para* substituents upon these rates has been shown[3–6] to be well correlated by the Hammett $\sigma\rho$ relationship. For the decompositions[4] of substituted benzoyl peroxides in dioxane, $\rho = 0.374$[5] at 80°. The perbenzoates decompose[5,6] in diphenyl ether with rates correlated with σ-constants by a ρ of -0.678 at 110.1°. These relatively small substituent effects, the largest differences in rate within a series corresponding to a factor of approximately ten, have been explained on the basis of an inductive effect. The ground state free energy of the molecules is increased or decreased by changing the magnitude of an unfavorable dipole–dipole interaction between the two fragments joined by the O–O bond.

The effect of *o*-substituents on decomposition rates has been known[7] for some time to be, at least in some cases, much larger than the effect of the corresponding *m*- or *p*-substituent. In general *o*-substituted benzoyl peroxides decompose more rapidly than the corresponding *p*-isomers by factors in the range 2–20. Cooper[7] observed an increase in rate of approximately 1000 when he compared the rate of decomposition of bis-(*o*-iodobenzoyl) peroxide with that of its *p*-isomer. On observing an increase in rate with the size of the *o*-substituent in a series of bis-(*o*-halobenzoyl) peroxides, Cooper postulated that the acceleration reflected a steric effect depending on the space-filling properties of the substituent.

Leffler,[8,9] in a careful study of the decomposition of the same iodo-substituted peroxide, confirmed the magnitude of the rate enhancement observed by Cooper[7] and suggested that its origin lay in the operation of a "heavy atom" effect,[9] the inhomogeneous magnetic field around the iodine nucleus enhancing the probability of an electronic singlet–triplet transition in the nearby O–O bonding electrons. Alternative explanations involving "trapping, by a concerted process or otherwise, of a nascent intermediate" were also suggested by Leffler.[9]

In a previous communication,[1] we presented preliminary evidence that the thermal decompositions of *t*-butyl *o*-iodoperbenzoate and of *t*-butyl *o*-(methylthio)-perbenzoate are actually *anchimerically*[10] *accelerated* through the action of the *ortho* groups. Decomposition through a singlet transition state (represented for *t*-butyl *o*-(methylthio)-perbenzoate by canonical forms I and II) stabilized

---

[1] For Part I see J. C. Martin and W. G. Bentrude, *Chemistry & Industry*, 192 (1959).

[2] Taken from the Ph.D. thesis of W. G. Bentrude, University of Illinois, June, 1961. Presented in part before the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 46-O of Abstracts.

[3] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).

[4] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[5] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[6] A. T. Blomquist and I. A. Bernstein, *J. Am. Chem. Soc.*, **73**, 5546 (1951).

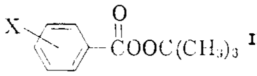
[7] W. Cooper, *J. Chem. Soc.*, 3106 (1951).

[8] J. E. Leffler, C. C. Petropoulos and R. D. Faulkner, *Chemistry & Industry*, 1238 (1956).

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

[10] S. Winstein, C. R. Lindegren, H. Marshall and L. Ingraham, *ibid.*, **75**, 147 (1953).

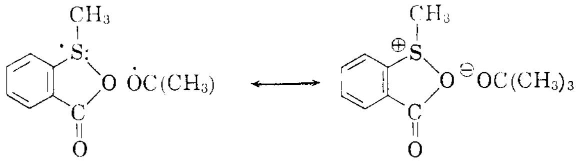
TABLE I

DECOMPOSITION OF  IN CHLOROBENZENE

Run	X	P_0,[a] mole/l.	Inhibitor	T, °C.	k,[e] sec.$^{-1}$
1	*o*-CH_3S	0.042	None	50.1	$(2.42 \pm 0.04) \times 10^{-4}$
2	*o*-CH_3S	.21	None	50.1	$(2.47 \pm .05) \times 10^{-4}$
3	*o*-CH_3S	.42	None	50.1	$(3.55 \pm .09) \times 10^{-4}$
4	*o*-CH_3S	.042	1 *M* sty[b]	50.3	$(1.94 \pm .02) \times 10^{-4}$
5	*o*-CH_3S	.042	0.2 *M* sty	50.2	$(1.88 \pm .01) \times 10^{-4}$
6	*o*-CH_3S	.042	0.2 *M* AN[c]	50.2	$(1.90 \pm .03) \times 10^{-4}$
7	*o*-CH_3S	.042	0.02 *M* S[d]	50.2	$(2.51 \pm .06) \times 10^{-4}$
8	*o*-CH_3S	.042	None	34.8	$(3.96 \pm .08) \times 10^{-5}$
9	*o*-CH_3S	.042	None	39.7	$(7.77 \pm .14) \times 10^{-5}$
10	*o*-CH_3S	.042	None	69.8	$(1.96 \pm .03) \times 10^{-3}$
11	*p*-CH_3S	.042	None	120.4	$(1.75 \pm .05) \times 10^{-4}$
12	*o*-I	.031	None	85.0	$(4.02 \pm .04) \times 10^{-5}$
13	*o*-I	.031	None	102.4	$(2.58 \pm .02) \times 10^{-4}$
14	*o*-I	.031	None	118.8	$(1.32 \pm .02) \times 10^{-3}$
15	*o*-$(CH_3)_3C$	.040	None	100.1	$(3.81 \pm .02) \times 10^{-5}$
16	*o*-$(CH_3)_3C$	.040	None	119.8	$(4.50 \pm .09) \times 10^{-4}$
17	*o*-$(CH_3)_3C$	.040	None	135.9	$(2.38 \pm .03) \times 10^{-3}$
18	*o*-C_6H_5S	.032	None	39.7	$(1.01 \pm .02) \times 10^{-4}$
19	*o*-C_6H_5S	.032	None	53.8	$(5.23 \pm .06) \times 10^{-4}$
20	*o*-C_6H_5S	.032	0.2 *M* sty	53.8	$(4.58 \pm .07) \times 10^{-4}$
21	*o*-C_6H_5S	.032	None	70.0	$(2.62 \pm .04) \times 10^{-3}$

[a] P_0 is initial perester concentration. [b] sty means styrene. [c] AN represents acrylonitrile. [d] S means sulfur. [e] Errors expressed as standard deviations, 68% confidence limits.

by bond formation between oxygen and the neighboring group was postulated. In this paper results are presented which confirm this view.



I II

Results

Peresters.—The peresters decomposed in this study were routinely synthesized in 20 to 34% yields from the acyl chlorides and *t*-butyl hydroperoxide by a modification of the method of Bartlett and Hiatt.[11] The aromatic acid percursors were commercially available or synthesized by literature procedures with the exception of *o*-(phenylthio)-benzoic acid. The published synthetic procedures leading to this acid involved[12a] the fusion of potassium *o*-chlorobenzoate and sodium thiophenolate in the presence of copper bronze or[12b] the reaction of sodium thiophenolate with *o*-carboxyphenyldiazonium ion. Neither of these procedures gave satisfactory yields in our hands. As an alternative method, methyl *o*-(phenylthio)-benzoate was prepared (in 42% yield) by the phenylation (with a diphenyliodonium salt) of sodium *o*-carbomethoxythiophenolate in methanol. This procedure is similar to that of Beringer, *et al.*,[13] for the phenylation of sodium *o*-carbomethoxyphenolate.

Rate Studies.—The results of careful rate studies of the first-order thermal decompositions in chlorobenzene of five substituted *t*-butyl perbenzoates appear in Table I. Rates were measured by following the disappearance of the perester carbonyl stretching frequency by infrared spectroscopy.

For purposes of comparison, the rates of decomposition of these peresters relative to that of *t*-butyl perbenzoate are compiled in Table II. Rates were computed from the activation parameters given.

