The Accelerated Decomposition of Benzoyl Peroxide in the Presence of Sulfides and Disulfides[1]

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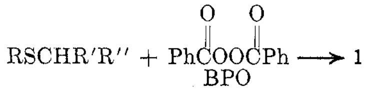
Benzoyl peroxide (BPO) decomposes at an accelerated rate in the presence of aliphatic sulfides or disulfides. The effect is most dramatic for methyl sulfide: 0.5 M methyl sulfide in carbon tetrachloride increases the rate constant for BPO disappearance by about 10^4 over that for pure CCl_4, and BPO decomposes with explosive speed in neat methyl sulfide. These reactions have been shown to be ionic processes by a series of experiments using free-radical scavengers, oxygen, and polymerizable and nonpolymerizable olefins. The sulfides and disulfides are oxidized to the sulfoxide or thiolsulfinate, respectively. Other products that have been isolated in one or more of these reactions include benzoic acid, benzoic anhydride, olefin, an α-benzoyloxy sulfide, and polysulfides. The reactions are first order in disulfide or sulfide, and first order in peroxide. We suggest a mechanism for all of these reactions in which the O–O bond of BPO undergoes nucleophilic attack by the sulfur compound to produce an intermediate **1** which exists in two resonance structures, **2** and **3**. We have included the nonionic structure **3** in the description of the intermediate since the change from CCl_4 to methanol as solvent produces a rate enhancement of only a factor of 11, a smaller effect than would be expected for a totally ionic reaction. The intermediate **1** can decompose by a number of paths. For example, attack by the benzoate ion on the carbonyl carbon produces benzoic anhydride and the sulfoxide, and attack on the α hydrogen produces an ylide and benzoic acid. This system is compared and contrasted with similar work in the literature. In cases where a small concentration of a rather ineffective sulfur compound is used, some of the BPO undergoes normal homolysis in competition with the ionic decomposition. It is interesting, therefore, to inquire whether this homolysis might occur at an accelerated rate due to the presence of the sulfur compound. Several studies in the literature suggest that such an assisted homolysis might be expected.[3-5] Data on the rate of polymerization of styrene in the presence of BPO and disulfides, however, show that all of the radicals in this system are produced by the normal, unimolecular decomposition of BPO, and no assisted homolysis occurs. Some data on the effect of sulfur compounds on the rate of decomposition of *tert*-butyl perbenzoate, propionyl peroxide, lauroyl peroxide, *tert*-butyl peroxylate, and *n*-nitrophenylazotriphenylmethane also are given.

Benzoyl peroxide (BPO) decomposes at an accelerated rate in the presence of aliphatic sulfides or disulfides. The effect is most dramatic for methyl sulfide: 0.5 M methyl sulfide in CCl_4 increases the rate of BPO decomposition by 10^4 over that for pure CCl_4, and BPO decomposes at an explosive rate in pure methyl sulfide. The sulfur compounds which we have studied (Table I) include compounds of the type RSR and RSSR where R = methyl, propyl, isobutyl, *sec*-butyl, *tert*-butyl, or phenyl. A mechanism which is consistent with all of our evidence involves the nucleophilic attack of the sulfur compound on the O–O bond of BPO and the initial formation of an intermediate **1**, where R is an alkyl group in the case of sulfides and a thiyl group for disulfides (eq 1).



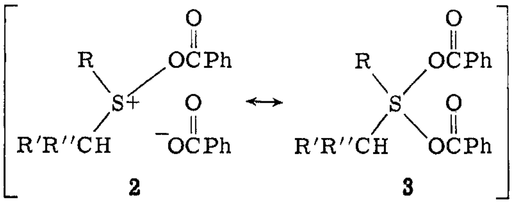
$$\mathrm{RSCHR'R''} + \underset{\mathrm{BPO}}{\mathrm{Ph\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}Ph}} \longrightarrow \mathbf{1} \qquad (1)$$

$\mathbf{1} \longrightarrow$ products including sulfoxide (from sulfides) or thiolsulfinate (from disulfides), benzoic acid, benzoic anhydride, olefin, and polysulfides

In order to clarify the distinctions to be made later in this paper, it is useful to define the following terms. *Homolysis* implies simple, unimolecular bond scission to form free radicals;[3a] *assisted homolysis* is homolysis of higher molecularity than unity which occurs at an accelerated rate (a process we have previously referred to as molecule-induced homolysis[3b]); *heterolysis* is unimolecular bond scission to form ions (*e.g.*, SN1); and *assisted heterolysis* is heterolysis of molecularity greater than unity (*e.g.*, SN2). In the discussion to follow, we establish that sulfur compounds interact with BPO to accelerate the rate of its heterolysis, and that this process, eq 1, competes with the normal homolysis of BPO. Our data also show that no accelerated homolysis occurs.

The exact nature of the intermediate **1** requires discussion. An extensive series of studies using free-radical scavengers, which will be presented below, as well as the products produced in these reactions, prove conclusively that eq 1 is not a radical reaction.[3a] However, the small rate effect produced by increasing solvent polarity suggests that the transition state leading to **1** does not have unit charge separation.[3c] There are two possible explanations for this. In the first, **1** is an ion pair but the transition state leading to its formation is very reactantlike and has developed very little charge separation; in the second, intermediate **1** itself is not totally ionic in nature but has some covalent character. We cannot choose between these two possibilities conclusively, but because of analogies to other work in the literature we have formulated eq 1 in terms of the latter possibility. In this explanation, intermediate **1** is a resonance hybrid of ionic and covalent structures **2** and **3**.

There is precedent for both **2** and **3**. Structures



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[2] (a) John Simon Guggenheim Fellow, 1970–1971; NIH Special Postdoctoral Fellow, Summer, 1971. (b) Abstracted in part from the Ph.D. Dissertation of H. T. Bickley, Louisiana State University, 1971.

[3] (a) If the product of the reactivity and concentration of the sulfur compound is such that assisted heterolysis, eq 1, is slow, then the normal homolysis of BPO occurs in competition with the catalyzed ionic reaction. (b) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 118–126, 180–186, 290; (c) p 119; (d) pp 223–227; (e) p 244.

