1 h. After cooling to room temperature, the phosphorus compounds were removed under vacuum, yielding a semisolid residue. This was taken up in hot methanol. The azo compound (264 mg, 72%) was isolated as long needles. A second recrystallization furnished material, mp 210-211 °C. During a study of the fluorescence properties of this compound, the presence of an impurity was revealed in the excitation spectrum. Sublimation (105-130 °C (0.05 mm)) removed this impurity; NMR δ 2.21 (AB q); UV (benzene) λ_{max} 366 nm (ϵ 129); MS, *m/e* 238, 240, 242 ($m^+ - N_2$); calcd for $C_6H_8Br_2$ ($m^+ - N_2$), 237.8992; found, 237.8990.

Nitrogen quantum yields were determined on a photochemical merry-go-round using a Hanovia 450-W medium-pressure mercury arc lamp and filters to isolate the desired wavelength (366 nm direct or 313 nm sensitized). Solutions were degassed and sealed in Pyrex tubes, N_2 evolution being measured with a Toepler pump and gas buret. The initial absorbance was arranged to be about 3 and conversions were kept below 20%. A solution of 2,3-diazabicyclo[2.2.1]hept-2-ene plus benzophenone was employed as the actinometer ($\Phi_r = 1.0$). The temperature of the merry-go-round water bath was regulated to ±0.1 °C with a RFL Industries proportional controller.

Fluorescence lifetimes were determined utilizing a Lambda Physik EMG 101 nitrogen (337 nm) or xenon fluoride (351 nm) excimer laser and a Hewlett-Packard HP1741A storage oscilloscope. The desired emission was isolated wtih a Bausch and Lomb grating monochromator. The sample was degassed in a 1 cm^2 cell equipped with a glass well that protruded into the solution. Temperature was monitored by measuring the resistance of a calibrated thermistor placed in the well. The temperature of the cell was regulated by a cooling-heating block connected to a Neslab circulating bath. The scope traces were photographed and digitized to produce data files that were analyzed on a PDP 11/70 computer and a Hewlett-Packard 2648A graphics terminal. All fluorescence decays were first order.

Product Studies. Solutions of DBO in C_6H_6 or **2** in C_6H_5F were degassed and sealed in Pyrex tubes. Irradiation was done using a Hanovia 450-W mercury lamp and appropriate filters to isolate the 366-nm (direct) or 313-nm (Ph_2CO sensitized) line. Products were analyzed on an Antek 300 FID gas chromatograph with $^1/_8$ in. × 20 ft. stainless steel column of 20% XE-60 on Chromosorb P at 80 °C. DBO gave two peaks,[4] 1,5-hexadiene being identified by comparison of retention time with that of the known compound. Products of **2** were isolated by preparative GC (15% XE-60, 20 ft × 0.25 in., 80 °C) and their NMR spectra compared with those of the known compounds.[56] The first peak (retention time 13.3 min) was 1,4-dimethylbicyclo[2.2.0]hexane and the second (retention time 20.0 min) was 2,5-dimethyl-1,5-hexadiene.

A solution of **17** in C_6D_6 was irradiated at 366 nm for 20 min at 6 °C. An NMR of the solution showed δ 2.74 (s, 4 H), 5.36 (br s, 2 H), 5.67 (d, J = 2 Hz, 2 H), 7.60 (m, 10 H). On the basis of this spectrum, the product is assigned as 2,5-diphenylhexa-1,5-diene, a known substance.[57] The same product was formed on heating **17** to 200 °C. A similar experiment using azoalkane **3** gave an NMR spectrum corresponding to the known hydrocarbon 2-phenyl-1,5-hexadiene.[58]

Attempted Trapping of Cation 25. **7** (20 mg) was added to 3 mL of a saturated solution of NaOAc in AcOH. A few drops of CH_2Cl_2 were required to keep all reactants in solution. The mixture was irradiated for 2 h through Pyrex, with a Hanovia 450-W lamp. AcOH was then evaporated, and ~1 mL of $CDCl_3$ was added to the remaining solid. After filtration through K_2CO_3, NMR showed that no detectable amount of bridgehead acetate had formed (absence of δ 2.0 peak).

Acknowledgment. We thank the National Science Foundation and The Robert A. Welch Foundation for financial support. Some of the reported fluorescence lifetimes were determined at the Center for Fast Kinetics Research in Austin, TX, and we are grateful to Dr. M. A. J. Rodgers for his help.

Registry No. **1**, 87373-47-5; **2**, 49570-30-1; **3**, 87373-48-6; **4**, 25863-08-5; **5**, 87420-89-1; **6**, 39898-44-7; **7**, 3993-62-2; **8**, 87373-49-7; **9**, 87373-52-2; **10**, 87373-55-5; **13** (R = Br), 87373-53-3; DBO, 3310-62-1; biacetyl, 431-03-8; chrysene, 218-01-9; 9-fluorenone, 486-25-9; 1,3,5-cyclooctatriene, 1871-52-9; dimethyl azodicarboxylate, 2446-84-6; *exo*-7,8-dicarboxymethoxy-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene, 87373-50-0; 4-methyl-2,4,6,10-11-pentaazapentacyclo[5.5.4.0^{2,6}.0^{8,12}.0^{13,16}]hexadec-10-ene-3,5-dione, 87373-51-1; *trans*-1,4-dibromo-1,4-dinitrosocyclohexane, 87373-54-4.

---

(56) Srinivasan, R. *Int. J. Chem. Kin.* **1969**, *1*, 133 "Selected Nuclear Resonance Spectral Data"; Haas, C. E., Ed.; Thermodynamics Research Center: College Station, TX, 1978.

(57) Marvel, C. S.; Gall, E. I. *J. Org. Chem.* **1960**, *25*, 1784.

(58) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4417.

Reaction of Nucleophiles with Electron Acceptors by S_N2 or Electron Transfer (ET) Mechanisms: *tert*-Butyl Peroxybenzoate/Dimethyl Sulfide and Benzoyl Peroxide/*N*,*N*-Dimethylaniline Systems[1,2]

William A. Pryor*[1a] and William H. Hendrickson, Jr.[1b]

Contribution from the Departments of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and the University of Dallas, Irving, Texas 75061.

Received January 12, 1983. Revised Manuscript Received July 2, 1983

Abstract: This paper is one of a series that probes the reactions of nucleophiles with peroxides, reactions that can occur either by an initial S_N2 reaction or by an electron-transfer (ET) reaction. The products and kinetics are reported for the reaction of dimethyl sulfide and a series of ring-substituted aryl methyl sulfides with *tert*-butyl peroxybenzoate (TBP) and four ring-substituted TPB's. Kinetic analysis allows the separation of the rate constants for unimolecular homolysis (k_1) and those for the decomposition of the TBP by the sulfide (k_2). The bimolecular reaction is accelerated by electron-withdrawing substituents in the TBP; for example, when 3,5-$(NO_2)_2$-TBP is used, k_2/k_1 is 12 000. The products that are formed are consistent with a radical process; however, this evidence is not regarded as conclusive. Experiments with both limiting galvinoxyl and excess galvinoxyl, as well as with styrene, indicate that radicals are produced in sulfide-TBP reactions, but the yield of radicals is small (see Table VII). Solvent effects (Table I) and substituent effects (Table II) are not useful for distinguishing S_N2 and ET pathways. The kinetic isotope effect produced by substituting deuterium in the nucleophile is reported for the $(CD_3)_2S$ reaction with TBP and $(NO_2)_2$-TBP and also for the reaction of dimethylaniline-d_6 with benzoyl peroxide. This isotope effect is suggested to be a more reliable probe of the nature of the initial reaction (i.e., S_N2 or ET). Surprisingly, the isotope effects indicate that the dimethylaniline-BPO system involves an S_N2 reaction and the dimethyl sulfide-TBP system involves ET, although the former pair gives about a 10-fold higher yield of free radicals.

In recent years, a lengthening list of reactions that had been thought to occur by ionic reactions has been found to involve free-radical chain reactions, at least under some conditions.[3] Some of the most interesting reactions that are of this type are sub-

0002-7863/83/1505-7114$01.50/0

stitution processes.[4]

Nucleophiles can react with suitable substrates either by the familiar S_N2 reaction or by a radical-mediated process initiated by an electron-transfer (ET) reaction. In recent years, a number of groups have studied the reactions of nucleophiles with peroxides, in particular, since peroxides generally give products in an irreversible step upon either one- or two-electron transfer processes.[5]

These reactions also model some of the features of a group of biological oxidations in which one-electron processes often occur.[6] For example, the reaction of benzoyl peroxide with *N,N*-dimethylaniline (DMA) has been studied in great detail; an almost quantitative yield of benzoic acid, methylaniline, and formaldehyde is obtained after workup, along with small yields of products such as *p*-benzoyloxydimethylaniline that suggest the presence of benzoyloxyl radicals in the reaction. Similarly, the demethylation of nitrogen-containing drugs (including DMA) catalyzed by hemeproteins or prostaglandin synthetase involves free-radical intermediates and produces formaldehyde along with the demethylated drug.[6] These types of reactions can be represented by the generalized scheme shown in eq 1.

$$R_2N\text{-}CH_3 \xrightarrow{\text{oxidation}} R_2\dot{N}^+\text{—}CH_3 \xrightarrow{(\text{-H}\cdot)} R_2N^+\text{=}CH_2 \xrightarrow{H_2O} R_2N^+H_2 + CH_2O \quad (1)$$

In the case of nucleophiles and peroxides, the initial reaction can occur by an initial ET or by nucleophilic displacement on the O–O bond of the peroxide, and it generally is extremely difficult to determine which mechanism prevails in any particular case.[2,5] The kinetics and the products of these reactions generally can be rationalized by both mechanisms, and more subtle factors such as solvent polarity effects also are unable to select mechanisms in an unambiguous way.[2a] Even the accelerated production of free radicals cannot be taken as conclusive proof for an ET mechanism, since an S_N2 displacement reaction can lead to an intermediate that homolyzes faster than does the peroxide itself.[2,5,7,8] There even is some uncertainty as to whether the ET and S_N2 mechanisms represent entirely independent pathways, or whether they form a continuum with borderline cases having partial bonding and characteristics of both types of mechanisms.[5i] Furthermore, borderline cases can be expected: the kinetic isotope effect data we have reviewed[2b] as well as the data of other authors[5] indicate that a spectrum of experimental responses occurs when a series of such peroxide–nucleophile reactions is studied. On kinetics criteria alone, of course, it is extremely difficult to separate a "merged" mechanism from simultaneous occurrence of independent ET and S_N2 reactions. Nevertheless, our current working hypothesis is that ET and S_N2 pathways represent independent and distinguishable mechanisms, and we have interpreted our data in this way.