The apparent first-order rate constant for the decomposition of *t*-butyl *o*-(methylthio)-perbenzoate was reduced by about 22% by the addition of the inhibitors, styrene or acrylonitrile (by comparison of runs 1, 4, 5 and 6). Further, a tenfold increase in initial perester concentration caused a 47% increase in the apparent first-order rate constant (comparison of runs 1 and 3). Although first-order plots remained linear throughout the concentration range, the results stated show that the unimolecular decomposition of *t*-butyl *o*-(methylthio)-perbenzoate is accompanied by an induced decomposition of higher than first order.[14] Activation parameters were determined from runs in which no inhibitor was added. For the decomposition of *t*-butyl *o*-(phenylthio)-perbenzoate at 53.8° the apparent first-order rate constant was decreased only 12% by the presence of 0.2 *M* styrene (from runs 19 and 20).

---

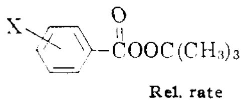
(11) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(12) (a) I. Goldberg, *Ber.*, **37**, 4526 (1904); (b) W. S. Weedon and H. W. Doughty, *Am. Chem. J.*, **33**, 386 (1905).

(13) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2708 (1953).

(14) A part of the rate increase observed on going to the more concentrated solution may be attributed to the change in medium on going from the dilute to the more concentrated solution. A forthcoming publication (J. C. Martin, W. G. Bentrude and D. L. Tuleen) will present evidence for a dependence on solvent polarity for this decomposition which is larger than usually expected for free-radical reactions. For a discussion of polar solvent effects in free-radical reactions, see J. E. Leffler, "The Reactive Intermediates in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 251.

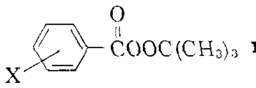
TABLE II

DECOMPOSITION OF  IN CHLOROBENZENE

X	Rel. rate at 60°	Rel. rate at 120.4°	$\Delta H^{\ddagger}$, kcal./mole[d]	$S^{\ddagger}$, e.u.[d]
o-C_6H_5S	2.78×10^4 $(2.45 \times 10^4)^b$	...	23.0 ± 0.03	−3.4 ± 0.2
o-CH_3S	1.81×10^4 $(1.41 \times 10^4)^c$	...	22.6 ± .2	−5.5 ± 1.3
o-I	54.1	...	28.0 ± .3	−0.8 ± 1.7
o-$(CH_3)_3C$	3.8	...	34.2 ± .5	12.5 ± 3.5
p-CH_3S	..	3	....	....
H[a]	1	1	33.5	7.8

[a] In *p*-chlorotoluene.[15] [b] Corrected for 12% induced decomposition. [c] Corrected for 22% induced decomposition. [d] The values for the activation parameters and their standard deviations were calculated from the absolute rate equation of Eyring using the method of least squares.

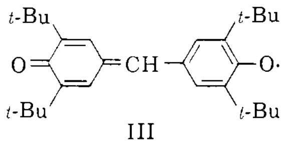
TABLE III

DECOMPOSITION OF  IN CHLOROBENZENE

Run	Perester	$P_0 \times 10^{3a}$	$G_0 \times 10^{4b}$	T, °C.	Atmosphere	$k \times 10^{5,c}$ sec.$^{-1}$	% linearity
22	o-CH_3S	9.00	6	39.5	N_2	2.16^d	80
23	o-CH_3S	9.00	6	39.5	N_2	2.15^d	82
24	o-CH_3S	9.00	3	39.4	N_2	2.16^d	76
25	o-CH_3S	4.50	6	39.4	N_2	...	Non-lin.
26	o-CH_3S	5.13	6	39.4	N_2	...	Non-lin.
27	o-CH_3S	9.00	6	39.5	Air	2.68 ± 0.005^c	80
28	o-CH_3S	9.00	6	39.4	Air	$2.55 \pm .01^c$	87
29	o-CH_3S	9.00	3	39.4	Air	$2.52 \pm .007^c$	94
30	o-CH_3S	4.50	6	39.4	Air	$2.63 \pm .008^c$	75
31	o-C_6H_5S	5.74	6	39.3	Air	$5.02 \pm .017^c$	85
32	o-C_6H_5S	2.87	6	39.3	N_2	$4.82 \pm .07^c$	90
33	o-C_6H_5S	5.74	3	39.3	Air	$5.01 \pm .02^c$	90
34	o-C_6H_5S	2.87	6	39.3	Air	$5.05 \pm .03^c$	85
Av.	o-CH_3S	Runs 28–30		39.4	Air	2.59	
Av.	o-C_6H_5S	Runs 31–34		39.3	..	4.98	

[a] P_0 is initial perester concentration in moles/liter. [b] G_0 is initial galvinoxyl concentration in moles/liter. [c] Rate constants and standard deviations by method of least squares. [d] Least squares treatment was not performed on this run, rate constant was obtained graphically from linear portion of curve.

Table III contains results obtained in chlorobenzene solvent by the use of the colored radical III, Coppinger's radical[16] or "galvinoxyl."[17,18] This radical absorbs strongly in the visible portion



III

of its spectrum.

Radical counting was carried out with scavenger concentrations in the range 6 × 10^{-4} M. To follow the scavenger concentration as a function of time the wave length 570 mμ (ϵ 760) was used. This wave length corresponds to a shoulder near the intense peak at 435 mμ. With pure solvent at this scavenger concentration, reproducible kinetic runs, linear to 75–94% completion, were obtained (Table III).

Purity of solvent is a necessity which cannot be overemphasized in connection with the decompositions measured by the scavenger reaction. Chlorobenzene, distilled from phosphorus pentoxide after drying over calcium chloride, gave solutions of galvinoxyl which were rapidly decolorized. When the solvent was further purified by distillation from potassium hydroxide pellets, chlorobenzene was obtained in which a galvinoxyl blank was stable, in the presence or absence of oxygen, over the time of the perester runs.

Oxygen has little apparent effect upon the radical-capture processes in the decomposition of *t*-butyl *o*-(phenylthio)-perbenzoate (comparison of runs 32 and 34) as the rate constants and linearity of the optical density *versus* time relation are nearly the same for runs in air and in thoroughly degassed samples under nitrogen. For *t*-butyl *o*-(methylthio)-perbenzoate an effect of oxygen is seen at 9.00 × 10^{-3} M initial perester concentration. Runs in which solutions had been degassed and over which was then introduced an atmosphere of nitrogen gave reproducible, largely linear plots of optical density *versus* time at two initial values of galvinoxyl concentration (see runs 22, 23 and 24). At half concentrations of initial perester, however, the plots from degassed runs were slightly concave upward (runs 25 and 26) and the rate of

---

(15) A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951).

(16) G. M. Coppinger, *ibid.*, **79**, 501 (1957).

(17) P. D. Bartlett, Abstracts of Papers, 16th National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June, 1959, p. 91.

(18) P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

galvinoxyl consumption was reduced. In the presence of air no dependence of rate upon either initial galvinoxyl or perester concentration was seen. The efficiency of radical scavenging apparently is increased in the presence of oxygen. Runs in duplicate (not all listed in Table III) confirmed the effects of the variation of reactant and oxygen concentrations in each case.

Rate constants determined using galvinoxyl as scavenger are compared with those obtained by infrared analysis (constants calculated from activation parameters in Table II) in Table IV.

TABLE IV

EFFICIENCY OF RADICAL CAPTURE WITH GALVINOXYL AS RADICAL SCAVENGER IN THE DECOMPOSITION OF IVa AND IVb AT 39.4°

Perester	$k \times 10^5$, sec.$^{-1}$ By i.r.	By galvinoxyl	$k_{\text{galv.}}/k_{\text{i.r.}}$
IVa	6.53 (5.10)[a]	2.59	0.40 (0.51)[a]
IVb	9.65 (8.49)[b]	4.98	0.52 (0.59)[b]

[a] Corrected for assumed 22% induced decomposition. [b] Corrected for assumed 12% induced decomposition.

Product Studies.—Products of the decomposition of a degassed sample of *t*-butyl *o*-methylthioperbenzoate in chlorobenzene are given in Table V.