TABLE I

RATE CONSTANTS FOR THE REACTION OF BPO WITH SULFIDES AND DISULFIDES IN CCl_4[a]

Sulfide or disulfide	$10^2[\mathrm{BPO}]_0$	$10^2[\mathrm{RSR}]_0$ or $10^2[\mathrm{RSSR}]_0$	Temp, °C	10^4k, sec^{-1}[b]	$10^4k'$, M^{-1} sec^{-1}[c]
None	4.0		41	0.002	
Methyl sulfide	4.0	48.6	41	46.5	100.0
Propyl sulfide	4.0	31.7	41	26.8	91.0
Isobutyl sulfide	4.0	4.80	41		68.0[c]
Isobutyl sulfide	4.0	9.84	41		55.0[c]
Isobutyl sulfide	4.0	19.1	41		61.0[c]
Isobutyl sulfide	4.0	31.9	41		57.0[c]
Isobutyl sulfide	4.0	37.3	41	25.0	67.0
sec-Butyl sulfide	4.0	31.8	41	3.8	12.6
tert-Butyl sulfide	4.0	32.5	41	1.19	3.90
tert-Butyl disulfide	1.1	Neat	41	3.9	0.72
None	5.0		60	0.02	
tert-Butyl sulfide	4.1	64.2	60	15.0	23.0
Methyl disulfide	4.1	63.7	60	3.64	5.7
Ethyl disulfide	4.1	64.3	60	2.40	3.7
tert-Butyl disulfide	4.1	64.2	60	2.37	3.7
Isobutyl disulfide	4.1	63.8	60	2.24	3.5
Propyl disulfide	4.1	63.8	60	2.24	3.5
Isopropyl disulfide	4.1	64.1	60	1.03	1.7
sec-Butyl disulfide	4.1	64.1	60	0.90	1.4
None	0.8		100	3.2	
tert-Butyl sulfide	1.2	17.7	100	61.0	360.0
Phenyl sulfide	1.1	84.2	100	25.8	31.0
Methyl disulfide	1.7	17.0	100	16.3	101.0
Propyl disulfide	1.2	17.9	100	15.1	87.0
tert-Amyl disulfide	1.1	17.8	100	12.2	71.0
tert-Butyl disulfide	1.1	5.06	100		120.0[f]
tert-Butyl disulfide	0.77	8.86	100	7.3	83.0
tert-Butyl disulfide	1.0	18.0	100	12.8	71.0
tert-Butyl disulfide[d]	1.1	18.6	100	12.1	65.0
tert-Butyl disulfide	8.90	17.5	100		92.0[c]
tert-Butyl disulfide	16.2	17.6	100		50.0[f]
tert-Butyl disulfide[e]	1.1	18.6	100	13.3	72.0

[a] The initial concentration of reactants is indicated by the subscript zero. [b] First-order rate constant k for the disappearance of BPO; calculated by computer from raw data assuming that the sulfur compound's concentration does not change. [c] The second-order rate constant k' in eq 4a; calculated by dividing the first-order rate constant k by the average concentration of sulfide or disulfide for runs where the sulfur compound is present in eightfold excess or more. In the cases in which a value of k is not given, k' was determined directly using the integrated form of the second-order rate law, eq 4a. [d] Degassed. [e] 0.2 M styrene added. [f] Calculated using eq 4b; see text.

analogous to **2** have been suggested in the reaction of amines with BPO[4] and in the decomposition of mercaptide-substituted peroxy esters.[5] Covalent compounds which have structures analogous to **3** have recently been isolated by Martin[6a,b] and by Kapovits and Kalman,[6c] and Martin has reviewed the support for such a formulation.[6a] Moffatt has postulated a related tetravalent sulfur compound as an intermediate in sulfoxide–carbodiimide reactions.[6d]

We have studied the reaction of a number of sulfides and disulfides with BPO (Table I). The product mixtures from both types of compounds are similar, suggesting that these reactions involve a similar mechanism and proceed through intermediate **1** (R is alkyl for sulfides and thiyl for disulfides).

After our investigation was completed we discovered that Horner[4b] previously had observed that sulfides enhance the rate of decomposition of BPO. He also postulated the involvement of the nonbonded electrons on sulfur in a reaction which is first order in sulfide and first order in peroxide. However, it is not clear from his report whether the reaction goes by a radical or ionic mechanism.

Horner observed the presence of sulfoxides, α-benzoyloxy substitution products (**4**),[7] benzoic anhydride, and benzoic acid as products from the reaction of BPO with sulfides,[4b] and he postulated that the reaction between BPO and sulfides involves the initial combination of two species followed by the decomposition of the intermediate complex by competitive radical and polar paths. Horner suggested that the most

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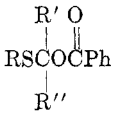
(4) (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 590–596; (b) L. Horner and E. Jurgens, *Justus Liebigs Ann. Chem.*, **602**, 135 (1957).

(5) (a) W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.*, **84**, 1561 (1962); (b) D. L. Tullen, W. G. Bentrude, and J. C. Martin, *ibid.*, **85**, 1938 (1963); (c) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964); (d) J. C. Martin and T. W. Koenig, *J. Amer. Chem. Soc.*, **86**, 1771 (1964).

(6) (a) J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2339 (1971); (b) J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2341 (1971); (c) I. Kapovits and A. Kalman, *Chem. Commun.*, 649 (1971); (d) see, for example, J. C. Moffatt, *J. Org. Chem.*, **26**, 1909 (1971).

(7) (a) An α-substitution product also has been reported in a recent investigation of the reaction of BPO with $(RS)_2CH_2$; the products are benzoic acid and $PhCOOCH(SR)_2$: K. Gollmer and H. Ringsdorf, *Makromol. Chem.*, **121**, 227 (1969). (b) The α-substitution product is the only product in the reaction of sulfides with *tert*-butyl perbenzoate in the presence of copper salts as catalysts. The mechanism is probably the mixed ion–radical pathway of the Kharasch reaction. See G. Sosnovsky, *Tetrahedron*, **18**, 15 (1962), and for reviews, G. Sosnovsky, *Angew. Chem., Int. Ed. Engl.*, **3**, 269 (1964), and W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 138–145. (c) L. Bateman and K. R. Hargrave, *Proc. Roy. Soc., Ser. A*, **224**, 389, 399 (1954); D. Barnard, *J. Chem. Soc.*, 489 (1956); K. R. Hargrave, *Proc. Roy. Soc., Ser. A*, **235**, 55 (1956). (d) The literature is reviewed by R. Hiatt in "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 73–78. (e) R. Curci, R. A. Di Prete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 740 (1970).



$\mathrm{RS\underset{R''}{\overset{R'}{C}}O\overset{O}{\overset{\|}{C}}Ph}$

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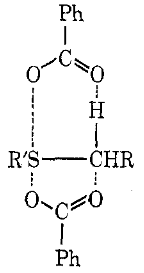
likely mechanism for the formation of the α-substitution product involves the cyclic structure shown below.[4b]



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This structure is similar to one proposed by Oae and Kise[8] to rationalize an ^{18}O exchange between a sulfoxide and acetic anhydride. They suggest that the exchange involves an equilibrium between a cyclic structure similar to **5** and one like **2** ↔ **3**.