Table I. Solvent Effects on the Rate of the Dimethyl Sulfide–TBP Reaction[a]

solvent	E_T	$k_{obsd} \times 10^5$ (s^{-1})
carbon tetrachloride	32.5	1.5
benzene	34.5	1.7
tert-butyl alcohol	43.9	2.2
acetic acid	51.2	5.2
methanol	55.5	2.5

[a] The solvent consists of that named plus 0.05 M TBP, 1.0 M dimethyl sulfide, and 0.2 M styrene; the temperature 80 °C. The E_T values are from Abraham, M. H. *Prog. Phys. Org. Chem.* 1974, *11*, 1.

Table II. Substituent Effects on Rate Constants for the TBP–Dimethyl Sulfide Reaction

substituent in TBP	E_a[a] (kcal/mol)	$k_1 \times 10^5$[b] (s^{-1})	$k_2 \times 10^5$[c] (M^{-1} s^{-1})	k_2/k_1 (M^{-1})
p-CH_3O	35.7 ± 2.0	0.10	0.89	8.9
H	34.0 ± 0.3	0.088	1.46	17.
p-Cl	36.8 ± 0.9	0.042	3.34	80.
p-NO_2	34.9 ± 1.7	0.029	15.5	535.
3,5-$(NO_2)_2$	40.1 ± 0.5	0.011	134.0	12 000.

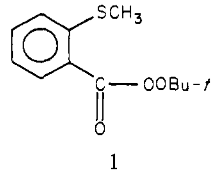
[a] Calculated from an Arrhenius plot of k_1 measured in CCl_4 containing 0.2 M styrene at 110, 120, and 130 °C. Complete data are given in ref 2d. [b] At 80 °C, calculated from an Arrhenius plot. [c] In CCl_4, 1.0 M dimethyl sulfide, 0.2 M styrene, 0.01 M peroxyester at 80 °C.

In this paper, we report a detailed study of the reaction of dimethyl sulfide with *tert*-butyl peroxybenzoate. We also review our kinetic isotope effect (KIE) method[2b] to distinguish ET and S_N2 pathways in the reactions of nucleophiles with peroxides, and we report the application of this test to the reactions of $(CH_3)_2S$ and $(CD_3)_2S$ with *tert*-butyl peroxybenzoate (TBP) and benzoyl peroxide (BPO) and the reaction of DMA/DMA-d_6 with BPO.

Results

Kinetics of the Dimethyl Sulfide–TBP Reaction. The rate of decomposition of TBP is accelerated by a factor of 17 in 1.0 M dimethyl sulfide in CCl_4, and the reaction follows pseudo-unimolecular kinetics. The observed rate constant (k_{obsd}) is the sum of the rate constant for unimolecular peroxyester homolysis (k_1) and the term for the bimolecular, sulfide-assisted decomposition, $k_2[CH_3SCH_3]$. Values of k_2 were determined by subtracting the contribution of peroxyester homolysis from the total reaction rate measured by infrared analysis in 1.0 M dimethyl sulfide.

Peroxybenzoates are susceptible to induced decomposition;[9] for example, Bentrude and Martin reported that the rate of decomposition of **1** decreased 22% when 0.2 M styrene was added to the reaction mixture.[10] When 0.2 M styrene was added to dimethyl sulfide–TBP reaction solution, k_{obsd} decreased by 28%; therefore, all of the reactions were run in 0.2 M styrene to prevent induced decomposition.



1

---

(1) (a) Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803. (b) Department of Chemistry, University of Dallas, Irving, Tex. 75061.

(2) Some of these results have been reported elsewhere in preliminary form: (a) Pryor, W. A.; Hendrickson, W. H., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 1580. (b) Pryor, W. A.; Hendrickson, W. H., Jr. *Ibid.* **1975**, *97*, 1582. (c) Pryor, W. A.; Hendrickson, W. H., Jr. *Tetrahedron Lett.* **1983**, *24*, 1459. (d) Taken in part from the dissertation of W. H. Hendrickson, Jr., Louisiana State University, 1974.

(3) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. Bilevich, K. A.; Okhlobystin, O. Yu. *Russ. Chem. Rev.* **1968**, *37*, 954.

(4) See, for example, Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663.

(5) (a) Church, D. F.; Pryor, W. A. *J. Org. Chem.* **1980**, *45*, 2866. (b) Dixon, B. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 3068. (c) Zupancic, J. J.; Horn, K. A.; Schuster, G. B. *Ibid.* **1980**, *102*, 5279. (d) Koo, J. Y.; Schuster, G. B. *Ibid.* **1978**, *100*, 4496. (e) Okamoto, K.; Takeuchi, K.; Murai, O. *Tetrahedron Lett.* **1981**, 2785. (f) Hull, L. A.; Davis, G. T.; Rosenblatt, D. H.; Williams, H. K. R.; Weglein, R. C. *J. Am. Chem. Soc.* **1967**, *89*, 1163. (g) Chalfont, G. R.; Perkins, M. J. *J. Chem. Soc. B* **1971**, 245. (h) Nugent, W. A.; Bertini, F.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 4945. (i) Walling, C.; Zhao, C. *Tetrahedron* **1982**, *38*, 1105. (j) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187.

(6) (a) For a review see: Kalyanaraman, B. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, in press; Vol. VI. Mason, R. P. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1982; Vol. V, pp 181 ff. (b) Griffin, B. W. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.: Plenum Press: New York, 1979; pp 773 ff. (c) Laskey, J. M.; Sivarajah, K.; Mason, R. P.; Kalyanaraman, B.; Abou-Donia, M. B.; Eling, T. E. *J. Biol. Chem.* **1981**, *256*, 7764. (d) Maruyama, K.; Otsuki, T. *Chem. Lett.* **1982**, 1. (e) Sun, F. F. *Fed. Proc.* **1981**, *40*, 752.

(7) Walling, C. In "Free Radicals in Solution"; Wiley: New York, 1957; pp 590 ff.

(8) Pryor, W. A. In "Free Radicals"; McGraw-Hill: New York, 1966; pp 98 and 99.

(9) (a) Blomquist, A. T.; Ferris, A. F. *J. Am. Chem. Soc.* **1951**, *73*, 3412. (b) Walling, C.; Azar, J. C. *J. Org. Chem.* **1968**, *33*, 3888.

(10) Bentrude, W. G.; Martin, J. C. *J. Am. Chem. Soc.* **1962**, *84*, 1561.

Table III. Rate Constants for Reaction of Aryl Methyl Sulfides with *tert*-Butyl *p*-Chloroperoxybenzoate and Benzoyl Peroxide

substituent	*p*-Cl-TBP[a] $k_2 \times 10^5$ $M^{-1}\ s^{-1}$	BPO[b] $k_2 \times 10^3$ $M^{-1}\ s^{-1}$
p-CH_3O	1.82	3.39
p-$(CH_3)_3C$	0.87	1.69
p-CH_3	0.78	1.65
H	0.38	0.83
p-Cl	0.17	0.54
p-Br		0.43

[a] 0.01 M *p*-Cl-TBP, 1.0 M sulfide, 0.2 M styrene, CCl_4, 80 °C. [b] 0.01 M BPO, 0.10 M sulfide, CCl_4, 40 °C.

Solvent Effects. Rate constants of the TBP–dimethyl sulfide reaction were measured by iodometric titration in five solvents (Table I).[2d] With the exception of acetic acid, the reaction rates are virtually independent of solvent polarity. For example, a graph of log k vs. E_T yields a straight line with a slope of 0.009.[11] The relatively large rate increase observed in acetic acid may be the result of an acid-catalyzed reaction similar to that observed in the reaction of sulfides with *tert*-butyl hydroperoxide.[12]

Substituent Effects. Values of k_1 extrapolated to 80 °C from Arrhenius plots of kinetic data collected at higher temperatures, values of k_2, and activation energies for peroxyester homolysis[13-15] are given in Table II for TBP and several ring-substituted peroxyesters. The Hammett plot of log k_2 vs. σ gives a ρ value of $+1.34 \pm 0.03$ ($r = 0.999$).[2d] This ρ value is similar to that found for the reaction of TBP with triphenylphosphine ($\rho = +1.24$).[16]

As shown in Table II, electron-withdrawing groups in the phenyl ring of TBP greatly accelerate the rate of the sulfide-assisted decomposition but retard the rate of peroxyester homolysis; therefore, k_1 makes an increasingly smaller contribution to k_{obsd} as the electron-withdrawing ability of substituents increases. This difference can be utilized to minimize the amount of homolysis that competes with the assisted decomposition. For example, *tert*-butyl *p*-methoxyperoxybenzoate is decomposed by 1.0 dimethyl sulfide only nine times faster than it homolyzes, whereas *tert*-butyl 3,5-dinitroperoxybenzoate undergoes the bimolecular reaction 1.2×10^4 times faster than unimolecular homolysis. Thus, for 3,5-$(NO_2)_2$-TBP, $k_2/k_1 = 12\,000$ and unimolecular homolysis accounts for only 0.008% of the total rate of decomposition of the peroxyester.