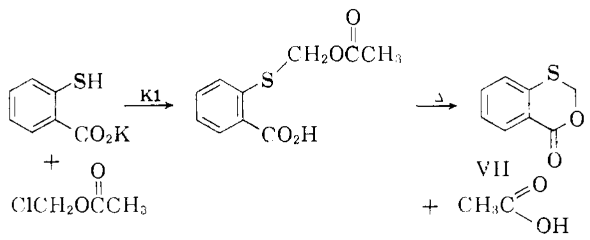
TABLE V

PRODUCTS FROM DECOMPOSITION OF *t*-BUTYL *o*-(METHYLTHIO)-PERBENZOATE (0.32 *M*) IN CHLOROBENZENE AT 70°

Product	Mole/mole of perester
Carbon dioxide	0.015
Isobutylene	.012
t-Butyl alcohol	.62
Acetone	.21
3,1-Benzoxathian-4-one	.12
o-(Methylthio)-benzoic acid	.30
Diphenyl disulfide 2,2'-dicarboxylic acid	.04
Three unidentified acids	..
Mole % *t*-butyl residue identified	85
Mole % acid residue identified	48
Weight % unidentified acids	26[a]

[a] Based on total weight non-distillable residue.

The identity of the 3,1-benzoxathian-4-one (VII) was suggested by the results of microanalysis and by the presence of hydrogens having a single sharp n.m.r. absorption peak at $\tau = 4.6$ in carbon tetrachloride and confirmed by comparison with a material synthesized by an adaption of the method used by Mowry[19] for the analogous 2-methyl-3,1-benzoxathiane-4-one.



The products of the decomposition of *t*-butyl *o*-(phenylthio)-perbenzoate were also isolated and are recorded in Table VI.

TABLE VI

PRODUCTS FROM THE DECOMPOSITION OF *t*-BUTYL *o*-(PHENYLTHIO)-PERBENZOATE (0.16 *M*) IN CHLOROBENZENE

Product	Mole/mole of perester[a,b]
Carbon dioxide[d]	0.007
Isobutylene[d]	.33
t-Butyl alcohol[d]	.39
Acetone[d]	.32
Diphenyl sulfoxide 2-carboxylic acid[e]	.17
o-(Phenylthio)-benzoic acid[e]	.28
Diphenyl diphenyl disulfide 2,2'-dicarboxylate[e]	.52
Unidentified compound[c,e]	..

[a] Mole % *t*-butyl residue identified, 104%. [b] Mole % acid residue identified, 97%. [c] 3% by weight of non-volatile products. [d] Volatile products determined from a run at 70°. [e] Non-volatile products determined from a run at 90°.

The isobutylene was determined by a combination of manometric measurements, infrared spectroscopy and gas-liquid phase chromatography (g.l.p.c.). The presence of a large proportion of isobutylene in the volatile products is supported by the n.m.r. spectrum of the crude decomposition reaction mixture.

When the *t*-butyl *o*-(phenylthio)-perbenzoate decomposed at room temperature in the absence of solvent, the products in Table VII were isolated by chromatography on silica gel.

TABLE VII

NON-VOLATILE PRODUCTS OF THE DECOMPOSITION OF *t*-BUTYL-*o*-(PHENYLTHIOPERBENZOATE AT ROOM TEMPERATURE WITHOUT SOLVENT

Product	Wt. % of total products
o-(Phenylthio)-benzoic acid	9
Diphenyl sulfoxide 2-carboxylic acid	42–47
Methyl *o*-(phenylthio)-benzoate	32
Unidentified compound[a]	13–18

[a] The unidentified compound is the same as that isolated from the decomposition in solution (Table VI).

Discussion

Nature of the Substituent Effect.—It is clear that the presence of an *o*-methylthio or an *o*-phenylthio grouping within the molecule of a substituted *t*-butyl perbenzoate renders it remarkably unstable. The thermal decomposition of such a substituted perbenzoate is accelerated by a factor of 10^3–10^4 relative to that of the unsubstituted perbenzoate. The acceleration of the perester decomposition produced by a *p*-methylthio group (a factor of three) is, in contrast, no larger than that which would be expected to result from the operation of an inductive influence such as has been postulated to explain the rate effects of other *p*-substituents in *t*-butyl perbenzoate decompositions.[6]

It appears, therefore, that the extraordinarily large accelerating influences of the *o*-methylthio and *o*-phenylthio groups operate directly through space in a manner which requires the proximity of the sulfide sulfur and the O–O bond being broken. At least three theories may be advanced to explain the dramatic rate enhancement seen in the decompositions of these peresters: (a) The first would propose that the strain imposed upon the molecule by non-bonding steric interactions be-

---

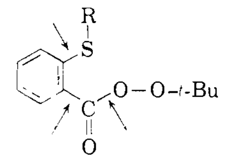
[19] D. T. Mowry, W. H. Yanko and E. L. Ringwald, *J. Am. Chem. Soc.*, **69**, 2358 (1947).

tween the *o*-substituent and the perester *t*-butoxy group is relieved as the O–O bond is lengthened on going to the transition state. Our rate studies indicate, however, that the *o*-*t*-butyl substituent has only a minor effect on the rate of decomposition (a fourfold increase relative to the rate for the unsubstituted perbenzoate). The contrastingly large acceleration provided by the less bulky sulfide substituents would seem clearly to indicate that their effect is largely electronic rather than steric in origin.

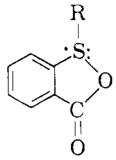
(b) If the effect of the sulfide groupings in the *o*-position were a manifestation of the so-called "heavy atom" effect,[20] *i.e.*, an effect of the inhomogeneous magnetic field about the sulfur nucleus acting to increase the probability of a forbidden singlet–triplet transition (one must now assume that passing through the transition state involves an electronic transition), the *o*-iodo substituent should cause an even greater rate enhancement than the sulfide sulfur substituent, because the iodine has the greater nuclear charge and nuclear magnetic moment. Note, however, that the *ortho* iodine increases the decomposition rate by a factor of fifty, whereas the sulfide sulfur *o*-substituents give a rate increase of several thousand-fold. A neighboring-group effect based on magnetic catalysis, as suggested by Leffler[8,9] in the bis-(*o*-iodobenzoyl) peroxide case, is unlikely here and probably is not operative in the peroxide analogy.

(c) Thirdly, one may postulate a singlet transition state in which the sulfur participates in a bonding interaction similar to that involved in ionic reactions. The transition state for decomposition may be represented by the canonical forms I and II. Structure I requires that sulfur expand its valence shell to accommodate nine electrons. (The odd electrons in I are, of course, to be considered paired in this representation.) This then is an anchimerically assisted decomposition leading to radical products. Previous possible examples of such an anchimeric assistance in a radical reaction have been based on the observation of very small accelerations with a resulting uncertainty of interpretation (see ref. 1 for a discussion of this point).

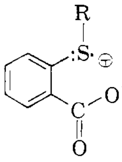
In a large number of perester decompositions, many of them involving simultaneous multiple bond cleavages, Bartlett and Hiatt found a correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ which suggested that the favorable $\Delta H^{\ddagger}$ for the decomposition of the more unstable peresters was obtained at the expense of restrictions of rotational degrees of freedom which were reflected in an unfavorable $\Delta S^{\ddagger}$. It was possible to discern from an inspection of their data, and a knowledge of the courses taken by the decompositions of individual peresters, ranges of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ characteristic of decompositions involving the restriction of rotation about 0, 1, 2 or 3 bonds on going to the transition state. It is interesting that the activation parameters for the decompositions of those of our peresters which decompose at an enhanced rate fall in the range of values observed by Bartlett and Hiatt[11] for perester decompositions in which the approach to the transition state involves the loss of rotational freedom about three bonds. Whether or not one wishes to push this agreement to the limit of postulating that three rotational degrees of freedom are frozen out on going to the transition states for the decompositions for which we postulate an anchimeric acceleration, it is certainly significant that the $\Delta H^{\ddagger}$ is drastically lowered for the sulfide peresters and is also lowered, although to a lesser degree, for *t*-butyl *o*-iodoperbenzoate. All three have negative entropies of activation. These changes in $\Delta S^{\ddagger}$ (from 7.8 e.u. for *t*-butyl perbenzoate) are certainly significant. The combination of lowered $\Delta H^{\ddagger}$ and lowered $\Delta S^{\ddagger}$ is compatible with a transition state in which stabilization is gained at the expense of rotational freedom as pictured by structures Ia and Ib. A loss of rotational freedom might be expected about the three bonds in IV which are indicated by arrows if the postulated reaction pathway is the correct one.