Some years ago, Bateman and his coworkers discovered that hydroperoxides react with sulfides in a process that produces sulfoxide,[7c] and the groups of Modena and of Edwards have studied these reactions in detail.[7d,e] In the absence of oxygen, the reaction is ionic and involves nucleophilic attack by sulfur in a mechanism not unlike that proposed here, but the product mixture is simpler. One unexpected and interesting feature of the hydroperoxide reaction, which we will later see is shared by the reaction studied here, is that the rate is not markedly affected by solvent polarity.[7e] Another striking similarity of hydroperoxides and BPO is that both undergo an accelerated decomposition in amines, and, for both peroxidic materials, the amine-accelerated reaction appears to be complex and to involve both homolytic and heterolytic paths.[4,7d]

Results

Kinetic Studies.—We have studied the kinetics of the reaction of BPO with sulfides and disulfides by monitoring the disappearance of BPO by infrared spectrometry. The reaction is first order in BPO and first order in the sulfur compound. All the sulfides are more reactive toward BPO than even the most reactive disulfide, probably because of the greater nucleophilicity of sulfides.[9] Data on the order of reactivities of a series of sulfides and disulfides are given in Table I. As R varies, the order of reactivity for the sulfides increases in the order phenyl < *tert*-butyl < *sec*-butyl < isobutyl < propyl < methyl. The disulfides follow a similar pattern but the rate constants are more compressed. This order suggests a steric effect which, as would be expected, is more pronounced in sulfides than in disulfides.[10] The lower nucleophilicity of aryl sulfides or disulfides relative to their alkyl analogs also is expected.[9]

The Ionic Nature of the Reaction. Effects of Scavengers.—We have eliminated the possibility that our results are due to a radical reaction of BPO which is accelerated by sulfur compounds by studying the effects of scavengers. If BPO is allowed to thermally decompose in CCl_4 in the presence of galvinoxyl, 89% of the radicals theoretically formed are scavenged. However, the addition of sulfur compounds diminishes the equivalents of galvinoxyl which are destroyed, indicating that an increasing fraction of the BPO decomposes by a nonradical process in the presence of increasing concentrations of disulfides. If a sufficient amount of sulfur compound is added, BPO reacts entirely by a nonradical process and no galvinoxyl is destroyed[3a] (see Table II).

TABLE II

THE REACTION OF BPO WITH DISULFIDES IN CCl_4 IN THE PRESENCE OF GALVINOXYL

10^3 $[BPO]_0$	$10^3[G]_0$[a]	Disulfide	$[RSSR]_0$	Galvinoxyl decolorized, %	Temp, °C
2.39	3.91	Isobutyl	0.281	0	60
8.79	3.60	*tert*-Butyl	3.05	0	80
0.046	3.59	*tert*-Butyl	0.170	19.2	80
0.015	4.16	None		89.0	80

[a] Galvinoxyl.

The data of Table III show the effect of sulfur compounds on the rate of polymerization of styrene. As the concentrations of the sulfur compounds are increased, a larger fraction of the BPO decomposes by a nonradical mechanism and R_P decreases. The rate constants for the assisted heterolysis of BPO, eq 1, are unaffected by the presence of styrene (Table I). Oxygen also does not affect these rate constants (Table I). (The last column in Table III will be discussed below.)

We also have used nonpolymerizable olefins to test for a radical component of the reaction. If BPO is allowed to decompose in CCl_4 in the presence of 2-methyl-1-butene, the olefin is consumed by the addition of CCl_4 to the double bond in a radical chain reaction. However, if the reaction is carried out in the presence of a sulfur compound, for example, *tert*-butyl disulfide (TSST), there is very little decrease in the olefin concentration, indicating that radicals are not formed (see Table IV).

It is known that if phenyl radicals from phenylazotriphenylmethane are generated in TSST–CCl_4 mixtures, 80% of the phenyl radicals can be accounted for as benzene, chlorobenzene, and *tert*-butyl phenyl sulfide.[11] However, the products of the decomposition of BPO in TSST–CCl_4 mixtures do not include these products; rather, the phenyl groups are accounted for as benzoic anhydride and benzoic acid, as is consistent with a nonradical mechanism. (It actually was this discrepancy that led to our study of the BPO system.)

Assisted Homolysis.—As the data of both Tables II and III show, in the presence of sufficiently low concentrations of sulfur compounds, and particularly those which are relatively inefficient at assisting heterolysis, a fraction of the BPO decomposes by a free-radical

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[8] S. Oae and M. Kise, *Tetrahedron Lett.*, 2261 (1968).

[9] J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).

[10] G. Modena and L. Malioli, *Gazz. Chim. Ital.*, **87**, 1306 (1957).

[11] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 273 (1970).

TABLE III

THE RATE OF POLYMERIZATION OF STYRENE INITIATED BY BPO AND OTHER INITIATORS AT 60° IN THE PRESENCE OF DISULFIDES

Disulfide	$[RSSR]_0$	Initiator	$[Styrene]_0$	Time, hr	Polymer, mg	10^5R_P (M sec^{-1})[d] obsd	R_P/R_P Obsd[d]	R_P/R_P Calcd[e]
None		BPO[a]	8.34	5.0	290, 306	4.23, 4.44		
tert-Butyl	0.191	BPO[a]	8.14	5.0	129.0	1.91	0.4	0.5
Isobutyl	0.183	BPO[a]	8.05	5.0	94.0	1.83	0.4	0.4
tert-Butyl	0.596	BPO[a]	7.37	5.0	67.0	0.920	0.2	0.1
tert-Butyl	0.963	BPO[a]	6.75	5.0	47.0	0.581	0.1	0.03
Methyl	0.198	BPO[a]	8.13	5.0	54.0	0.817	0.2	0.4
tert-Amyl	0.234	BPO[a]	7.89	5.0	69.0	1.97		
None		LPO[b]	8.34	0.74	72.0	12.1		
tert-Butyl	0.21	LPO[b]	7.99	0.74	115.0	11.6		
None		AIBN[c]	8.34	1.30	83.0	4.9		
tert-Butyl	0.21	AIBN[c]	7.99	1.30	74.0	4.0		

[a] Molarities are calculated at 60°. BPO is 0.01 M. [b] Lauroyl peroxide (LPO) is 0.011 M. [c] Azobisisobutyronitrile (AIBN) is 0.014 M. [d] R_P is the rate of polymerization (in M/sec) for the control run in the absence of disulfide; R_P' is that for the run containing sulfur compound. [e] Calculated using eq 3 and assuming that the sulfur compound diverts some BPO to decompose by an ionic reaction and does not accelerate the normal rate of homolysis of BPO. See text.

TABLE IV

EFFECT OF *tert*-BUTYL DISULFIDE ON THE DECOMPOSITION OF BPO IN THE PRESENCE OF 2-METHYL-1-BUTENE AT 60°[a]

$[TSST]_0$	Olefin concentration Initial	Olefin concentration Final
0	0.458	0.0059
0.582	0.569	0.531

[a] BPO is 0.337 M.

mechanism.[3a] It is interesting, therefore, to inquire whether the rate at which this fraction undergoes homolysis is affected by the presence of the sulfur compounds. Such an effect would not be unexpected.[3b,4,5] A number of types of compounds which have nucleophilic character are able to interact with peroxides to accelerate homolysis.[3b] However, our studies using styrene demonstrate that the rate of homolysis of BPO is not affected by the presence of the sulfur compounds.