A series of ring-substituted aryl methyl sulfides were allowed to react with *tert*-butyl *p*-chloroperoxybenzoate to evaluate the substituent effects on the sulfide molecule. (The chloro-substituted peroxyester was used since its ratio of k_1/k_{obsd} is smaller than that for TBP itself.) Table III presents these data; a Hammett plot of the data has a slope of -1.68 ± 0.05, $r = 0.999$ (omitting the point for the methoxy derivative, which is off the correlation line).[2d]

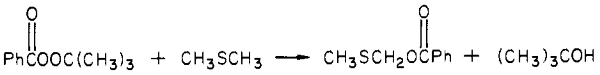
The substituent effect for the reaction of benzoyl peroxide with ring-substituted aryl methyl sulfides also was studied (Table III). The ρ value for this reaction is -1.30 ± 0.13 ($r = 0.985$), again omitting the methoxy derivative.[2d]

Product Analysis of the Dimethyl Sulfide Reaction with TBP and BPO. The products of the TBP–dimethyl sulfide reaction were determined by GLPC analysis of a reaction carried out in CCl_4 and 0.2 M styrene. The major products are benzoyloxydimethyl sulfide (**2**, 96%) and *tert*-butyl alcohol (91%); at least six minor products were detected but not identified, but no dimethyl sulfoxide, *tert*-butyl benzoate, acetone or benzoic acid are detected. Thus, reaction 2 accounts for greater than 90% of the products observed.

Table IV. Rate of Galvinoxyl Disappearance in the Dimethyl Sulfide–TBP Reaction[a]

[peroxyester]	$R_T \times 10^8 M\ s^{-1}$ [b]	$R_1 \times 10^8 M\ s^{-1}$ [c]	$R_2 \times 10^8 M\ s^{-1}$ [d]	R_2/R_1
	tert-Butyl *p*-Methoxyperoxybenzoate[e]			
0.0025	4.1	0.35	0.2	0.6
0.010	5.4	1.3	0.5	0.4
0.025	7.7	3.5	0.6	0.2
0.050	12.2	7.0	1.6	0.2
			av	$0.3_5 \pm 0.19$
	tert-Butyl Peroxybenzoate[f]			
0.010	3.0	1.0	0	0
0.025	4.7	2.5	0.2	0.1
0.050	7.3	4.6	0.7	0.2
0.10	12.4	9.4	1.0	0.1
			av	0.1 ± 0.08
	tert-Butyl *p*-Chloroperoxybenzoate[g]			
0.010	3.1	0.75	0.2	0.3
0.025	4.4	1.5	0.6	0.4
0.050	7.0	3.0	1.7	0.6
0.10	11.1	6.0	2.8	0.5
			av	$0.4_5 \pm 0.13$
	tert-Butyl *p*-Nitroperoxybenzoate[h]			
0.0025	1.1	0.08	0.3	4.0
0.010	2.8	0.40	1.7	4.2
0.025	4.4	0.70	3.0	4.3
0.050	9.4	1.5	7.2	4.8
			av	4.3 ± 0.3

[a] 6.0×10^{-4} M galvinoxyl in CCl_4 at 80 °C. [b] Rate of galvinoxyl disappearance in 1.0 M dimethyl sulfide–peroxyester solution. [c] Rate of galvinoxyl disappearance due to peroxybenzoate homolysis. [d] Calculated by $R_2 = R_T - R_1 - R_B$ using R_B values determined from Figure 1. [e] $R_B = 3.6 \times 10^{-8}$ M/s. [f] $R_B = 2.0 \times 10^{-8}$ M/s. [g] $R_B = 2.3 \times 10^{-8}$ M/s. [h] $R_B = 0.7 \times 10^{-8}$ M/s.



$$PhC(=O)OOC(CH_3)_3 + CH_3SCH_3 \longrightarrow CH_3SCH_2OC(=O)Ph + (CH_3)_3COH \quad (2)$$

2

Radical Production in the Sulfide-Assisted Reaction of TBP. Our interest in the sulfide–TBP reaction originated with our observation that compound **1** gives a substantial yield of radicals, but the reaction of sulfides with BPO gives no radical products.[17] We therefore were interested in studying radical production in a reaction that is more analogous to the reaction of **1**, namely, the reaction of dimethyl sulfide with TBP, eq 2.

1. Limiting Galvinoxyl. The radical yield in peroxide decomposition reactions can be measured by trapping the radicals with galvinoxyl.[18] When the peroxyester is present in excess, its concentration remains constant and the rate of radical production is related to the rate of disappearance of scavenger. In the presence of 1.0 M dimethyl sulfide, the total rate of radical production in the peroxyester–dimethyl sulfide reaction (R_T) is the sum of the rate of radical production from unimolecular peroxyester homolysis (R_1) and the rate of radical production by the sulfide-assisted decomposition (R_2) (eq 3). In eq 3, f_1 is the fraction of the

$$R_T = R_1 + R_2 = 2(f_1k_1 + f_2k'_2)[\text{TBP}] \qquad (3)$$

unimolecular homolysis that yields scavengeable free radicals, f_2 is the fraction of the bimolecular reaction that forms scavengeable free radicals, and k'_2 is the pseudo-unimolecular rate constant for the bimolecular reaction in 1.0 M dimethyl sulfide.

---

(11) For a review of solvent effects on reaction rates, see: Abraham, M. H. *Prog. Phys. Org. Chem.* **1974**, *11*, 1. Ahmad, I.; Tollin, G. *Biochemistry* **1981**, *20*, 5925. Kosower, E. M. In "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968; pp 187 ff.

(12) Edwards, J. O.; Fortnum, D. H. *J. Org. Chem.* **1962**, *27*, 407.

(13) A Hammett plot of log k_1 at 120 °C vs. σ constants gives a ρ value of -0.38 ± 0.08 ($r = 0.934$). A better correlation is obtained using σ^+ constants ($\rho = -0.33 \pm 0.03$, $r = 0.985$). Other reported ρ values for TBP homolysis are -0.57 in diphenyl ether[14] and -0.34 in undecane.[15]

(14) Bloomquist, A. T.; Berstein, I. A. *J. Am. Chem. Soc.* **1951**, *73*, 5546.

(15) Antonovskii, V. L.; Bezborodova, L. D.; Yasselman, M. E. *Russ. J. Phys. Chem.* **1969**, *43*, 1279.

(16) Denny, D. B.; Goodyear, W. F.; Goldstein, B. *J. Am. Chem. Soc.* **1961**, *83*, 1726.

(17) Pryor, W. A.; Bickley, H. T. *J. Org. Chem.* **1972**, *37*, 2885.

(18) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.

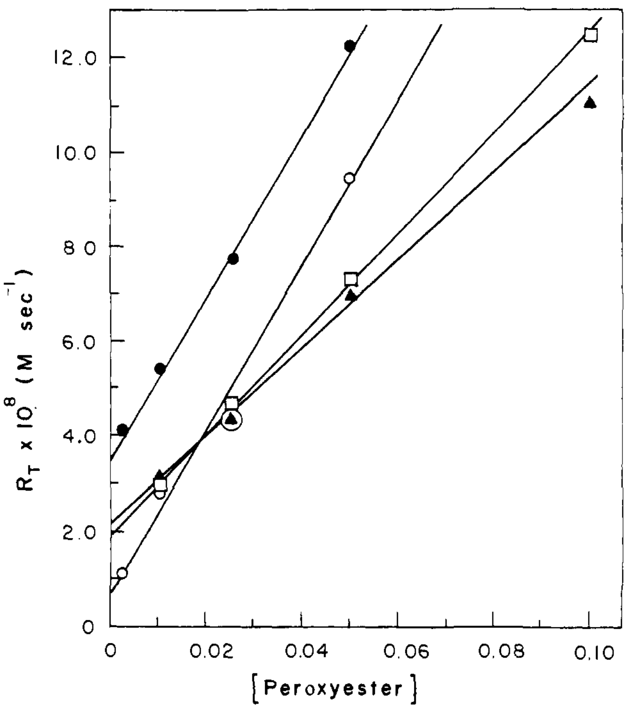


Figure 1. Plots of R_T vs. peroxyester concentration for the reaction of dimethyl sulfide with substituted TBP: initial dimethyl sulfide concentration, 1.0 M; initial galvinoxyl concentration, 6.0×10^{-4} M; ●, p-CH_3O-TBP; □, TBP; ▲, p-Cl-TBP; ○, p-NO_2-TBP.

Values of R_T and R_1 for four peroxyesters are reported in Table IV. Graphs of R_T vs. peroxyester concentration, which are shown in Figure 1, yield nonzero intercepts that are dependent on the nature of the peroxyester. We assume these intercepts are due to a galvinoxyl decomposition that is independent of peroxyester concentration, and we have treated this as equivalent to a blank reaction, R_B. The total rate of galvinoxyl disappearance is then the sum of R_1, R_2, and R_B, and values of R_2 can be found by subtracting R_1 and R_B from R_T. The ratio R_2/R_1 is given in the last column of Table IV and is independent of peroxyester concentration for each peroxyester. This independence shows that the method for making the blank correction gives self-consistent data.