If we introduce the usual assumption that the reverse of the dissociation reaction, radical combination, has a negligible activation energy, then the dissociation energy of the O–O bond (D_{O-O}) for the IVa or IVb is about 23 kcal./mole. This value is to be compared with D_{O-O} of approximately 34 kcal./mole for *t*-butyl perbenzoate. It is, therefore, clear that the intermediate radicals formed in the decomposition of the unstable peresters reported herein cannot be ordinary *o*-substituted benzoyloxy and *t*-butoxy radicals but must be stabilized in some remarkable manner to the extent of some 9 kcal. One might reasonably postulate that the radicals formed have structures represented by Va and Vb.[21]



Va. $R = CH_3$
b. $R = C_6H_5$



VI

Radical Nature of Products.—If we are to establish that this mechanism is to be classed as an anchimerically assisted bond homolysis we must

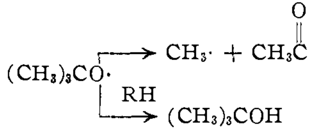
---

[20] M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

[21] While we prefer to write the structures of our postulated type of bridged radical as in V, the possible importance of resonance form VI in the description of the radical points up a similarity between the decompositions which are the subject of this study and the reactions between diacyl peroxides and tertiary amines [see C. Walling, "Free Radicals in Solution" John Wiley and Sons, Inc., New York, N. Y., 1957, for a discussion of this reaction]. The importance of this resonance form or, in a different rotational state, of this isomer of V in these decompositions will be discussed in the following part of this series[15] with the presentation of data bearing on the question.

first establish that the products are, indeed, free radicals rather than ions or singlet molecules. The first line of evidence bearing on this question may be discerned in the isolated products of these decompositions.

The volatile products from the decomposition of *t*-butyl *o*-(methylthio)-perbenzoate (IVa), *t*-butyl alcohol and acetone (Table V), are to be expected from a decomposition which yields intermediate *t*-butoxy radicals. The origin of acetone is particularly difficult to explain by a nonradical mechanism. A Criegee-type rearrangement, similar to that of 9-decalyl perbenzoate,[22a] could lead to acetone[22b] by a polar route involving the development of a partial positive charge on the *t*-butoxy fragment of the decomposing perester. Substituent effects, to be reported in a following paper,[16] establish that the polarization of the transition state is that predicted from canonical structure Ib. Such a polar route leading to acetone is, therefore, ruled out. Although neither methane nor ethane was detected in the decomposition products, it is possible that the methyl radicals expected from the reaction leading to acetone are incorporated in the unidentified acids or add to chlorobenzene.[23] Isobutylene is commonly formed in small amounts in the free-radical decompositions of *t*-butyl peresters.[11]



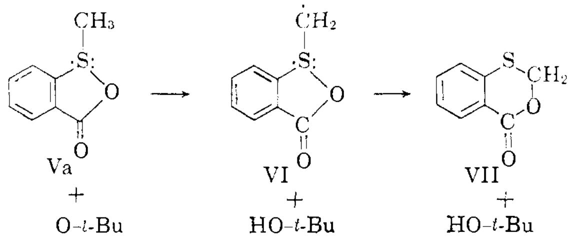
$$(CH_3)_3CO\cdot \rightarrow CH_3\cdot + CH_3\overset{\overset{O}{\|}}{C}CH_3$$
$$(CH_3)_3CO\cdot \xrightarrow{RH} (CH_3)_3COH$$

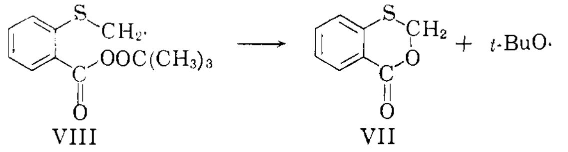
The presence of *o*-(methylthio)-benzoic acid among the decomposition products is not surprising and neither confirms nor rules out a radical decomposition mechanism. The origin of diphenyl disulfide 2,2′-dicarboxylic acid is obscure.

The complexity of products from the acid residue (non-distillable products) undoubtedly results from the presence of the S-methyl group. These methyl hydrogens are particularly labile to radical attack because of the radical-stabilizing influence of the adjacent sulfide sulfur and their abstraction leads to a multiplicity of products.

The complexity of this mixture made its separation extremely difficult and only the major components were isolated. The n.m.r. spectrum of the crude reaction mixture showed peaks (notably at $\tau = 3.65$) which were not present in any of the fractions obtained in the work up. This indicates that some of the initial products are extremely unstable.

Several mechanisms may be advanced to explain the origin of 3,1-benzoxathian-4-one (VII). It may arise from abstraction of hydrogen from the S-methyl group by the *t*-butoxy radical within the solvent cage (or by any other radical in the solution) followed by a rearrangement of the resulting diradical. These two steps may occur in a concerted manner. Alternatively, 3,1-benzoxathian-4-one (VII) may arise from an intramolecular attack of an S-methyl radical (VIII) on the oxygen of the O–O bond





The S-methyl radical could result from hydrogen abstraction from IVa by a radical species in solution. This is an interesting type of induced decomposition, and in view of the relatively large amount of radical-chain induced decomposition (about 22% of the over-all reaction at 50°) accompanying the primary decomposition, it seems quite likely that some type of abnormal inducing mechanism is operative. If the induced decomposition observed with this dissociation arises by the proposed intramolecular pathway, then styrene, which apparently halts the induced decomposition, should prevent the formation of 3,1-benzoxathian-4-one. An n.m.r. study was undertaken to determine the effect of added styrene upon the amount of heterocycle formed as measured by the intensity of the methylene–hydrogen peak at 5.10 τ (shifted 0.4 τ in chlorobenzene from the value determined in carbon tetrachloride). It was estimated that two to three times as much 3,1-benzoxathian-4-one was formed in the absence of styrene as when styrene (about 2 *M*) was present. Apparently the heterocycle is formed by a pathway which can be partially blocked by styrene. This fact excludes formation of all the heterocycle by a cage reaction and is consistent with the intramolecular induced decomposition mechanism. Of course, it may be only coincidental that styrene inhibits the induced decomposition and also reduces the amount of 3,1-benzoxathian-4-one formed. Styrene may be interrupting two separate and distinct pathways. However, the relatively small amount of induced decomposition accompanying the decomposition of *t*-butyl *o*-phenylthioperbenzoate (12% of the total rate) is further evidence that the S-methyl group is involved in promoting in some way the relatively large amount of induced decomposition observed with the methylthio analog. If all of the heterocycle is formed by this mechanism, then we must conclude that styrene is not effective in halting all induced decomposition.

While some of these products are indicative of a free-radical process, many of them could equally well have resulted from an ionic or molecular mechanism. Our failure to identify all of the products makes any attempt to draw further conclusions from these results unsatisfying.

---

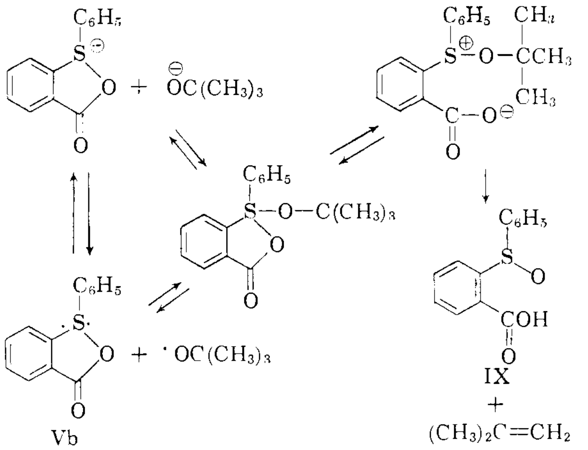
(22) (a) R. Criegee, *Ann.*, **560**, 127 (1948); (b) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **83**, 956 (1961).

(23) It is not unusual for decompositions of *t*-butyl peresters in chlorobenzene to produce little or no methane or ethane.[11] See M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 5981 (1954), for evidence of a major "loss" of methyl radicals in benzene solution, presumably as a result of addition of the radicals to the aromatic ring.