In the absence of sulfur compounds, the rate of the BPO-initiated polymerization of styrene is given by

$$R_P = \frac{[M]}{\delta}\{k_d f[\mathrm{BPO}]_0 e^{-k_d t}\}^{0.5} \tag{2a}$$[3d]

where $\delta = k_t^{0.5}/k_p$, k_t and k_p are the rate constants for termination and propagation in the polymerization of styrene, k_d is the rate constant for unimolecular homolysis of BPO, f is the efficiency of BPO at initiating polymerization, and $[M]$ is the molarity of styrene. In the presence of sulfur compound, the BPO undergoes a competing pseudo-unimolecular ionic decomposition, eq 1, and the rate of polymerization, R_P, is given by

$$R_P' = \frac{[M]}{\delta}\{k_d f[\mathrm{BPO}]_0 e^{-(k_d+k)t}\}^{0.5} \tag{2b}$$

where k is the first-order rate constant taken from Table I for the appropriate sulfur compound and concentration. Thus, the ratio R_P'/R_P, given in eq 3, depends only on kt. Table III compares values of this ratio calculated in this way with those observed, and the agreement is excellent. This agreement implies that all of the polymer produced in styrene–disulfide–BPO mixtures can be accounted for by the usual rate constant for unimolecular homolysis of BPO; no accelerated homolysis occurs.

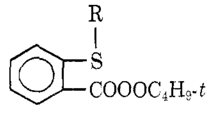
$$R_P'/R_P = e^{-kt/2} \tag{3}$$

In this connection it is appropriate to make some remarks about the methods used to calculate rate constants. When only negligible amounts of homolysis occurs, k' was calculated using eq 4a. (See the footnotes to Table I for details.) If an appreciable fraction of the BPO undergoes homolysis, eq 4a is not accurate and eq 4b was used. Values of k_d were taken from runs in pure CCl_4 and the instantaneous concentration of the sulfur compound was expressed in terms of its initial concentration, the moles of BPO reacted, and the fraction of the reaction which was heterolytic. This gave satisfactory values of k' even for runs in which the initial concentrations of the sulfur compound and the BPO were equal and where a large fraction of the reaction was homolytic. For example, in a run at 100° with $[\mathrm{BPO}]_0 = 0.16\ M$ and $[tert\text{-butyl disulfide}]_0 = 0.17\ M$, $10^4k'$ is calculated to be 50 ± 20. This value can be compared with a value of about $78 \pm 10 \times 10^{-4}$ predicted from runs at higher concentrations of *tert*-butyl disulfide (Table I).

$$-\mathrm{d}[\mathrm{BPO}]/\mathrm{d}t = k'[\mathrm{BPO}][\text{sulfur compound}] \tag{4a}$$

$$-\mathrm{d}[\mathrm{BPO}]/\mathrm{d}t = k'[\mathrm{BPO}][\text{sulfur compound}] + k_d[\mathrm{BPO}] \tag{4b}$$

The Effect of Sulfur Compounds on Other Peroxides and Initiators.—The literature cited in the introduction suggests that eq 1 might be a general process. Furthermore, Martin, *et al.*, have found that the thiyl-substituted perester **6** gives a greatly accelerated homolysis relative to unsubstituted *tert*-butyl perbenzoate.[5] Quite surprisingly, they also find that the rate of decomposition of **6** increases on increasing the polarity of the solvent.[5b] Therefore, they have suggested that the transition state for the assisted homolysis of **6** includes the dipolar resonance structure **7**.[5]



6, $R = C_6H_5$ or $t\text{-}C_4H_9$

We have performed some preliminary experiments on other initiators to determine the generality of eq 1. Table V shows that sulfur compounds hardly affect the rate of decomposition of azo compounds, as would be expected.[3b] Interestingly, diacyl peroxides are much

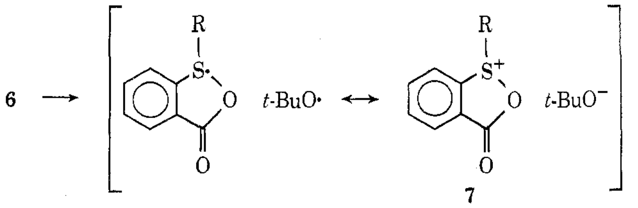
TABLE V

THE EFFECT OF SULFUR COMPOUNDS ON THE RATE OF DECOMPOSITION OF SEVERAL OTHER INITIATORS

Initiator[a]	$[I]_0 \times 10^2$	Sulfur compd[b]	$[RSR]_0$ or $[RSSR]_0$	Solvent	Temp, °C	10^4k, sec^{-1}
TBP	1.99	None		CCl_4	120	1.58
TBP	1.99	None		CCl_4	120	1.67
TBP	2.16	TSST	0.172	CCl_4	120	1.44
TBP	2.56	TSST	Neat[c]		120	1.38
TBP	2.02	Me_2S	0.178	CCl_4	120	29.3
TBPOx	1.59	None		CCl_4	39	0.79
TBPOx	1.72	TSST	0.204	CCl_4	39	0.98
TBPOx	1.67	TSST	Neat[c]		39	0.98
PPO	2.56	None		CCl_4	80	0.79
PPO	2.67	*i*-Bu_2S	0.182	CCl_4	80	5.8
PPO	2.57	TSST	Neat[c]		80	3.4
LPO	1.26	None		CCl_4	80	1.23
LPO	1.28	TSST	0.178	CCl_4	80	1.31
LPO	1.23	TSST	Neat[c]		80	3.2
NAT	0.229	None		CCl_4	60	0.83
NAT	0.313	TSST	Neat[c]		60	0.88

[a] The abbreviations are: TBP, *tert*-butyl perbenzoate; TBPOx, di-*tert*-butyl peroxylate; PPO, propionyl peroxide; LPO, lauroyl peroxide; NAT, *p*-nitrophenylazotriphenylmethane. [b] TSST is *tert*-butyl disulfide; Me_2S is methyl sulfide; and *i*-Bu_2S is isobutyl sulfide. [c] The sulfur compound is the solvent.

less accelerated than is BPO. For example, the decomposition of propionyl peroxide is increased in rate some tenfold by 0.2 *M* isobutyl sulfide, conditions under which the decomposition of BPO is increased over 10^3.



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(Compare Tables I and V.) Similarly, the decomposition of lauroyl peroxide is three times faster in neat *tert*-butyl disulfide than in CCl_4, whereas this change in solvent increases the rate of decomposition of BPO by 10^3. The rate of decomposition of di-*tert*-butyl peroxylate is hardly affected by *tert*-butyl disulfide.

tert-Butyl perbenzoate (TBP) represents an intermediate case. As might be expected from Martin's work,[5] its rate of decomposition is substantially increased by sulfur compounds; however, it is much less sensitive than is BPO. For example, 0.2 *M* methyl sulfide in CCl_4 increases the rate of decomposition of TBP by 20-fold and BPO by 10^4. (Compare Tables I and V.)

We did not perform the extensive scavenger and solvent variation studies with these initiators which would allow us to decide whether these increased rates are due to assisted heterolysis or homolysis. However, one piece of evidence indicates that the effect for TBP is due at least partially to an ionic process similar to that for BPO. A large-scale run at 120° with methyl sulfide and TBP modeled after the run shown in Table V gave a white precipitate which was collected and recrystallized, and the nmr was determined in CCl_4. Its spectrum was identical with that of the α-substitution product **4** ($R = CH_3$, $R' = R'' = H$) obtained from the methyl sulfide–BPO reaction (singlets at 2.22 and 5.32 ppm and aromatic absorption at about 7.8 ppm; relative intensity 3:2:5).