2. **Excess Galvinoxyl.** When the peroxyester-sulfide reaction is carried out in excess galvinoxyl and the reaction is followed to completion, the efficiency of radical production can be determined from the amount of galvinoxyl consumed (eq 4: $[G]_0$ = initial

$$f_2 = ([G]_0 - [G]_f)/2[\text{peroxyester}] \qquad (4)$$

galvinoxyl concentration, $[G]_f$ = final galvinoxyl concentration), and k_{obsd} can be calculated from the rate of galvinoxyl disappearance (eq 5).[19]

$$\ln \frac{[G] - [G]_f}{[G]_0 - [G]_f} = k_{obsd}t \qquad (5)$$

For accurate results with the excess scavenger method, R_B and R_1 must be much smaller than R_2; therefore, only the two nitro-substituted peroxyesters are usable. The data are shown in Table V; a correction for the blank reaction was made where applicable. The validity of the results is supported by the reasonably satisfactory agreement between k_{obsd} measured with galvinoxyl and by infrared analysis (Table V). The values of f_2 are shown in Table V and indicate that about 2% of the peroxyester-dimethyl sulfide reaction produces scavengeable free radicals.

3. **Styrene Polymerization.** We have also used styrene as a scavenger to confirm the galvinoxyl scavenging experiments. Styrene polymerization has been used by both Walling and O'Driscoll to determine radical yields in the DMA-BPO system.[20] Values of R_T/R_1 for the peroxyester-dimethyl sulfide reaction determined by styrene polymerization are given in Table VI; details of the method are given in the Experimental Section.[2d] Each of the four peroxyesters studied by this method accelerated the polymerization of styrene in the presence of dimethyl sulfide, but the R_T/R_1 ratios are small, as in the galvinoxyl experiments. Nitro-substituted aromatic compounds inhibit the polymerization of styrene. The rate of the thermal polymerization of styrene is retarded about twofold by 0.05 M nitrobenzene (see legend to Table VI), and 0.05 M m-dinitrobenzene completely inhibits the polymerization even in the presence of 0.05 M TBP. Thus, the rates of polymerization initiated by p-NO_2-TBP are slower than for TBP itself (see Table VI), but there is a substantial acceleration for the solutions containing 1.0 M dimethyl sulfide relative to the solutions containing only the peroxyester. The $(NO_2)_2$-TBP entirely inhibited the polymerization and consequently could not be studied by this method.

Table V. Radical Production in the Dimethyl Sulfide-TBP Reaction Determined Using the Excess Galvinoxyl Method[a]

peroxyester	concn, M	$k_{IR} \times 10^5$ [b] (s^{-1})	$k_{obsd} \times 10^5$ [c] (s^{-1})	$G_B/(G_0 - G_f)$[d]	f_2[e]	R_T/R_1[f]
p-NO_2-TBP	0.010	15.5	10.9	0.61	0.016	12
p-NO_2-TBP	0.022	15.5	14.5	0.21	0.020	19
3,5-$(NO_2)_2$-TBP	0.027	134	160	0	0.014	730
3,5-$(NO_2)_2$-TBP[g]	0.025	126[h]	119[h]	0	0.016	620

[a] 1.0 M dimethyl sulfide, 1.0×10^{-3} M galvinoxyl in CCl_4 at 80 °C. [b] Rate constant for peroxyester disappearance determined by infrared. [c] Rate constant for peroxyester disappearance calculated by eq 5. [d] Fraction of total galvinoxyl disappearance due to the blank reaction. [e] Calculated by eq 4. [f] $R_T = 2f_2k_{obsd}[TBP]_0$. [g] 0.50 M dimethyl-$d_6$ sulfide. [h] $2k_{obsd}$.

Table VI. Radical Production in the Dimethyl Sulfide-TBP Reaction Measured by Styrene Polymerization[a]

peroxyester	$R_p{}^0 \times 10^4$ [b]	$R_p \times 10^4$ [c]	R_T/R_1[d]
p-CH_3O-TBP	1.4	1.5	1.3
TBP	1.0	1.2	1.4
p-Cl-TBP	0.98	1.1	1.6
p-NO_2-TBP	0.17[e]	0.44[e]	20

[a] Solvent is styrene containing 0.05 M peroxyester, 80 °C, 1 h reaction time. [b] Rates of polymerization (in M/s) in the absence of dimethyl sulfide, corrected for the spontaneous polymerization rate in the absence of peroxyester, $R_{p,thermal} = 1.2 \times 10^{-5}$ M/s. [c] R_p in the presence of 1.0 M dimethyl sulfide, corrected for the thermal polymerization in the presence of 1.0 M dimethyl sulfide, $R_{p,thermal} = 2.0 \times 10^{-5}$ M/s. [d] Calculated using eq 15. [e] Reaction time 1.5 h, corrected for the thermal polymerization rate in the presence of 0.05 M nitrobenzene, $R_{p,thermal} = 0.9 \times 10^{-5}$ M/s.

Radical Production Efficiency. In order to directly compare efficiencies of radical production for different peroxyesters, it is necessary to estimate values of f_2. At equal peroxyester concentrations and in excess dimethyl sulfide, the ratio of R_2 to R_1 is given by eq 6, and rearrangement yields an expression for f_2 (eq 7).

$$\frac{R_2}{R_1} = \frac{2f_2k'_2[\text{TBP}]}{2f_1k_1[\text{TBP}]} \qquad (6)$$

$$f_2 = \frac{f_1R_2/R_1}{k'_2/k_1} \qquad (7)$$

Values of f_2 derived from eq 7 are a measure of radical production from the dimethyl sulfide-peroxyester reaction relative to the efficiency of radical production from the unimolecular homolysis of the peroxyester, f_1; for simplicity we have assumed that f_1 is unity. The method also assumes that the radicals produced by the bimolecular reaction are trapped with the same

---

(19) Lamb, R. C.; Rogers, F. F.; Dean, G. C., Jr.; Voigt, F. W. J. Am. Chem. Soc. 1962, 84, 2635.

Table VII. Comparison of the Efficiency of Radical Production in the Dimethyl Sulfide–TBP Reaction Using Three Methods[a]

	limiting galvinoxyl			excess galvinoxyl		styrene polymerization	
peroxyester	k_2/k_1	R_2/R_1[b]	$f_2 \times 100$[c]	R_2/R_1[d]	$f_2 \times 100$[c]	R_2/R_1[e]	$f_2 \times 100$[c]
p-CH_3O-TBP	8.9	0.4	4.5			0.3	3.4
TBP	17.	0.1	0.6			0.4	2.4
p-Cl-TBP	81.	0.4	0.5			0.6	0.7
p-NO_2-TBP	535.	4.3	0.8	15	2.8	19.	3.6
3,5-$(NO_2)_2$-TBP	12 000.			730	6.1		

[a] The solvent for the galvinoxyl experiments is CCl_4, 80 °C, with and without 1.0 M dimethyl sulfide. That for the styrene experiments is styrene, 80 °C, containing additives and peroxyester as explained in Table VI. [b] From Table IV. [c] Calculated by eq 7. [d] From Table V, $(R_T/R_1) - 1$. [e] From Table VI, $(R_T/R_1) - 1$.

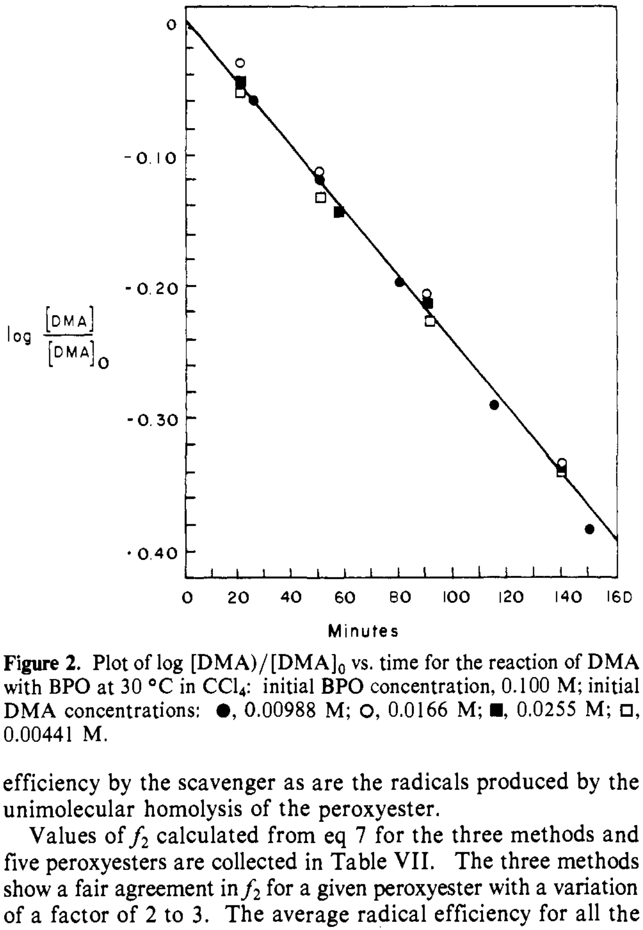


Figure 2. Plot of log $[DMA]/[DMA]_0$ vs. time for the reaction of DMA with BPO at 30 °C in CCl_4: initial BPO concentration, 0.100 M; initial DMA concentrations: ●, 0.00988 M; ○, 0.0166 M; ■, 0.0255 M; □, 0.00441 M.