The products from the decomposition of *t*-butyl *o*-(phenylthio)-perbenzoate were, on the other hand, essentially all identified. The absence of the reactive methylthio grouping in the decomposition mixture apparently results in a product mixture much less complex and, incidentally, more characteristic of a free-radical process.

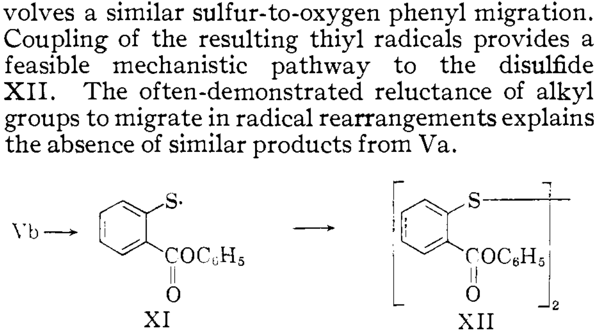
The amount of decarboxylation in the decomposition of *t*-butyl *o*-(phenylthio)-perbenzoate in chlorobenzene, as mirrored in carbon dioxide evolution, is again negligible. The volatile products contain the characteristic products from *t*-butoxy radicals, acetone (32%) and *t*-butyl alcohol (39%). The latter is found in a considerably smaller proportion than that formed in the presence of the hydrogen donating methylthio grouping of the previously described perester (62%). The absence of a good hydrogen donor in the reaction medium allows, in this case, the more effective competition of a reaction yielding isobutylene. Isobutylene is found in much larger amounts (~33%) in this product mixture than in those from the decompositions of most *t*-butyl peresters.

We may speculate that the large amount of isobutylene results, in part, from a reaction yielding another observed product, diphenyl sulfoxide 2-carboxylic acid (IX). Such products could be formed either from an ion pair or a radical pair intermediate. One plausible formulation is shown below. The postulate that the sulfoxide oxygen comes from the *t*-butoxy group of the original perester is to be tested using oxygen-18 tracer techniques.

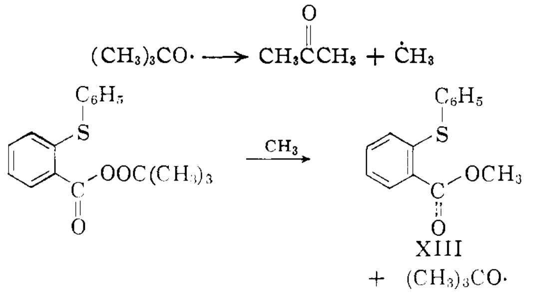


The observed *o*-(phenylthio)-benzoic acid in the product mixture might reasonably be expected to result from the proposed intermediate Vb by a simple abstraction of hydrogen from the solvent.

The major product, diphenyl diphenyl disulfide 2,2′-dicarboxylate (XII), accounting for 52% of the carboxylate residues, is most easily explained on the basis of a free-radical mechanism. Rearrangement of the proposed bridged radical Vb to give the thiyl radical XI has a close analogy in the rearrangement which occurs[24] in the radical decomposition of 2,2′-diphenoxybenzoyl peroxide giving 25% of phenyl salicylate. DeTar and Hlynsky[24] have postulated that this product is the result of an oxygen-to-oxygen phenyl migration in the intermediate carboxylate radical. In our case the conversion of Vb to the thiyl radical XI involves a similar sulfur-to-oxygen phenyl migration. Coupling of the resulting thiyl radicals provides a feasible mechanistic pathway to the disulfide XII. The often-demonstrated reluctance of alkyl groups to migrate in radical rearrangements explains the absence of similar products from Va.



The non-volatile products of the decomposition at room temperature of the phenylthio perester IVb without solvent (Table VII) differ principally from those formed in chlorobenzene solution in that a much larger amount of diphenyl sulfoxide 2-carboxylic acid (IX) is produced and an appreciable amount (32% by weight) of methyl *o*-(phenylthio)-benzoate (XIII), a product not observed in chlorobenzene solution, is observed. This latter compound could result from a radical-chain, induced decomposition involving the methyl radical in the two-step sequence shown below. Such a process would be expected to be much more important in the highly concentrated pure substrate than in the dilute solutions in chlorobenzene.


$$(CH_3)_3CO\cdot \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_3 + \dot{C}H_3$$

The occurrence of phenyl migration in the decomposition of *t*-butyl *o*-(phenylthio)-perbenzoate (IVb) suggests that the rate enhancement which is observed might be explained in terms of phenyl participation rather than sulfur participation. Similarly, the acceleration provided the decomposition of IVa by the neighboring methylthio group might be the result either of sulfur participation or of participation by neighboring hydrogen of the methylthio group. The near coincidence in rates for the two peresters suggests an explanation for the rate enhancement which involves a structural feature common to both, *i.e.*, the sulfur atom. Any other explanation requires an objectionably high degree of coincidence. Preliminary studies[25] indicate that the decomposition of *t*-butyl *o*-phenoxyperbenzoate is not appreciably more rapid than that of *t*-butyl perbenzoate. This suggests that phenyl participation is not important, at least in the oxygen analog of IVb.

Radical Scavenging Experiments.—A second line of evidence for the free-radical nature of these

---

[24] D. F. DeTar and A. Hlynsky, *J. Am. Chem. Soc.*, **77**, 4411 (1955).

[25] J. C. Martin and E. H. Drew, unpublished work.

decompositions involves experiments designed to trap radical intermediates using reactions distinctively free-radical in nature.

The copolymerization of styrene and methyl methacrylate at 50° initiated by perester IVa yields, under identical conditions, thirty times as much of a 1:1 copolymer as does a benzoyl peroxide initiated reaction. This is not, however a direct measure of the efficiency of radical production. The most convincing evidence that these are, indeed, largely free-radical decompositions is to be found in the results recorded in Table III involving the use of the radical scavenger "galvinoxyl" III.[16–18] This scavenger has been very effectively used in studies of several homolytic perester decompositions.[17,18] In our studies the disappearance of galvinoxyl in the presence of a large excess of perester is found to be zero order until 80–94% of the scavenger is destroyed. Knowing the perester concentrations, we may calculate first-order rate constants for the rates of formation of radicals in solution. Comparison of these rate constants with those determined by infrared spectrophotometry for the disappearance of the perester (Table IV) allows us to say that, under the conditions employed, more than half (51% for IVa and 59% for IVb) of the number of radicals expected if each perester molecule yields two free radicals is detected by reaction with the scavenger. A limited study using the more familiar scavenger, diphenylpicrylhydrazyl (DPPH),[26] showed similar results. As the efficiency of DPPH was only approximately 40% that of galvinoxyl, we were led to employ the latter scavenger in most of our work.

The fate of the remaining portion of the decomposed perester molecules which are not accounted for in the galvinoxyl study remains to be explained. Other perester decompositions[18] have shown efficiencies of scavenging as low as those found here, presumably for similar reasons. One or a combination of the following factors could explain the apparent inefficiency of galvinoxyl: (1) Explanations of apparent radical inefficiencies based on the inability of scavenger reactions to compete with geminate recombinations are not particularly meaningful for non-decarboxylative perester decompositions. However, if the concept of geminate recombination is expanded to include other reactions between original radical pairs before they become kinetically free, then one can imagine a whole class of geminate reactions. The inefficiency of a scavenger might then be explained by the inability of the scavenger reaction to compete with the geminate reactions.

The importance of this possibility merits discussion in the light of products isolated. Among the products of decomposition of *t*-butyl *o*-(methylthio)-perbenzoate (IVa), the heterocycle 3,1-benzoxathian-4-one (VII) has already been discussed in terms of its possible origin by a cage reaction. The possible formation of diphenyl sulfoxide 2-carboxylic acid (IX) by a geminate reaction of free radicals has also been discussed.

(2) Galvinoxyl may not be efficient enough to capture all radicals which survive the geminate reactions and become kinetically free. If such were the case we would expect[27] that the rate of the scavenging reaction would not then be independent of scavenger concentration. In the studies reported here, the rate of scavenger disappearance was constant over a twofold range of initial scavenger concentration. Within a run, the relation between scavenger and time was linear, often over more than 90% of a run covering a tenfold range of scavenger concentration.