Thus, our results suggest that the enhanced homolysis found by Martin, *et al.*, for **6** represents a special case.[12] When the peroxide linkage and the sulfur atom are in separate molecules, as in TBP and methyl sulfide, the reaction appears to be ionic. Furthermore, it is much less accelerated than is the comparable reaction of BPO. Another interesting feature is that Martin, *et al.*, find that the *tert*-butyl perbenzoate **6** gives similar rate accelerations with R equal to either methyl or phenyl.[5] With BPO, phenyl sulfide is much less efficient at accelerating heterolysis than is methyl sulfide (Table I).

All of the data discussed above can be summarized by postulating that the intramolecular sulfur atom of **6**, for a reason not entirely clear, accelerates homolytic scission more than heterolytic, but that the opposite is true when external sulfur compounds interact with BPO or TBP.

Effects of Solvent Polarity.—The rate of disappearance of BPO in the BPO–TSST system was studied in a series of solvents with different values of Kosower's *Z* values.[13a] (See Table VI.) The reaction rate does increase with increasing solvent polarity but less so than would be expected for a typical ionic reaction.[13b] There are two possible explanations for this. One is that the transition state leading to **1** is not far along the reaction coordinate and little charge separation has

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[12] One of the most striking features of the work reported here is the contrast between the BPO–sulfide reaction and the decomposition of *tert*-butyl *o*-phenylthiolperbenzoate (**6**) studied by Martin, *et al.*[5] Our reaction shows a smaller effect of solvent polarity than does Martin's, yet our reaction is ionic and his seems to be entirely radical. One possibility which could partially reconcile the two sets of data should be mentioned. We showed that our reaction was ionic by scavenger studies carried out in the least polar solvents we studied (such as CCl_4 and styrene), and, therefore, it is clear that our reaction remains ionic in more polar solvents. Martin, *et al.*, carried out most of their scavenger studies in chlorobenzene,[5a] and it is conceivable that a portion of the decomposition of their perester **6** occurs in more polar solvents such as methanol by an ionic mechanism. Professor Martin has informed us that the evidence for formation of radicals from **6** in methanol solution lay in the observation of zero-order galvinoxyl disappearance. Clearly, more research is necessary both on the decomposition of **6** in very polar solvents and on that of *tert*-butyl perbenzoate in sulfide solvents to unravel ionic and radical components of these reactions, and both we and Professor Martin intend to pursue these studies further.

[13] (a) For a discussion of E_T see E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 305. (b) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill, New York, N. Y., 1962, pp 106–107, discusses the rate increases to be expected from increasing solvent polarity in ionic and radical reactions involving sulfur compounds.

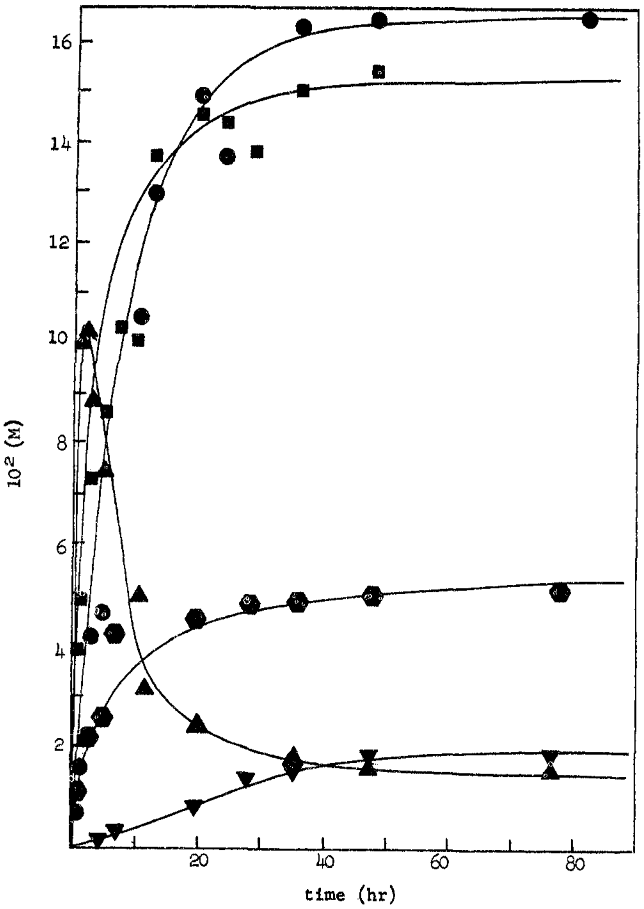

Figure 1.—A plot of the products of the reaction of 0.102 M BPO and 0.632 *M tert*-butyl sulfide (TST) in CCl_4 at 80° as a function of time. The products are coded as follows: benzoic acid ●, benzoic anhydride ▲, isobutylene ■, TSST ⬢, TS_3T ▼.

TABLE VI

RATE OF REACTION OF BPO WITH *tert*-BUTYL DISULFIDE AS A FUNCTION OF SOLVENT POLARITY AT 80° [a]

Solvent	10^4k, sec^{-1}	E_T[b]
CCl_4	2.72	32.5
$CHCl_3$	6.3	39.1
PhH	3.66	34.5
PhCl	4.00	37.5
CCl_4[c]	3.17	32.5
CCl_4[d]	3.42	32.5
$(CH_2Cl)_2$	6.5	42.0
CH_2Cl_2	7.4	41.1
CH_3OH	27.7	55.0

[a] The initial concentration of BPO is 0.02 *M*; that of TSST is 0.2 *M*. [b] See ref 13a. [c] This sample contains 0.0072 *M* Cl_3CCO_2H. [d] This sample contains 0.0256 *M* Cl_3CCO_2H.

developed. In the second possibility, the transition state is similar to the intermediate **1**, but **1** is a resonance hydride of structures like **2** and **3** with an appreciable contribution from the covalent structure.[14]

The small effect which we find for eq 1 when the polarity of the solvent is increased is even more surprising when compared with the results of Martin, *et al.*,[5] for the decomposition of **6**. They find that the