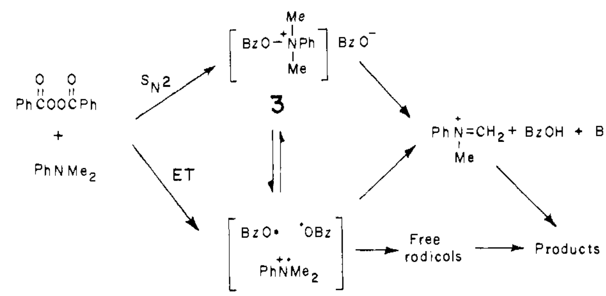
efficiency by the scavenger as are the radicals produced by the unimolecular homolysis of the peroxyester.

Values of f_2 calculated from eq 7 for the three methods and five peroxyesters are collected in Table VII. The three methods show a fair agreement in f_2 for a given peroxyester with a variation of a factor of 2 to 3. The average radical efficiency for all the reactions if 2.5 ± 1.9%. By comparison, the decomposition of BPO accelerated by dimethylaniline produces free radicals with an efficiency of 10–20%,[20a,c] and peroxyester **1** produces radicals with an efficiency of about 50%.[10]

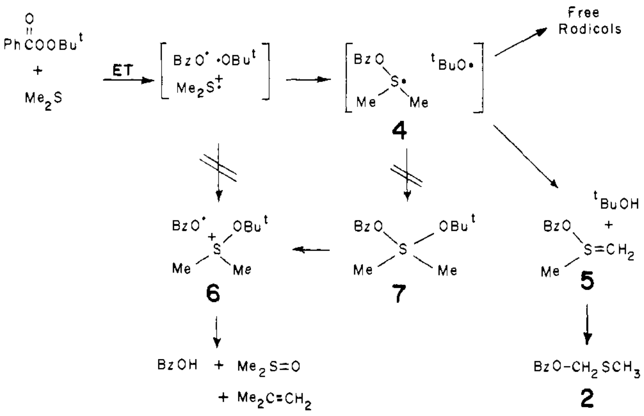
Isotope Effect Method for Distinguishing S_N2 and ET Mechanisms. The β-deuterium kinetic isotope effect (KIE) was measured for the reactions of dimethyl sulfide and dimethyl-d_6 sulfide with both TBP and $(NO_2)_2$-TBP. In addition, isotope effects were measured for the reaction of the sulfide with *tert*-butyl hydroperoxide and BPO, both of which are not thought to produce radicals in reaction with dimethyl sulfide.[17] The reactions were carried out in excess dimethyl sulfide, and rate constants were determined under pseudo-unimolecular conditions. The results, displayed in Table VIII, show that the peroxyester reactions give normal isotope effects (i.e., k_H/k_D greater than unity), whereas the hydroperoxide and BPO reactions give inverse isotope effects.

We have also applied the KIE test to the BPO–DMA system.[2c] Reproducible rate constants were obtained by the use of styrene to retard induced decomposition, as discovered by Walling and O'Driscoll,[20] and by the simple but novel expedient of using BPO as the flooded reagent. Under these conditions the reaction is first order in amine (see Figure 2). Our second-order rate constant using excess BPO is 0.97×10^{-3} M^{-1} s^{-1}, in good agreement with that of Walling and Indictor[20a] of 1.17×10^{-3} M^{-1} s^{-1} using excess DMA (both at 30 °C in solutions containing styrene). The agreement of the second-order rate constants, obtained under pseudo-unimolecular conditions with either of the two reactants present in excess, is the strongest possible evidence for the first-order kinetic dependence on each reactant and the overall biomolecular nature of the reaction. The KIE data are given in Table VIII and show an inverse isotope effect.

Scheme I



Scheme II



Discussion

The difficulty in experimentally distinguishing between S_N2 and ET mechanisms for the reactions of nucleophiles with peroxides is illustrated in Scheme I, which shows pathways for product formation in the benzoyl peroxide–dimethylaniline system. The difficulties arise because the radical intermediates can be formed either directly by an ET reaction or by homolysis of intermediate **3**, which is produced in an S_N2 process and could undergo homolysis faster than does benzoyl peroxide itself. Several workers have favored an ET mechanism for this system;[7,8,21,22] in contrast, Walling has attributed radical formation in this system to the homolysis of intermediate **3**.[7]

Argument for an ET Mechanism for the TBP–Dimethyl Sulfide Reaction. The TBP–dimethyl sulfide reaction is similar to the BPO–DMA reaction in that both reactions produce scavengeable free radicals and the reaction products are consistent with either an ET or S_N2 mechanism. The TBP–dimethyl sulfide reaction produces a 96% yield of methyl benzoyloxydimethyl sulfide(**2**),

---

(20) (a) Walling, C.; Indictor, J. *J. Am. Chem. Soc.* **1958**, *80*, 5814. (b) O'Driscoll, K. F.; White, P. J. *J. Polym. Sci., Part B* **1963**, *1*, 597. (c) O'Driscoll, K. F.; Lyons, P. F.; Patsiga, R. *J. Polym. Sci., Part A* **1965**, *3*, 1567. (d) O'Driscoll, K. F.; Ricchezza, E. N. *Makromol. Chem.* **1961**, *47*, 15. (e) O'Driscoll, K. F. In "Organic Peroxides"; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1, pp 609 ff.

(21) Horner, L. *J. Polym. Sci.* **1955**, *18*, 438.

(22) Pobedimskii, B. G.; Buchachenko, A. L.; Neiman, M. B. *Russ. J. Phys. Chem.* **1968**, *42*, 748.

Table VIII. Kinetic Isotope Effects for Reactions of Dimethyl-d_6 Sulfide and Dimethylaniline-d_6 with Some Peroxide Compounds

peroxide	nucleophile		k_H, $M^{-1}\,s^{-1}$	k_D, $M^{-1}\,s^{-1}$	k_H/k_D
tert-butyl hydroperoxide[a]	Me_2S		1.46×10^{-4}	1.68×10^{-4}	
			1.71×10^{-4}	1.75×10^{-4}	
			1.59×10^{-4}		
			1.66×10^{-4}		
		av	$1.59 \pm 0.1 \times 10^{-4}$	$1.72 \pm 0.05 \times 10^{-4}$	0.92 ± 0.09
benzoyl peroxide[b]	Me_2S		9.81×10^{-3}	11.8×10^{-3}	
			9.76×10^{-3}	10.8×10^{-3}	
		av	$9.78 \pm 0.03 \times 10^{-3}$	$11.3 \pm 0.7 \times 10^{-3}$	0.87 ± 0.06
benzoyl peroxide[c]	$PhNMe_2$		0.990×10^{-3}	1.078×10^{-3}	
			0.949×10^{-3}	1.025×10^{-3}	
			0.981×10^{-3}	1.055×10^{-3}	
			0.966×10^{-3}	1.030×10^{-3}	
		av	$0.97 \pm 0.02 \times 10^{-3}$	$1.04 \pm 0.02 \times 10^{-3}$	0.93 ± 0.03
TBP[d]	Me_2S		1.60×10^{-5}	1.56×10^{-5}	
			1.68×10^{-5}	1.57×10^{-5}	
			1.63×10^{-5}	1.42×10^{-5}	
		av	$1.64 \pm 0.04 \times 10^{-5}$	$1.52 \pm 0.08 \times 10^{-5}$	1.08 ± 0.08
3,5-$(NO_2)_2$-TBP[d]	Me_2S		1.36×10^{-3}	1.26×10^{-3}	
			1.32×10^{-3}	1.26×10^{-3}	
		av	$1.34 \pm 0.03 \times 10^{-3}$	1.26×10^{-3}	1.06 ± 0.03

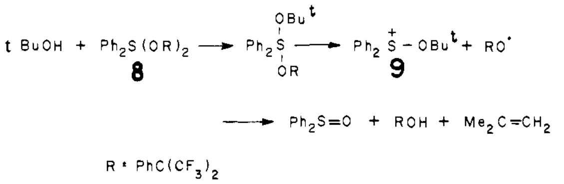
[a] In *tert*-butyl alcohol at 80 °C, determined by iodometric titration. [b] In CCl_4 at 40 °C, determined by infrared. [c] In CCl_4 at 30 °C, determined by GC analysis of DMA. Initial BPO concentration was 0.1 M and DMA was 0.01 M. [d] In CCl_4 at 80 °C, determined by infrared.

91% *tert*-butyl alcohol, and 2–3% of scavengeable radicals. An ET mechanism that is consistent with the observed products is shown in Scheme II. The initial transfer of an electron from dimethyl sulfide to TBP results in a peroxyester radical anion and a sulfide radical cation. The peroxyester radical anion is very unstable and rapidly decomposes to a benzoate anion and a *tert*-butoxyl radical, preventing reversible electron transfer.[23]

An electron transfer from dimethyl sulfide to TBP is not unreasonable. Nucleophilic displacements on TBP are much slower than on BPO, and ET should be able to compete effectively with the slower nucleophilic displacement. Electron-transfer reactions have been observed on 1-phenylethyl peroxybenzoate with electron donors that are poor nucleophiles (such as diphenylanthracene).[5b]

The reactive intermediates, *tert*-butoxyl radical, benzoate anion, and the dimethyl sulfide cation-radical, are formed together in a solvent cage.[5h] Diffusion produces free *tert*-butoxyl radicals and **4**; the low yield of scavengeable free radicals can be explained by the rapid disproportionation of **4** and *tert*-butoxyl radicals to yield nonradical products, *tert*-butyl alcohol and the benzoyloxy ylide **5**. Ylide **5** has previously been identified in the Pummerer rearrangement of sulfonium salts[24] and as an intermediate in the BPO–dimethyl sulfide reaction.[17] Rearrangement of **5** produces the ultimate product, methyl benzoyloxymethyl sulfide (**2**).