This criterion (independence of rate on scavenger concentration) would not be a valid one if the scavenger failed to react at all with one of two dissimilar radicals generated in a decomposition. If such were the case the scavenger efficiency would remain, independent of scavenger concentration, at 50% (in the absence of any geminate reactions of radicals generated in the decomposition). Our data have been interpreted as meaning that up to 59% of the expected radicals are captured. While this is greater than the 50% maximum efficiency expected if only one type of radical (presumably the *t*-butoxy or methyl) were scavenged, it is not sufficiently greater to make us certain that this is not the situation. A very inefficient capture of one type of radical might increase the efficiency somewhat above 50% while not introducing a sufficiently large kinetic dependence on galvinoxyl concentration to make a pronounced deviation from the zero-order dependence expected for efficient scavenging of all radicals that escape the cage. The plausibility of such an explanation depends in part on our acceptance of the possibility that only a small fraction of generated radicals fails to escape the cage.

(3) The peresters may decompose by competing radical and non-radical mechanisms. The activation energies for the competing processes would not be expected to be the same (although they could, by coincidence, be identical) and, in the temperature range where competition is favored, a plot of log (k/T) *vs.* $1/T$ would probably not be linear. This plot is found to be linear over a 30–35° range for the peresters under consideration. If, however, the competition between ionic and free-radical pathways occurs after a rate-determining step shared in common between the two paths, the linearity of the activation plot would not allow us to rule on the plausibility of a competing ionic process. Evidence tending to rule out this possibility, namely that the percentage of radicals trapped or that the percentage of characteristically free-radical products is essentially independent of solvent polarity, is presented in the following part of this series.[15]

Until the results of a complete study of the products of the reaction with galvinoxyl are in hand, it is not possible to rule out either 1 or 2, above, as explanations of scavenger inefficiency. Either is compatible with the observed kinetic results.

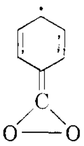
***t*-Butyl *o*-*t*-Butylperbenzoate.**—The kinetic studies on the decomposition of *t*-butyl *o*-*t*-butylperbenzoate are interesting with respect to the possibility put forth by Bartlett and Hiatt[11] that the benzoyloxy radical is stabilized by some type

---

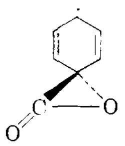
(26) A. Henglein, *Makromol. Chem.*, **15**, 188 (1955).

(27) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

of resonance interaction with the benzene ring. This postulate was made in possible explanation of the lower $\Delta H^{\ddagger}$ for *t*-butyl perbenzoate decomposition (33.5 kcal./mole) compared with that for *t*-butyl peracetate (38 kcal./mole). The similarity in $\Delta H^{\ddagger}$ for the decompositions of the *o*-*t*-butyl (34.2 kcal./mole) and the unsubstituted perbenzoates argues against structure XIV or any other which requires coplanarity of the carboxyl group and the ring as a representation of such an interaction. The bulky *o*-*t*-butyl substituent would make such a planar structure one of very high energy which would, therefore, not make a significant contribution to the stabilization of the transition state. This would lead us to expect a $\Delta H^{\ddagger}$ for the *o*-*t*-butylperbenzoate similar to that for the peracetate.



XIV



XV

If the similarity in $\Delta H^{\ddagger}$ for the two reactions does, indeed, reflect a similar degree of resonance stabilization for the benzoyloxy and the *o*-*t*-butylbenzoyloxy radicals, it is necessary to invoke an interaction in a conformation such as is pictured in XV, an α-lactone-type structure similar to that postulated by Walling,[28] as a possible intermediate in certain induced decomposition reactions of benzoyl peroxide. Another, perhaps more palatable, explanation for the small size of the increase in $\Delta H^{\ddagger}$ accompanying the introduction of the *o*-*t*-butyl substituent would account for the difference in the perbenzoate and the peracetate in terms of the ground state dipole–dipole interactions mentioned earlier.[4]

Experimental[29]

Materials.—Chlorobenzene, cyclohexane, methylene chloride and pentane were purified by shaking with concentrated H_2SO_4, washing with aqueous base and distilling. Pyridine was fractionally distilled from barium oxide. *t*-Butyl hydroperoxide (Lucidol Corporation) was distilled through a short column using a Dry Ice condenser; b.p. 32–33° (15 mm.).

***t*-Butyl *o*-(Methylthio)-perbenzoate (IVa).**—Technical grade thiosalicylic acid was converted to *o*-(methylthio)-benzoic acid by the method of Zincke and Siebert.[31] The resulting acid was converted to the acid chloride by the method of McClelland and Warren.[32]

In 125 ml. of dry ether were dissolved *t*-butyl hydroperoxide (2.75 g., 0.033 mole) and pyridine (3.12 g., 0.0395 mole). To this solution, stirred at −12°, was added, dropwise, over a period of 2 hr., a solution of *o*-(methylthio)-benzoyl chloride (4.67 g., 0.0231 mole) in 250 ml. of dry ether. The reaction mixture was stirred 9 days at approximately −10°. The ether-insoluble material was removed by filtration, the filtrate concentrated to 75 ml. and chromatographed on 250 g. of basic alumina at −15°. Ether was used as eluent. The perester, a white solid, was obtained analytically pure in 36% yield after one recrystallization from ether–pentane; 1.92 g., 0.0083 mole, m.p. 55.2–55.7°, single infrared peak at 1738 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{16}O_3S$: C, 59.96; H, 6.71. Found: C, 60.09; H, 6.69.

The ether-insoluble side product from this reaction, *o*-(methylthio)-benzoic anhydride, was separated from the pyridine hydrochloride by dissolving the amine salt in water. The water-insoluble solid was recrystallized from ether–pentane to give white needles, m.p. 122.0–122.5°, infrared peaks at 1710 and 1772 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_3S_2$: C, 60.35; H, 4.43. Found: C, 60.45; H, 4.45.

The anhydride was saponified with alcoholic potassium hydroxide to yield, upon acidification, *o*-(methylthio)-benzoic acid (m.p. 168.5–169°, mixed m.p. 168.5–169°).

***t*-Butyl *p*-(Methylthio)-perbenzoate.**—*p*-(Methylthio)-benzoyl chloride was prepared from *p*-mercaptobenzoic acid by the method of Buu-Hoi and Lecocq.[33] The perester was prepared by the addition, over a 3-hr. period at −20°, of an ether solution of *p*-(methylthio)-benzoyl chloride (3.9 g., 0.195 mole) to a stirred, ether solution of *t*-butyl hydroperoxide (2.1 g., 0.025 mole) and pyridine (2.6 g., 0.033 mole). After 3 days at −20°, the reaction mixture was concentrated and chromatographed on basic alumina at −20° to give the perester, a light-yellow oil, in 29% yield (1.35 g., 0.0056 mole), infrared maximum at 1734 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{16}O_3S$: C, 59.96; H, 6.71. Found: C, 60.22; H, 6.81.

***t*-Butyl *o*-Iodoperbenzoate.**—Pure *o*-iodobenzoic acid was converted in 85% yield to the acid chloride by the method of Wachter[34]; m.p. 35–40° (lit.[34] 35–40°). This acid chloride was converted to the perester by the same procedure described above for IVa. The perester, a white solid, was obtained in 33% yield, m.p. 45.5–46.0°, infrared maximum at 1746 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{13}IO_3$: C, 41.27; H, 4.09. Found: C, 41.47; H, 4.33.

***t*-Butyl *o*-Butylperbenzoate.**—*o*-*t*-Butylbenzoic acid[35] was converted to the acid chloride by treatment for 4 hr. with an excess of boiling thionyl chloride. Distillation at reduced pressure gave the acid chloride in 88% yield, b.p. 140–141° (20 mm.).

Anal. Calcd. for $C_{11}H_{13}OCl$: C, 67.18; H, 6.66. Found: C, 67.25; H, 6.81.