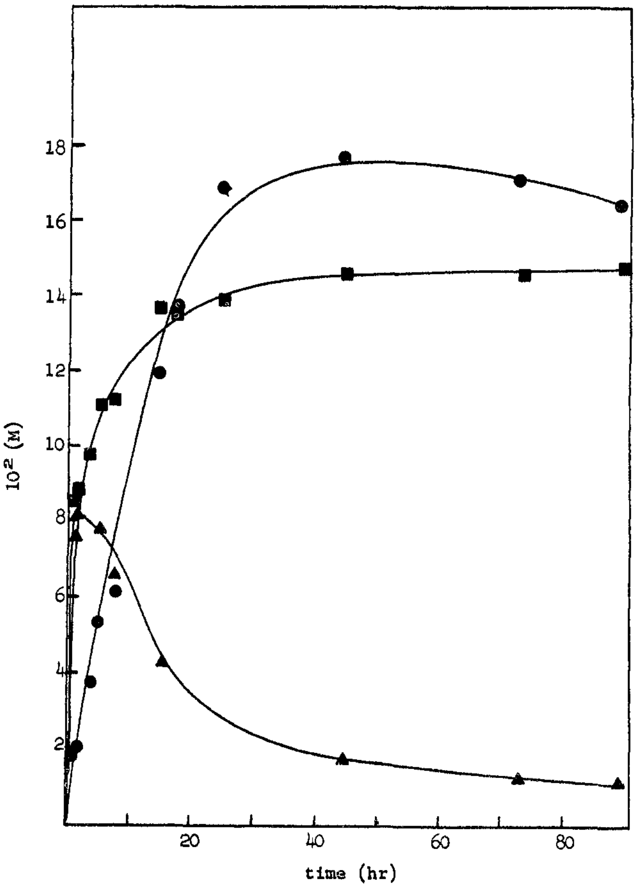

Figure 2.—A plot of the products of the reaction of BPO and TSST *in* CCl_4 *at 80° as a function of time:* $(BPO)_0$ = 0.102, $(TSST)_0$ = 0.632; benzoic acid ●, benzoic anhydride ▲, isobutylene ■.

solvents cyclohexane, chlorobenzene, and methanol give rate constants for the decomposition of **6** which increase in the ratio 0.07:1:47. The rate increase they observed in going from chlorobenzene to methanol is about six times greater than we find (Table VI). It certainly is unexpected that the BPO–sulfide reaction, with a small solvent effect, is entirely ionic in mechanism, whereas the decomposition of **6**, with a large solvent effect, is entirely radical.[12] However, it should be stressed that *neither* eq 1 nor the decomposition of **6** is accelerated by more polar solvents to the degree that a completely ionic reaction would be.[13] Thus, the transition state both for eq 1 and for the decomposition of **6** has some dipolar character but does not involve unit charge separation.

Products.—Table VII shows typical data on the nature of the products from both BPO–sulfide and BPO–disulfide reactions, and Figures 1 and 2 plot product data for *tert*-butyl sulfide and disulfide, respectively. The products consist of benzoic acid and benzoic anhydride, olefin, polysulfides, and the α-substitution product **4** for those sulfur solvents that possess an α hydrogen. The material balance for the phenyl groups is quite good throughout the reaction (Table VII). Since the sulfur solvents were usually present in excess, material balances in sulfur are difficult to obtain. Polysulfide–sulfur (formally in the zero valance state) is produced. Both disulfide and trisulfide products were isolated from the reactions of *tert*-butyl sulfide (Figure 1), and mass spectral evidence for the presence

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[14] The solvent studies (Table V) were done using *tert*-butyl disulfide, the least reactive sulfur solvent which was studied. It seemed possible that a larger solvent effect might have been observed if a more reactive sulfur solvent were used. However, preliminary results using isobutyl sulfide indicate that the rate enhancement due to changing the solvent from CCl_4 to methanol is about the same with this more reactive sulfide as that shown in Table VI for *tert*-butyl disulfide.

TABLE VII

REACTION PRODUCTS OF BPO WITH SULFIDES AND DISULFIDES IN CCl_4 AT 80°

$[BPO]_0$, *M*	Sulfide or disulfide	Initial [RSR] or [RSSR], *M*	Time, hr	$10^2[PhCO_2H]$, *M*	$10^2[(PhCO)_2O]$, *M*	$10^2[R(-H)]$,[a] *M*	10^2 [α-substituted product],[b] *M*
0.102	*tert*-Butyl sulfide	0.632	0.5	0.6	10.0	4.0	
			1.0	1.6	10.2	5.0	
			3.0	4.2	8.9	7.3	
			5.0	4.7	7.4	8.7	
			10.3	10.6	5.0	10.0	
			20.0	15.0	2.5	14.7	
			36.0	16.0	1.9	15.1	
0.104	Methyl sulfide	0.397	0.5	3.3	6.9		3.9
			5.0	6.1	4.2		5.9
			10.0	6.1	3.4		6.0
0.0503	*tert*-Butyl disulfide	0.704	0.5	1.0	3.9	4.2	
			1.0	1.2	4.2	4.2	
			5.0	2.1	4.0	5.0	
			7.5	3.4	2.8	5.2	
			17.0	8.2	1.7	7.1	
0.0491	*tert*-Amyl disulfide	1.70	0.5	2.0	3.0	3.6	
			2.0	2.2	2.6	4.0	
			3.0	2.4	2.6	4.6	
			12.0	2.9	2.5	4.9	
			22.0	5.0	2.1	4.9	

[a] Olefin formed from R group on sulfide or disulfide. [b] This is **4** shown in text.

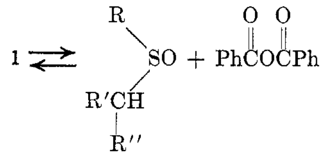
of tetra- and pentasulfides was obtained from reaction mixtures of the BPO–TSST system.

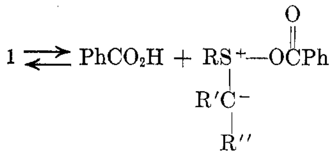
The order in which products are formed is revealing. Anhydride is produced early in the reaction and then disappears (Figures 1 and 2). Notice particularly that the olefin is formed earlier than is benzoic acid (Figures 1 and 2).

Temperature Coefficients.—The Arrhenius activation energies for the reaction of BPO with *tert*-butyl sulfide, *tert*-butyl disulfide, methyl disulfide, and propyl disulfide are 17, 18, 19, and 20 kcal/mol, respectively, calculated from the data in Table I. The Arrhenius *A* factor is approximately $10^9\ M^{-1}\ sec^{-1}$ for all of these reactions, a rather typical value for a second-order ionic reaction.

Discussion

Sulfides.—Several modes of decomposition are available to **1**, and sulfides and disulfides give somewhat different product mixtures. We will discuss the reactions of sulfides first. (1) Intermediate **1** can revert to starting materials. (2) The benzoate anion can attack the carbonyl carbon of the cation fragment in **1** to produce benzoic anhydride and a sulfoxide (eq 5). (3) If the sulfide possesses a hydrogen α to sulfur, the benzoate anion can abstract a proton to form benzoic acid and an ylide (eq 6) which can subsequently rearrange to produce the α-substitution product (eq 7).


(5)



$$1 \rightleftarrows \mathrm{PhCO_2H} + \underset{\substack{| \\ \mathrm{R'C^{-}} \\ | \\ \mathrm{R''}}}{\mathrm{RS^{+}}}\mathrm{{-}O\overset{\overset{O}{\|}}{C}Ph} \tag{6}$$

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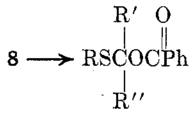
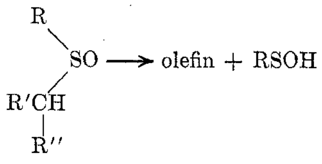
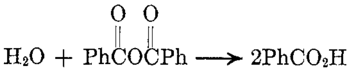


$$\mathbf{8} \longrightarrow \mathrm{RS}\underset{\substack{| \\ \mathrm{R''}}}{\overset{\substack{\mathrm{R'} \\ |}}{\mathrm{C}}}\mathrm{O\overset{\overset{O}{\|}}{C}Ph} \tag{7}$$

Johnson and Phillips[15] have studied the Pummerer rearrangement of sulfonium salts. Their results indicate the initial formation of an ylide in a rate- and product-determining step; the ylide then leads to product *via* a sulfur-stabilized carbonium ion. It is likely, therefore, that the reaction shown in eq 7 involves the formation of an ion pair and the subsequent recombination of the ions to form the α-substitution product. The subsequent reactions are shown in eq 8–11 and will be discussed below.