One could envision the combination of the dimethyl sulfide cation–radical and the *tert*-butoxyl radical to form **6**, which would undergo rapid decomposition to isobutylene and dimethyl sulfoxide (see Scheme II). For example, the dehydration of *tert*-butyl alcohol by sulfurane **8** is complete within seconds in chloroform at −50 °C (eq 8).[25] The postulated intermediate in this reaction is the *tert*-butoxysulfonium ion **9** which yields diphenyl sulfoxide and isobutylene. Compound **6** can be generated in situ by the reaction of dimethylmethoxysulfonium fluoroborate with sodium *tert*-butoxide in *tert*-butyl alcohol (eq 9).[26] The observed products were isobutylene and dimethyl sulfoxide. Since dimethyl sulfoxide is not an observed reaction product in the dimethyl sulfide–TBP reaction, **6** cannot be an intermediate in that system.

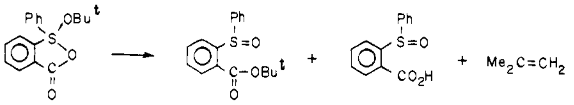


$$t\text{BuOH} + \underset{\mathbf{8}}{Ph_2S(OR)_2} \longrightarrow Ph_2\overset{OBu^t}{\underset{OR}{S}} \longrightarrow \underset{\mathbf{9}}{Ph_2\overset{+}{S}-OBu^t} + RO^{\cdot} \longrightarrow Ph_2S{=}O + ROH + Me_2C{=}CH_2 \qquad (8)$$

$$R = PhC(CF_3)_2$$

$$Me_2S^{+}{-}OMe\ BF_4^{-} \xrightarrow[\text{NaOBu-}t]{t\text{-BuOH}} \underset{\mathbf{6}}{Me_2S^{+}{-}OBu\text{-}t} \rightarrow Me_2S{=}O + Me_2C{=}CH_2 \qquad (9)$$

The sulfurane **7** also could be envisioned as an intermediate; **7** could be formed by combination of **4** with a *tert*-butoxyl radical. A similar sulfurane, **10**, has been studied by Martin.[27] Decomposition of **10** in chloroform gives the products shown in eq 10; no acetone or *tert*-butyl alcohol as detected. Decomposition of **7** would be expected to occur by a similar ionic pathway to yield dimethyl sulfoxide. The absence of dimethyl sulfoxide in the reaction products excludes the formation of **7** as a reaction intermediate and as a possible source of free radicals in Scheme II.



10

(10)

S_N2 Mechanism for the TBP–Dimethyl Sulfide Reaction. The products of the TBP–dimethyl sulfide reaction also can be rationalized as proceeding from an initial nucleophilic displacement, as shown in Scheme III. The absence of dimethyl sulfoxide in the products requires that displacement occurs at the benzoyloxy peroxidic oxygen to form the dimethylbenzoyloxysulfonium ion **11** instead of at the *tert*-butoxy oxygen to form **6**. Nucleophilic displacement is expected at the benzoyloxy oxyyen because it is more electropositive and less hindered than the *tert*-butoxy oxygen.[16] Intermediate **11** would form **2** and *tert*-butyl alcohol by a Pummerer rearrangement via the ylide **5**.[24]

---

(23) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 774.

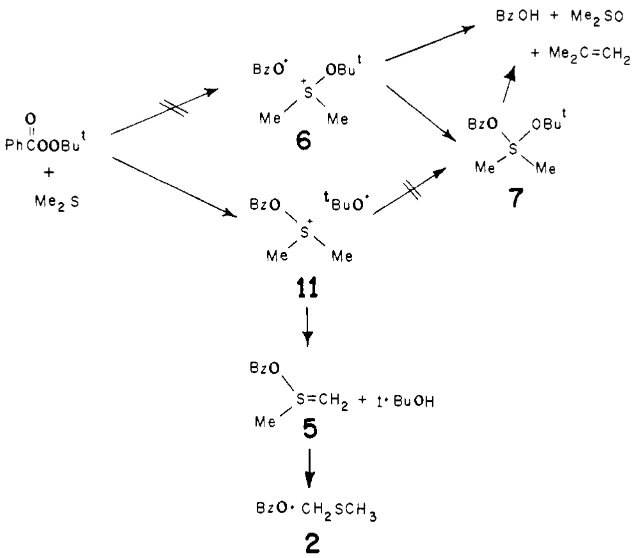
(24) Johnson, C. R.; Phillips, W. G. *J. Am. Chem. Soc.* **1969**, *91*, 682.

(25) (a) Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5003. (b) Martin, J. C. In "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; p 76.

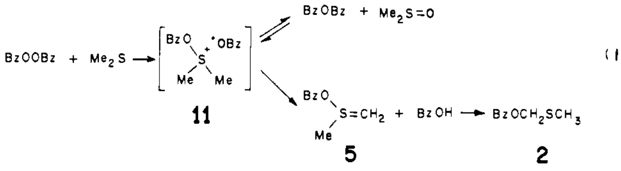
(26) Johnson, C. R.; Phillips, W. G. *J. Org. Chem.* **1967**, *32*, 1926.

(27) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 7851.

Scheme III



The displacement reaction in Scheme III is similar to the nucleophilic displacement of dimethyl sulfide on BPO (eq 11),[17]



(11)

and the sulfonium ion **11** and ylide **5** are intermediates in both reactions. Sulfurane **7** has already been shown to not be formed in the TBP–dimethyl sulfide reaction. Evidently, *tert*-butoxide preferentially abstracts a proton from **11** to form **5** rather than combining to form **7**. In the BPO–dimethyl sulfide reaction, dimethyl sulfoxide and benzoic anhydride are formed as intermediates by the nucleophilic displacement of benzoate anion on the benzoyloxydimethylsulfonium ion.[17] A similar reaction in the TBP–dimethyl sulfide system would yield dimethyl sulfoxide and *tert*-butyl benzoate. These products are stable under the reaction conditions and were not observed.

It is conceivable[25b] that **4**, **7**, and **11** all are resonance structures of the same species. We do not favor this formulation in this system since **4** appears to give products different from those obtained from **7** and **11**. Compound **4** gives **2** and *tert*-butyl alcohol, as shown in Scheme II; **7** might be expected to give dimethyl sulfoxide and isobutylene as shown in Scheme II;[27] **11** also would give sulfoxide and isobutylene,[25] as shown by the experiments described in eq 8 and 9.

ET or S_N2? Schemes I, II, and III illustrate the difficulty in using reaction products to separate S_N2 and ET reaction mechanisms in these peroxide–nucleophile systems. Likewise, substituent effects are unable to distinguish S_N2 and ET mechanisms. Electron-withdrawing substituents in the *substrate* decrease the reduction potential and increase ET reaction rates. For example, the half-wave reduction potential for substituted BPO's gives a Hammet correlation with a ρ of +4.2.[28] The ET reactions listed in Table IX show a somewhat smaller sensitivity, as would be expected for chemical rather than electrochemical reduction. However, the rate of nucleophilic displacement also is increased by electron-withdrawing groups in the substrate. Thus, the ρ value of +1.3 observed in the reaction of dimethyl sulfide with substituted TBP's is consistent with either ET or S_N2.

Rates of S_N2 reactions are accelerated by electron-donating substituents in the *nucleophile*. For example, the reaction of ring-substituted aryl methyl sulfides with BPO has a ρ value of −1.3, as shown in Table IX.[2a] However, rates of ET reactions also are accelerated in the same way; for example, the Hammett plot of the half-wave oxidation potential for substituted DMA's gives a ρ of −0.70.[29] Table IX shows several reactions thought to involve ET in which the measured ρ value is negative when substituted donor molecules are studied. Electron-transfer reactions should show a linear correlation when the logarithms of the rate constants are plotted vs. oxidation potentials of the donors.[30] However, at the present time these data alone cannot distinguish ET reactions from nucleophilic displacements.[5,30,31]

Table IX. Reactions of Peroxides with Nucleophiles (Donors)

peroxide	donor	ρ^a peroxide	ρ^b donor	% radical^c	ref
BPO	PhNMe$_2$	+1.6^d	−2.7^e	18^f	38
BPO	Ph$_2$NOH	0.8		100	5g
BPO	Me$_2$S		−1.3^g	0	17
BPO	ArCH=CHAr	+1.2	−1.0^h	10^i	*j*
TBP	Me$_2$S	+1.3	−1.7	2	this work
TBP	Ph$_3$P	+1.2		0	16
o-PhS–TBP			−1.3	50	*k*
o-Ph$_2$C=CH–BPO		+0.7	−1.8	11	*l*

[a] Hammett equation ρ when substituents are in the Ar group of the peroxide. [b] Substituents in the Ar group of the nucleophile. [c] Percent of the total reaction that produces scavengeable free radicals. [d] Reference 20c. [e] Reference 20d. [f] Reference 20a. [g] Using ArSCH$_3$; this work. [h] Correlation using σ^+. [i] For reaction of *m,m'*-dibromobenzoyl peroxide with *trans-p,p'*-dimethoxystilbene. [j] Green, D. F.; Adam, W.; Cantrill, J. E. *J. Am. Chem. Soc.* 1961, *83*, 3461. [k] Tuleen, D. L.; Bentrude, W. G.; Martin, J. C. *Ibid.* 1963, *85*, 1938. [l] Koenig, T. W.; Martin, J. C. *J. Org. Chem.* 1964, *29*, 1520.