In 110 ml. of dry pentane were dissolved *t*-butyl hydroperoxide (5.35 g., 0.064 mole) and pyridine (6.1 g., 0.077 mole). This solution was cooled to −20°, stirred, and to it was added, over a 3-hr. period, a solution of *o*-*t*-butylbenzoyl chloride (9.55 g., 0.0486 mole) in 75 ml. of dry pentane. After additional stirring at −20° for 48 hr., the reaction mixture was washed at 0° with, successively, 10% sulfuric acid, 10% sodium carbonate and water and dried over magnesium sulfate. Evaporation of the pentane left an orange oil which was shown to be impure by the presence of two peaks in the 1700–1800 cm.$^{-1}$ region of its infrared spectrum. Further purification was effected by chromatography on basic alumina at −20°. The perester, a colorless oil, was obtained in 20% yield (2.45 g., 0.0097 mole) and showed a characteristic single infrared peak at 1762 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.90; H, 8.78. Found: C, 72.45; H, 8.78.

***t*-Butyl *o*-(Phenylthio)-perbenzoate (IVb).**—Sodium (2.2 g., 0.095 g. atom) was dissolved in 200 ml. of methanol.

---

[28] C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960).

[29] The authors wish to express their indebtedness to Mr. O. W. Norton for the nuclear magnetic resonance spectra, to Mr. Josef Nemeth and staff for the microanalyses, and to Mr. Paul McMahon and staff for the infrared spectra. Melting points are uncorrected. Spectra are recorded in full in the Ph.D. thesis of Wesley G. Bentrude, University of Illinois, 1961, available from University Microfilms, Inc., Ann, Arbor Mich. The n.m.r. spectra were obtained with a Varian Associates model 4300-2 spectrometer with a V-K3506 super stabilizer using a 60-mc. r.f. field. Chemical shifts are expressed in τ-units[30] (parts per million relative to tetramethylsilane taken as 10). In all cases tetramethylsilane was used as an internal reference.

[30] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[31] Th. Zincke and G. Siebert, *Ber.*, **48**, 1248 (1915).

[32] E. W. McClelland and L. A. Warren, *J. Chem. Soc.*, 2621 (1929)

[33] N. G. Ph. Buu-Hoi and J. Lecocq, *Bull. soc. chim. France*, 139 (1946).

[34] W. Wachter, *Ber.*, **26**, 1744 (1893).

[35] The authors wish to acknowledge the contributions of Mr. Earl C. Smith who prepared this compound by a modification of the method of E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939).

This solution was cooled to 0°, and a solution of methyl thiosalicylate (16 g., 0.095 mole) in 200 ml. of methanol was added. (The ester was prepared according to the procedure of Gattermann.[36]) The cold solution was then stirred and swept with nitrogen introduced through a sintered-glass gas-dispersion tube. A slurry of diphenyliodonium bromide (33 g., 0.095 mole), prepared according to Beringer, *et al.*,[13] in 200 ml. of methanol, was added in small portions over a period of several minutes. The stirred solution was refluxed for 1 hr. under an atmosphere of nitrogen. The reaction mixture was cooled overnight at 0° and filtered to remove the dimethyl ester of diphenyl disulfide 2,2'-dicarboxylic acid, 3 g., m.p. 132.5–134° (lit.[41] 134°) after recrystallization from ether–pentane.

Anal. Calcd. for $C_{16}H_{14}O_4S_2$: C, 57.46; H, 4.22. Found: C, 57.40; H, 4.21.

After removal of the disulfide ester, 10% aqueous sodium hydroxide (200 ml.) and ether (200 ml.) were added to the filtrate. The ether extract was saponified with boiling ethanolic potassium hydroxide. Water was added to the reaction mixture and the ethanol and iodobenzene were extracted with ether. Acidification of the aqueous phase with dilute hydrochloric acid gave the crude acid in 46% yield (10 g., 0.057 mole). Separation from further diphenyl disulfide 2,2'-dicarboxylic acid was effected by extraction of the *o*-(phenylthio)-benzoic acid with hot chloroform. The acid remaining after evaporation of the chloroform, 9.2 g. (42%), had m.p. 162–164° (lit.[12] 166–167°) and gave an infrared spectrum identical with the infrared spectrum of authentic *o*-(phenylthio)-benzoic acid.[12a]

Treatment of this acid with thionyl chloride for 24 hr. at room temperature gave the acid chloride, which was recrystallized from ether–pentane; yield 68%, m.p. 70–71°.

Anal. Calcd. for $C_{13}H_9OClS$: C, 62.78; H, 3.65. Found: C, 61.93; H, 3.80.

The perester was prepared from this acid by the method described above for IVa. The perester, a white solid, was obtained in 34% yield, m.p. 58–59°, sharp infrared peak at 1748 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{18}O_3S$: C, 67.52; H, 5.96. Found: C, 67.48; H, 6.01.

3,1-Benzoxathian-4-one.—By a procedure similar to that used by Mowry[19] for the synthesis of some related compounds, potassium thiosalicylate (115.5 g., 0.6 mole), chloromethyl acetate (65.1 g., 0.6 mole) and potassium iodide (2 g., 0.00012 mole) were dissolved in 400 ml. of methyl ethyl ketone. The reactants were refluxed 40 hr., after which solids were removed by filtration and extracted several times with ether. The ether extract and reaction mixture filtrate were combined and the solvents removed by distillation to leave a light brown oil. Attempted distillation of this material at 1.0 mm. gave only very volatile distillate, mostly acetic acid. The residue, a dark-brown, grease-like material (42 g.), gave, on chromatography on silica gel with chloroform eluent, the desired product, m.p. 47.0–47.5°, 10.0 g. (0.06 mole, 10%).

Anal. Calcd. for $C_8H_6O_2S$: C, 57.81; H, 3.64. Found: C, 58.08; H, 3.88.

Galvinoxyl.—Oxidation of 4,4'-methylenebis-(2,6-di-*t*-butylphenol) to the free-radical, galvinoxyl,[37] gave a material, m.p. 154.0–154.5°, with a visible spectrum in cyclohexane solution with maxima at 435 mμ, ϵ 154,000 (lit.[16] 420 mμ, ϵ 200,000) and 760 mμ, ϵ 600, and a shoulder at 570 mμ, ϵ 760.

Copolymerization of Styrene and Methyl Methacrylate Initiated by *t*-Butyl *o*-Methylthioperbenzoate.—In each of 3 flasks were placed 4.16 g. of styrene and 4.00 g. of methyl methacrylate, a 1:1 mole ratio. To one flask was added 3 mg. of *t*-butyl *o*-(methylthio)-perbenzoate, to another 3 mg. of benzoyl peroxide, to the third nothing. After 1 hr. at 50°, the monomers were removed at reduced pressure. The first flask contained 0.461 g. of non-volatile residue; the second flask, 0.016 and the third flask 0.015 g. The residue from the first (perester-containing) flask was analyzed.

Anal. (Polymer): C, 75.88; H, 7.78. Assuming these analyses to be accurate within the limits ±0.3, the analysis corresponds to that for a polymer containing 51.1 ± 0.9% methyl methacrylate units.

Procedure for Kinetic Runs Analyzed by Infrared Spectroscopy.—Solutions of perester of accurately known concentrations either sealed in glass tubes or contained in long-neck flask under nitrogen, were thermostated to within ±0.03°. Aliquots were quenched by cooling to −78°. Analysis was effected spectrophotometrically, using a Perkin–Elmer model 21 spectrophotometer at the frequency of the perester carbonyl band in the infrared (near 1750 cm.$^{-1}$). Beer's law was shown to obtain in each case in the concentration range in which measurements were made.

The rate constants were determined by the method of least squares. In all cases the plots using the experimentally measured infinity optical density, (O.D.)$_\infty$, were linear to at least 75% reaction. With the exception of the *o*-*t*-butyl perbenzoate, the measured infinity gave a completely linear plot for at least one of the temperatures at which rate measurements were made. In other cases plots using the measured infinity deviated from linearity after 2 or 3 half-lives, a deviation which could be removed by a very small correction of (O.D.)$_\infty$.

Procedure for Studies with Galvinoxyl as Radical Scavenger.—All runs were followed with a Cary model 14M recording spectrophotometer. The apparatus in which the decompositions were run consisted of a water-jacketed 5-cm. quartz cell modified by the attachment of 2 bulbs (to contain, separately, solutions of perester and radical scavenger). Water, with temperature regulated to within ±0.03°, was circulated through insulated tubing from a constant temperature bath directly through the jacket of the cell within the compartment of the spectrophotometer.