(8)

$$\mathrm{RSOH} \longrightarrow \text{olefin} + \mathrm{(S)} + \mathrm{H_2O} \tag{9}$$



$$\mathrm{H_2O} + \mathrm{Ph\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}Ph} \longrightarrow 2\mathrm{PhCO_2H} \tag{10}$$

$$n\mathrm{S} + \mathrm{R_2S} \longrightarrow \mathrm{RS}_{n+1}\mathrm{R} \tag{11}$$

We believe that the sulfoxide produced in eq 5 is the precessor of the olefin produced in these reactions (eq 8). However, it is possible to rationalize the products of eq 8–10 by different mechanisms. For example, the benzoate ion in **1** could be postulated to abstract a β hydrogen to yield olefin, benzoic acid, and RSOCOPh directly (eq 12).[16]

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[15] (a) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969); (b) K. F. O'Driscoll, "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley, New York, N. Y., 1970, pp 630–632; (c) K. F. O'Driscoll, "Structure and Mechanism in Vinyl Polymerization," T. Tsura and K. F. O'Driscoll, Ed., Marcel Dekker, New York, N. Y., 1969, pp 87–89.

[16] This possibility was suggested by a referee.

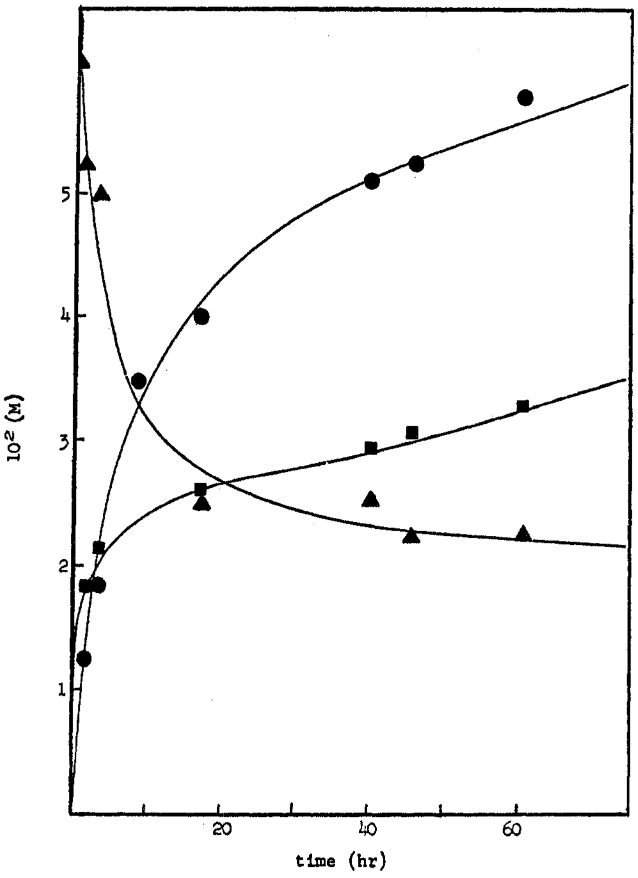
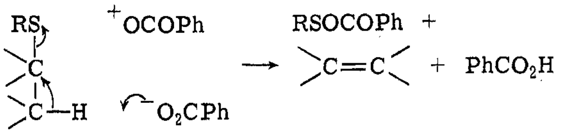


Figure 3.—A plot of the products of decomposition of *tert*-butyl sulfoxide in CCl_4 at 80° in the presence of benzoic anhydride: $(\text{sulfoxide})_0 = 0.0661$, $(\text{anhydride})_0 = 0.0614$; benzoic acid ●, benzoic anhydride ▲, isobutylene ■.



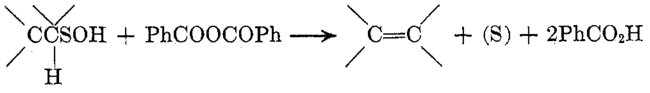
(12)

The RSOCOPh would then react with benzoic acid to yield sulfenic acid and anhydride.

$$\text{RSOCOPh} + \text{PhCO}_2\text{H} \longrightarrow \text{RSOH} + \text{PhCOOCOPh} \qquad (13)$$

This mechanism is not consistent with our data. Firstly, Figures 1 and 2 show that olefin formation precedes benzoic acid, whereas they would be produced together in eq 12. Secondly, in an independent study, *tert*-butyl sulfoxide was found to decompose to form isobutylene and, presumably, *tert*-butylsulfenic acid, and the rate of isobutylene formation did not change when benzoic anhydride was present. Furthermore, the rates of olefin and benzoic acid formation are similar in the BPO-*tert*-butyl sulfide and the sulfoxide–benzoic anhydride system (compare Figures 1 and 3).

Another possibility would be to formulate eq 9 and 10 as synchronous.



$$\text{H}\!-\!\overset{|}{\text{C}}\text{CSOH} + \text{PhCOOCOPh} \longrightarrow \text{C}\!=\!\text{C} + (\text{S}) + 2\text{PhCO}_2\text{H}$$

We prefer to formulate eq 9 and 10 separately, since Block[17] has evidence that water is produced in the similar decomposition of thiolsulfinates, RS(O)SR. He has proposed a mechanism involving a Cope rearrangement and the production of thiolsulfinic acid (RSSOH) as an intermediate. Note that the BPO reaction with disulfides would give thiolsulfinates in eq 1 and RSSOH in eq 8 instead of the sulfoxide and RSOH produced from sulfides.