Table X. Solvent Effects in the Reactions of Nucleophiles with Peroxides

reactants	slope of graph of log k vs. E_T^{a}	percent yield, scavengeable radicals	proposed mechanism
Me$_2$S + TBP	0.009	2	ET
o-Ph$_2$C=C–BPO^b	0.015	11	?
t-Bu$_2$S$_2$ + BPO^c	0.043	0	S_N2
PhNMe$_2$ + BPO^d	0.052	18	S_N2
Ph$_3$P + TBP^e	0.058	0	S_N2
o-PhS–TBP^f	0.12	50	?
diphenoyl peroxide + perylene^g	0.15		ET
(CH$_3$CH$_2$)$_3$N + CH$_3$CH$_2$I^h	0.23	0	S_N2

[a] For E_T values, see Table I. [b] Koenig, T. W.; Martin, J. C. *J. Org. Chem.* 1964, *29*, 1520. [c] Reference 17. [d] Reference 20a. [e] Reference 16. [f] Reference 10. [g] Reference 5d. [h] Richart, C.; Dimroth, K. *Fortschr. Chem. Forsch.* 1968, *11*, 1.

Attempts to distinguish ET and S_N2 mechanisms using the dependence of the rate on measures of the polarity of the solvent also are unreliable in these types of peroxide–nucleophile reactions. Data for the effect of solvent on several peroxide–nucleophile reactions are presented in Table X. All of the reactions are less sensitive to solvent effects than the reaction of ethyl iodide with triethylamine, but there appears to be no correlation between the solvent sensitivity and the amount of radical production or the proposed reaction mechanism.

The yield of free radicals, perhaps the most obvious parameter that might imply an ET mechanism, also is an unreliable probe of mechanism. Table X gives the yields of scavengeable radical for peroxide–nucleophile reactions, and they vary widely. However, an ET reaction may not yield scavengeable radicals, and systems that involve an initial S_N2 reaction may lead to an in-

---

(28) Schulz, V. M.; Schwarz, K. *Z. Chem.* **1967**, *7*, 176.

(29) Mann, C. K.; Barnes. K. K. In "Electrochemical Reactions in Non-Aqueous Systems"; Marcel Dekker: New York, 1970.

(30) (a) Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 5851. (b) Scandola, F.; Balzani, V.; Schuster, G. B. *Ibid.* **1981**, *103*, 2519. (c) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

(31) Walling, C. *J. Am. Chem. Soc.* **1980**, *102*, 6855.

Table XI. β-Deuterium Isotope Effects for Reactions of Nucleophiles (Donors) with Substrates

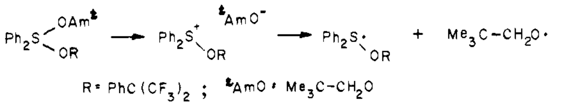
substrate	nucleophile	temp (°C)	mechanism	k_H/k_D[a]
CH_3OTs	$PhN(CD_3)_2$	51	S_N2	0.883 ± 0.008[b]
CH_3OTs	$PhP(CD_3)_2$	51	S_N2	0.952 ± 0.002[b]
t-BuOOH	CD_3SCD_3	80	S_N2	0.92 ± 0.09[c]
BPO	CD_3SCD_3	40	S_N2	0.87 ± 0.06[c]
BPO	$PhN(CD_3)_2$	30	S_N2	0.93 ± 0.03[c]
BPO	Ph_2NOD	25	ET	1.53[d]
ClO_2	$(CD_3)_3N$	25	ET	1.3[e]
TBP	CD_3SCD_3	80	ET	1.08 ± 0.08[c]
3,5-$(NO_2)_2$TBP	CD_3SCD_3	80	ET	1.06 ± 0.03[c]

[a] Per molecule. [b] Reference 34. [c] This work. [d] Reference 5g. [e] Reference 5f.

termediate that rapidly homolyzes, as originally pointed out by Walling.[7] The varying efficiency of cage recombination and the differing scavengeability of different radicals affects any comparisons that might be made.

Dimethyl Sulfide–TBP System: An ET Mechanism. Despite these difficulties in distinguishing mechanistic types, we believe that data on the dimethyl sulfide–TBP reaction can best be rationalized by an ET mechanism. This assignment is consistent with the product analysis: the benzoyloxydimethylsulfonium ion **11** and ylide **5** that would be formed in an S_N2 reaction (Scheme III) are known to be produced in the reaction of BPO with dimethyl sulfide. Since that reaction produces no scavengeable radicals, these intermediates must only undergo the nonradical decomposition shown in Scheme III.

Radicals could be proposed to originate from an electron transfer from *tert*-butoxide to **11**. Martin observed a radical pathway involving a possible electron transfer in the decomposition of alkoxy sulfuranes that cannot undergo elimination reactions (eq 12).[25a] A similar pathway may be envisioned for **11** in the presence of *tert*-butoxide (eq 13). However, when 0.1 M benzoic



$$Ph_2S(OAm^t)(OR) \longrightarrow Ph_2\overset{+}{S}-OR\ {}^tAmO^- \longrightarrow Ph_2\dot{S}-OR + Me_3C-CH_2O\cdot \quad (12)$$

$$BzO-\underset{\mathbf{11}}{\overset{+}{S}}Me_2 + t\text{-}BuO^- \rightarrow BzO-\dot{S}Me_2 + t\text{-}BuO\cdot \quad (13)$$

acid was added to a TBP–dimethyl sulfide reaction solution to intercept *tert*-butoxide ions, the rate of radical production was not reduced, indicating eq 13 cannot account for radical production. (This argument assumes, as seems reasonable, that the *tert*-butoxide in ion pair **11** is scavengeable by proton donors.)

Isotope Effects. The use of secondary kinetic isotope effects (KIE) for distinguishing S_N1 and S_N2 reactions is well known.[32,33] Inverse isotope effects are observed for S_N2 reactions when the nucleophile is deuterated in the β position; these inverse KIE can be attributed to increased force constants for bending vibrations in the transition state caused by steric crowding.[34] Data supporting inverse β-deuterium isotope effects for the S_N2 reactions of DMA and the analogous phosphine on methyl tosylate are presented in Table XI.

In contrast, normal hydrogen secondary KIE are expected when donors such as DMA or dimethyl sulfide undergo an ET reaction. The highest occupied orbital in such donors is predominantly a nonbonding orbital on the heteroatom; however, this orbital has a contribution that is bonding in the β-C–H stretching mode that is most important in determining β-deuterium secondary isotope effects.[35] Thus, weakened bonding at the β-C–H bond is expected in ET reactions, leading to normal KIE. For example, the spectra of dimethyl sulfide and dimethyl-d_6 sulfide show the deuterated compound to have a higher ionization potential by 230 cal/mol.[36] If this difference were fully realized at the transition state, the isotope effect for a ET reaction involving dimethyl sulfide would be predicted to be 1.39 at 80 °C.

Some examples of peroxide–nucleophile reactions for which the β-deuterium isotope effects are known are given in Table XI. The reactions of dimethyl sulfide with *tert*-butyl hydroperoxide and BPO, for which an S_N2 reaction might be expected, are indeed found to give inverse isotope effects as predicted. In contrast, the isotope effects for the reactions of dimethyl sulfide with both TBP and 3,5-$(NO_2)_2$-TBP are normal. One could argue, because of the rather large error limits, that the KIE for the reactions of dimethyl sulfide with TBP and with 3,5-$(NO_2)_2$-TBP are not significantly different from unity. Although this is true, the KIE are distinguishable from the inverse values expected for an S_N2 reaction, as indicated for the data in Table XI. Thus, while we cannot exclude a simultaneous occurrence of both S_N2 and ET pathways in these sulfide–peroxyester systems, the ET pathway must be the more important. Two reactions in the literature that had been concluded to involve an electron-transfer mechanism, the ClO_2–amine and BPO–hydroxylamine reactions shown in Table XI, also give normal KIE, in support of the usefulness of the isotope effect test to discriminate S_N2 and ET mechanisms.

Dimethyl Sulfide–TBP Reaction System and Possibility of an Artifactual Effect from a Primary Isotope Effect. In many of these systems, products can be rationalized as arising in a reaction in which an anion removes one of the β hydrogens, to give an ylide such as **5**, as shown in Scheme III. This reaction would have a primary KIE, and if the rate constant for this reaction is a part of k_{obsd}, then the large primary KIE for this proton abstraction could obscure a smaller secondary inverse KIE that might have occurred in an initial S_N2 reaction. This situation is observed in the reaction of phenyl methyl-d_3 sulfoxide with acetic anhydride, for which the kinetic isotope effect is 2.9.[37]

A similar primary KIE contribution could produce a normal isotope effect for the S_N2 reaction of dimethyl sulfide with TBP shown in Scheme III if the initial displacement reaction were reversible and if the reverse reaction were faster than decomposition of **11** to products.[2b] However, this rationalization for a normal isotope effect can be shown to be inapplicable to the reaction of dimethyl sulfide with TBP. The formation of **11** in Scheme III was shown to be irreversible by an experiment in which the cation in ion pair **11** was synthesized in situ from the dimethyl sulfide–BPO reaction and allowed to react with *tert*-butoxide ion. A solution of 0.10 M BPO was mixed with 0.40 M dimethyl sulfide in *tert*-butyl alcohol containing 0.05 M sodium *tert*-butoxide. Intermediate **11** is formed and, if the TBP–dimethyl sulfide reaction were reversible, **11** should react with the *tert*-butoxide to form TBP. However, no TBP was found.[2d] (We assume that **11**, formed originally with a benzoate ion as the counteranion in this experiment, is not bound in "too tight" an ion pair to exchange anions, as shown in eq 14.)

$$Me_2\overset{+}{S}(OBz)\ {}^-OBz + t\text{-}BuO^- \longrightarrow Me_2\overset{+}{S}(OBz)\ {}^-OBu\text{-}t + BzO^- \quad (14)$$

DMA–BPO Reaction: An S_N2 Mechanism. Tests of a variety of types and sophistication have proven unable to unambiguously establish the mechanism for the reaction of dimethylaniline with benzoyl peroxide.[2a,b,20,38] We have now applied the β-hydrogen

---

[32] Isotope effects are smaller for S_N2 than S_N1 reactions because of higher vibrational frequencies for deuterium in both substrate and nucleophile at the transition state;[33] these higher frequencies can be rationalized as being due to hybridization, steric, hyperconjugative, or inductive effects.[33e]

[33] (a) Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 2551. (b) Shiner, V. J., Jr.; Fisher, R. D. *Ibid.* **1971**, *93*, 2553. (c) Barclay, L. R. C.; Mercer, J. R.; Hudson, J. C. *Can. J. Chem.* **1972**, *50*, 3965. (d) Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418. (e) Wolfsberg, M. *Annu. Rev. Phys. Chem.* **1969**, *20*, 449.