The perester solution was introduced into one of the bulbs of the cell and an equal portion of the scavenger into the other. The solutions were carefully degassed and an atmosphere of nitrogen was introduced into the evacuated apparatus. The solutions were quickly mixed, the mixture was poured into the cell proper and the apparatus was placed in the cell compartment. With the spectrophotometer light source at a constant, pre-determined wave length, the variation of optical density of the solution in the cell with time was determined automatically, the relation being linear over 80–95% of the run in most runs.

The rate constants were determined from a correlation of optical density, (O.D.), with time by the method of least squares, where the values of (O.D.) were taken over the linear portion of each run.

Product Studies.—Apparatus and procedures similar to those described by Bartlett and Hiatt[11] were used to analyze products from decompositions carried to at least 10 half-lives. A vacuum line was used to analyze for gaseous products as described[11] and the remaining products were separated into volatile and non-volatile fractions by bulb-to-bulb distillation under high vacuum.

The liquid distillate was subjected to quantitative analyses for isobutylene, acetone and *t*-butyl alcohol using infrared spectrographic methods similar to those used in following the previously described kinetic runs. These analyses were confirmed by gas chromatography using an Aerograph A-90 chromatograph and comparing peaks with those of known standards.

The non-volatile residue was separated into fractions by fractional crystallization, when possible, or by chromatography on silica gel (28–200 mesh).

Products of the Decomposition of *t*-Butyl *o*-(Methylthio)-perbenzoate in Chlorobenzene.—The perester (0.785 g., 3.25 mmoles) was dissolved in 10 ml. of chlorobenzene. The solution was degassed and then heated at 70° for 1 hour.

(a) **Gaseous and Volatile Products.**—No condensable gases were detected. The condensed gases amounted to 114 ml. (at 32° and 14.7 mm.) or 0.09 mmole. After absorption of carbon dioxide, the amount was 132 ml. (at 32° and 5.6 mm.) or 0.04 mmole. Thus the amount of carbon dioxide was 0.05 mmole, or 1.5% based on moles of perester. The remaining gas (0.04 mmole or 1.2%) was transferred to a gas infrared cell. By comparison with the published A.P.I. spectrum[38] this gas was shown to be isobutylene.

---

(36) L. Gattermann, *Ber.*, **32**, 1150 (1899).

(37) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(38) "Catalogue of Infrared Spectral Data," American Institute Research Project 44, National Bureau of Standards, Vol. 2, No. 378.

The amount of *t*-butyl alcohol shown by infrared analysis to be in the chlorobenzene distillate was 2.02 mmole, 62%. By the same technique, the amount of acetone present was 0.68 mmole, 21%. That acetone and *t*-butyl alcohol account for about 95% of the volatile products was shown by gas chromatographic analysis.

(b) **Non-distillable Residue.**—The distillation residue, 2.432 g., from the decomposition of 2.763 g. (11.4 mmoles) of perester, a dark-yellow, partially solid material, was separated into its components by chromatography on silica gel (160 g. packed in a 60:40 mixture of methylene chloride–pentane) eluting with pentane, methylene chloride, ether and methanol to obtain the fractions

Component	Wt., mg.
3,1-Benzoxathian-4-one	230
o-(Methylthio)-benzoic acid	570
Diphenyl disulfide 2,2'-dicarboxylic acid	136
Unresolved residues	633

(c) **Effect of Styrene upon the Decomposition Products, as Studied by N.m.r.**—Into each of two n.m.r. sample tubes was introduced about 0.3 ml. of a 10% solution of the perester in chlorobenzene. Into one of the tubes was also introduced 60 mg. of styrene. Each tube was then carefully degassed on the vacuum line. A small amount of tetramethylsilane (degassed) was then distilled into the tube containing styrene. The tubes were sealed under vacuum and an n.m.r. spectrum was obtained for each sample. Spectra after decomposition were run at varying r.f. field and particular attention given to the absorption peak at 5.10 τ units, the position of the methylene resonance of authentic 3,1-benzoxathian-4-one in chlorobenzene. From the relative areas of this peak in each sample rough estimates were made of the relative amount of the heterocycle present. The decomposition in which no styrene was present showed evidence of only one half to one third as much of the heterocycle as was evidenced when styrene and tetramethylsilane were present.

Products of the Decomposition of *t*-Butyl *o*-(Phenylthio)-perbenzoate in Chlorobenzene.—A solution of the perester (0.500 g., 1.65 mmoles) dissolved in 10 ml. of chlorobenzene was degassed and sealed under vacuum. After 1.5 hr. at 70°, the flask was reattached to the vacuum line and the products analyzed.

(a) **Volatile Products.**—No non-condensable gases were detected. The condensable gas was shown by the procedure described above to consist of carbon dioxide (0.12 mmole, 0.7%) and isobutylene (0.089 mmole, 5.4%).

The amount of *t*-butyl alcohol in the chlorobenzene distillate was determined by infrared spectroscopic analysis (with confirmation by gas–liquid chromatography) to be 0.65 mmole or 39%; the amount of acetone, 0.52 mmole, 32%. Isobutylene, determined by gas chromatographic analysis using a column of polyethylene glycol on fire-brick, was present to the extent of 0.46 mmole or 28%. Combining this with the isobutylene in the gaseous fraction, the total isobutylene is 33%.

(b) **Non-distillable Residue.**—A degassed solution of the perester (1.376 g., 4.56 mmoles) in 30 ml. of chlorobenzene was decomposed at about 90°, the solution was opened to the atmosphere, cyclohexane was added and the solution was cooled to cause crystallization of products. A process of fractional crystallization, from a solvent made increasingly less polar by the addition of increments of pentane, was followed by chromatography on silica gel to effect a clean separation into four components.

Component	Wt., mg.
Diphenyl sulfoxide 2-carboxylic acid	192
o-(Phenylthio)-benzoic acid	290
Diphenyl diphenyl disulfide 2,2'-dicarboxylate (XII)	547
Unidentified	38

The diphenyl sulfoxide 2-carboxylic acid was identified by comparison with an authentic sample prepared by the method of Weedon and Doughty.[12b]

Identification of the diphenyl diphenyl disulfide 2,2'-dicarboxylate (XII), was effected by its alkaline hydrolysis to yield phenol, identified through its tribromo derivative, and diphenyl disulfide 2,2'-dicarboxylic acid. Final identification was made by showing its identity with an authentic sample prepared as follows[39]:

To phenyl thiosalicylate (1.0 g., 0.0043 mole, prepared after the manner of Mayer[40]) in 10 ml. of ethanol a solution of iodine in ethanol was added dropwise with stirring until the color of iodine persisted. The solution was diluted with 100 ml. of water and extracted with ether. Evaporation of the ether extracts yielded crude XII (0.80 g.), m.p. 109–113°. Recrystallization from ether yielded white crystals (0.23 g., 23%), m.p. 122–123°, with an infrared spectrum identical with that of the sample isolated from the perester decomposition.

Anal. Calcd. for $C_{26}H_{18}O_4S_2$: C, 68.41; H, 4.20. Found: C, 68.10; H, 3.96.

Non-volatile Products from the Decomposition of *t*-Butyl *o*-(Phenylthio)-perbenzoate without Solvent.—The products (190 mg.) of a decomposition of the pure perester over a period of days at room temperature were chromatographed on silica gel, eluting with methylene chloride–ether.

Component	Wt., mg.
Methyl *o*-(phenylthio)-benzoate	60
o-(Phenylthio)-benzoic acid	17
Diphenyl sulfoxide 2-carboxylic acid	95
Unidentified	25

Acknowledgments.—We wish to acknowledge the aid afforded this investigation by fellowships held by W. G. B. from the Abbott Laboratories (1957–1958) and the National Science Foundation (1959–1960). This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

---

(39) We wish to thank Mr. David Tuleen for carrying out this synthesis.

(40) F. Mayer, *Ber.*, **42**, 1132 (1909).