Sulfur atoms have been formulated as intermediates in eq 9 and 11, but it is probable that the polysulfide products are produced directly. A possible sequence could be

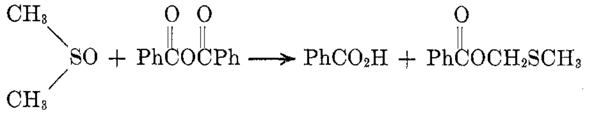
$$\text{RSOH} + \text{H}^+ \longrightarrow \text{RSOH}_2^+$$

$$\text{RSOH}_2^+ + \text{R}_2\text{S} \longrightarrow \text{R}_2\overset{+}{\text{S}}\text{SR} + \text{H}_2\text{O}$$

$$\text{R}_2\overset{+}{\text{S}}\text{SR} \longrightarrow \text{RSSR} + \text{R}^+$$

$$\text{R}^+ \longrightarrow \text{olefin} + \text{H}^+$$

There is evidence in the literature to support our postulation that the benzoate ion abstracts an α hydrogen from the dialkylbenzoxysulfonium cation in **1**. It is known, for example, that benzoic anhydride reacts with DMSO to produce benzoic acid and the α-substitution product (the Pummerer reaction).[15a] A Hammett plot of the reaction of substituted anhydrides with DMSO indicates that the rate-determining step is the nucleophilic attack of the sulfoxide oxygen on the carbonyl carbon of the anhydride.[18] Oae and Kise[8] have studied the reaction of acetic anhydride with phenyl methyl-d_3 sulfoxides. They found a ρ value of -1.60 and a k_H/k_D value of 2.85 at 120°. Sorenson[19] has postulated an analogous mechanism in the reaction of a mixed carboxylic–carbamic anhydride with DMSO.



$$(\text{CH}_3)_2\text{SO} + \text{PhCOOCPh} \longrightarrow \text{PhCO}_2\text{H} + \text{PhCOCH}_2\text{SCH}_3$$

Disulfides.—Disulfides react with BPO to produce benzoic acid, benzoic anhydride, olefin, and polysulfides in analogy with the reactions of sulfides. (See Table II and Figures 1 and 2.) However, disulfides give thiolsulfinates in eq 5 rather than sulfoxides. Attempts were not made to isolate thiolsulfinates from BPO–disulfide reaction mixtures, but there is indirect evidence that they are produced. In the methyl disulfide reaction mixture, an nmr peak at 5.50 ppm was observed which could arise from the presence of methyl thiolsulfinate. *tert*-Butyl thiolsulfinate was synthesized and shown to decompose to form isobutylene and polysulfides under the reaction conditions of the BPO–disulfide experiments. Block[17] studied the decomposition of several thiolsulfinates; the products are polysulfides, water, and either sulfenic acids or olefins (depending on whether the thiolsulfinate does or does not have α hydrogens).

Experimental Section

Materials.—Benzoyl peroxide was purchased from Matheson Coleman and Bell and was recrystallized several times from CCl_4–methyl alcohol. All sulfides and disulfides were purchased from either Eastman or Columbia and were distilled before use. Re-

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[17] E. Block, personal communication. We have independently found polysulfides as a decomposition product of both thiolsulfinates and sulfoxides. Since the submission of this paper, two communications of Block's have been published: *J. Amer. Chem. Soc.*, **94**, 642, 644 (1972).

[18] S. Iwanami, S. Arita, and K. Takeshita, *Yuki Gosei Kagaku Shi*, **26**, 375 (1968).

[19] W. R. Sorenson, *J. Org. Chem.*, **24**, 978 (1959).

agent grade CCl_4 was purchased from Matheson Coleman and Bell and was distilled before use.

Benzoyloxy Dimethyl Sulfide (BOMS).—BOMS has been isolated and purified from the reaction of BPO and methyl sulfide by using preparative gc. A 6-ft SE-30 column was used with the column temperature 110° and the inlet and detector temperature 205°. The nmr showed sharp singlets at 2.2 (3) and 5.32 ppm (2) and two broad peaks in the aromatic region, one centered at 7.45 (3) and the other at 8.05 ppm (2). The ir showed peaks at 5.78 (s), 6.21 (sh), 6.29 (sh), 6.70 (sh), 6.88 (m), 7.00 (b), 7.49 (sh), 7.60 (sh), 7.92 (b), 8.45 (sh), 9.15 (b), 9.32 (sh), 9.72 (sh), 10.70 (b), 12.40 (w), 13.30 (b), 14.03 (b), 14.54 μ (w). The boiling point was 83–84° (0.2 mm). *Anal.* Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.42; H, 5.75.

Benzoic Anhydride.—The isolation and identification of benzoic anhydride as an intermediate was achieved in the following manner. The reaction was monitored by ir and when the absorbance of the peaks at 1735 and 1790 cm^{-1} reached a maximum the reaction was quenched. Solvent and excess TSST were stripped off under vacuum, leaving a very viscous oil. This oil was soluble in CCl_4, and upon the addition of methyl alcohol white needlelike crystals were obtained. The material was recrystallized and gave a sharp melting point at 42°. The ir and nmr spectra were identical with literature values for benzoic anhydride. *Anal.* Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.26 H, 4.58.

Benzoic Acid.—The isolation and identification of benzoic acid as the final product in the reaction of BPO and TSST was achieved in the following manner. The reaction was monitored by ir and when the peak at 1700 cm^{-1} reached a maximum (accompanied by the disappearance of the peaks at 1735 and 1790 cm^{-1}) the reaction was quenched. The CCl_4 and excess sulfur compound were stripped off and the remaining material was twice recrystallized from CCl_4 and gave a sharp melting point at 121–122°. The ir and nmr spectra were identical with the literature values.

Procedure for Kinetic Runs.—The kinetic runs were carried out in sealed 1-cc glass ampoules in a constant-temperature bath. Reaction volumes were 0.6 cc and less than 1% of the CCl_4 solvent is in the vapor phase at 80°. Concentrations of reactants measured at room temperature differ negligibly from those present at 80°. Samples were removed at preselected times, thermally quenched, and stored in the refrigerator. After all samples had been removed, including infinity samples run to 10 half-lives, the concentration of the components of the reaction mixture was determined.

The disappearance of BPO was followed by ir on a Beckman IR-7 using the peak at 1770 cm^{-1}. Also the concentrations of benzoic anhydride and benzoic acid were monitored by ir using the peaks at 1735 and 1790 cm^{-1} for the anhydride and 1700 cm^{-1} for benzoic acid. All other products were determined by gc. The raw data were treated by a computer program to obtain a linear least squares fit of the data using the equation

$$\log (A - A_\infty) = -kt/2.303 + \log (A_0 - A_\infty)$$

where A is the optical density. A typical kinetic run consists of 14 points and two infinity readings, since the infinity reading has a strong influence on the calculated rate constant. The kinetics were studied over about 70% of the reaction. The correlation coefficient is generally 0.99 or better with the probable error in the slope about 1%.

Registry No.—Benzoyl peroxide, 94-36-0; BOMS, 19207-88-6; benzoic anhydride, 93-97-0; benzoic acid, 65-85-0; methyl sulfide, 75-18-3; propyl sulfide, 111-47-7; isobutyl sulfide, 592-65-4; *sec*-butyl sulfide, 626-26-6; *tert*-butyl sulfide, 107-47-1; *tert*-butyl disulfide, 110-06-5; methyl disulfide, 624-92-0; ethyl disulfide, 110-81-6; isobutyl disulfide, 1518-72-5; propyl disulfide, 629-19-6; isopropyl disulfide, 4253-89-8; *sec*-butyl disulfide, 5943-30-6; phenyl sulfide, 139-66-2; *tert*-amyl disulfide, 34965-30-5; styrene, 100-42-5; lauroyl peroxide, 105-74-8; azobisisobutyronitrile, 78-67-1; *tert*-butyl perbenzoate, 614-45-9; di-*tert*-butyl peroxylate, 110-05-4; propionyl peroxide, 3248-28-0; *p*-nitrophenylazotriphenylmethane, 16186-97-3.

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