[34] Kaplan, E. D.; Thorton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 6644.

[35] (a) Shiner, V. J., Jr. *ACS Monogr.* **1970**, *No. 167*, 139. (b) Sunko, D. E.; Borcic, S. *Ibid.* **1970**, *No. 167*, 167.

[36] McDiarmid, R. *J. Chem. Phys.* **1974**, *61*, 274.

[37] Oae, S.; Kise, M. *Tetrahedron Lett.* **1968**, 2261.

[38] Graham, D. M.; Mesrobian, R. B. *Can. J. Chem.* **1963**, *41*, 2938.

KIE test to this system, and the inverse isotope effect of 0.93 indicates the dominance of an S_N2 mechanism for this reaction, as originally suggested by Walling in 1957.[2c,7,20a]

The yield of scavengeable radicals from the DMA–BPO system is about 20%, whereas only about a 3% yield of radicals is obtained in the dimethyl sulfide–TBP system. Thus, the predominantly S_N2 reaction in the DMA–BPO system ultimately gives a larger yield of radicals than is obtained from the ET reaction of sulfides with TBP, reinforcing the unreliability of using the yield of radicals as a mechanistic probe in systems like these. Cage recombination of radicals, inherent radical stability, and other factors not connected with the nature of the primary reaction can determine the ultimate yield of scavengeable radicals.

It is surprising that dimethyl sulfide reacts with TBP by an ET reaction while the more easily reduced BPO reacts by S_N2. This may illustrate the sensitivity of the borderline region between these competing mechanisms to subtle structural changes.[30c] Benzoyl peroxide, being more susceptible to nucleophilic attack than is TBP, reacts with dimethyl sulfide by an S_N2 reaction. By comparison both the ET and S_N2 reaction rates are decreased in the comparable TBP reaction, but the S_N2 rate is reduced a larger amount, perhaps because the S_N2 reaction must occur at a "neopentyl"-type oxygen atom, a steric effect that would not be reflected in simple Marcus-type calculations.[30c] Therefore, dimethyl sulfide acts as a one-electron donor toward TBP.

Experimental Section

Materials. Sulfides were distilled from sodium hydroxide. Galvinoxyl was synthesized by H. T. Bickley using the method of Kharash and Joshi.[39] Styrene was washed with 10% sodium hydroxide and distilled at reduced pressure. Benzoyl peroxide was recrystallized from carbon tetrachloride–methanol. *tert*-Butyl peroxybenzoate (98%) was purchased from Lucidol and used without purification.

Aryl-Substituted Peroxybenzoates were synthesized from *tert*-butyl hydroperoxide and the appropriately substituted acid chloride by the method of Blomquist and Berstein.[14] The *p*-methoxy derivative, obtained as an oil, was purified by passing through a Florisil column. The other peroxyesters are solids and were recrystallized twice from hexane: *tert*-butyl *p*-chloroperoxybenzoate, mp 47–47.5 °C (lit.[9] 49°); *tert*-butyl *p*-nitroperoxybenzoate, mp 75–77 °C (lit.[14] 79°); *tert*-butyl 3,5-dinitroperoxybenzoate, mp 86–87 °C. Iodometric titration indicated that the peroxyesters were 98–100% pure, and the infrared spectra showed no absorption bands due to hydroperoxide, acid, or ester.

Aryl-substituted aryl methyl sulfides were synthesized by methylation of substituted thiophenols with dimethyl sulfate.[40]

Dimethyl-d_6 sulfide was synthesized by refluxing dimethyl-d_6 sulfoxide (Aldrich, 99+ atom % D) with ammonium bromide.[41] The ^1H NMR spectrum of the sulfide showed less than 1% protium impurity.

Dimethylaniline-d_6 was prepared by reducing trimethyl-d_9 phenylammonium iodide with lithium triethylborohydride.[42] Trimethyl-d_9-phenylammonium iodide was made by refluxing reaction of iodomethane-d_3 (Aldrich 99+ atom % D) with aniline.[2c,34]

Procedure for Kinetic Runs. Reaction samples were degassed and sealed under vacuum. Pseudo-unimolecular rate constants were determined as previously described[17] by following the disappearance of the peroxyester carbonyl absorbance at 1758 cm^{-1}.

Scavenger Methods. The disappearance of galvinoxyl was followed by monitoring the decrease in the absorption at 750 nm (ϵ 760).[10] See ref 2d, p 76, for details.

Styrene Polymerization. Reactions were carried out to a polymer conversion of 3–4%. The polymer was precipitated with methanol, filtered, and weighed.

The ratio of R_T/R_1 was calculated by eq 15, which was derived by

$$\frac{R_T}{R_1} = \left[\frac{k_1 + k'_2}{k_1} \frac{1 - e^{-k_1 t/2}}{1 - e^{-(k_1+k'_2)t/2}} \frac{\ln [M]_0^s/[M]_t^s}{\ln [M]_0/[M]_t} \right]^2 \qquad (15)$$

integration of the equations for peroxyester-initiated styrene polymerization in the presence and absence of dimethyl sulfide.[2d] In eq 15 $[M]_0$ and $[M]_t$ are the initial and final concentrations of sytrene in the absence of dimethyl sulfide and $[M]_0^s$ and $[M]_t^s$ are the initial and final concentrations of styrene in the presence of methyl sulfide.

At 80 °C styrene undergoes thermal polymerization and the amount of polymer formed in the reactions was adjusted for this by using eq 16.[20b]

$$R_{p,\text{corrected}} = [(R_{p,\text{obsd}})^2 - (R_{p,\text{thermal}})^2]^{1/2} \qquad (16)$$

DMA–BPO Reaction Kinetics. A kinetic run was made by placing 1-mL aliquots of 0.2 M BPO and 0.4 M styrene in CCl_4 and of 0.01 M *o*-dichlorobenzene and 0.02 M DMA in CCl_4 in separate arms of eight Y-shaped tubes. The tubes were degassed and sealed under vacuum. After equilibration at 30 °C the reaction was initiated by inverting the tubes. Tubes were removed at intervals and the reaction quenched by addition of 15 mL of 0.1 M sodium iodide in acetone. The resulting mixture was washed with 20 mL of 0.10 M sodium hydroxide and 20 mL of water. After drying over anhydrous Na_2SO_4 the solution was analyzed for DMA content by gas chromatography using *o*-dichlorobenzene as an internal standard. Pseudo-unimolecular rate constants were determined by a linear regression analysis of a semilogarithmic graph of dimethylaniline concentration vs. time. One reaction was followed to 90% completion; when plotted as a second-order equation, the plot was linear over the entire reaction.

Acknowledgment. This research was supported in part by grants from the National Institutes of Health to W. A. Pryor and the O'Hara Chemical Sciences Institute of the University of Dallas to W. H. Hendrickson and by National Science Foundation Grant CHE-7921514 to W. A. Pryor and GP-38051X1 to W. H. Hendrickson.

Registry No. *p*-$CH_3OC_6H_4SMe$, 1879-16-9; *p*-$(CH_3)_3CC_6H_4SMe$, 7252-86-0; *p*-$CH_3C_6H_4SMe$, 623·13-2; PhSMe, 100-68-5; *p*-ClC_6H_4SMe, 123-09-1; *p*-BrC_6H_4SMe, 104-95·0; *p*-CH_3O-TBP, 43084-97-5; *p*-Cl-TBP, 2203-13-6; *p*-NO_2-TBP, 16166-61-3; 3,5·$(NO_2)_2$-TBP, 55259-88-6; Me_2S, 75-18-3; TBP, 614-45-9; BPO, 94-36-0; DMA, 121-69-7; D, 7782-39-0.

---

[39] Kharasch, M. S.; Joshi, B. S. *J. Org. Chem.* **1957**, *22*, 1435.

[40] Gilman, H.; Beaber, M. *J. Am. Chem. Soc.* **1925**, *47*, 1449.

[41] Tranquille, M.; Fouassier, M.; Lautie-Mouneyrac, M. F.; Dizabo, P.; Forel, M. T. *C. R. Acad. Sci., Ser. C* **1970**, *270*, 1085.

[42] Cooke, M. P., Jr.; Parlman, R. M. *J. Org. Chem.* **1975**, *40*, 531.