1974

Electron Transfer in Peroxide - Nucleophile Interactions: the Reaction of Tert-Butyl-Peroxybenzoates With Sulfide.

William Harwell Hendrickson Jr

Louisiana State University and Agricultural & Mechanical College

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ELECTRON TRANSFER IN PEROXIDE-NUCLEOPHILE INTERACTIONS
THE REACTION OF TERT-BUTYL PEROXYBENZOATES WITH SULFIDE

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Chemistry

by
William H. Hendrickson, Jr.
B.S., Louisiana Tech University, 1970
December 1974
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</tr>
<tr>
<td>S</td>
<td>Sulfide</td>
</tr>
<tr>
<td>G</td>
<td>Galvinoxyl [2,6-di-tert-butyl-a-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyoxy]</td>
</tr>
<tr>
<td>[I]₀</td>
<td>The initial concentration of initiator</td>
</tr>
<tr>
<td>[M]</td>
<td>Concentration of monomer</td>
</tr>
<tr>
<td>[M]¹</td>
<td>Concentration of monomer in monomer-sulfide solution</td>
</tr>
<tr>
<td>Me₂S</td>
<td>Dimethyl sulfide</td>
</tr>
<tr>
<td>BPO</td>
<td>Benzoyl peroxide</td>
</tr>
<tr>
<td>DMA</td>
<td>Dimethylaniline</td>
</tr>
<tr>
<td>BOMS</td>
<td>Benzoyloxyethyl methyl sulfide</td>
</tr>
<tr>
<td>Bz₂O</td>
<td>Benzoic anhydride</td>
</tr>
<tr>
<td>Ac₂O</td>
<td>Acetic anhydride</td>
</tr>
<tr>
<td>Ac₂O₂</td>
<td>Acetyl peroxide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DMAO</td>
<td>Dimethylaniline N-oxide</td>
</tr>
<tr>
<td>Eₜ</td>
<td>The transition energy for the charge transfer band for pyridium N-phenol-betanine</td>
</tr>
</tbody>
</table>
ABBREVIATIONS AND SYMBOLS — Continued

CT  Charge transfer
ET  Electron transfer
\( k_H \) The unimolecular rate constant for perester homolysis
\( k_S \) The bimolecular rate constant for the reaction of sulfide with perester
\( k'_S \) The pseudounimolecular rate constant for the reaction of sulfide with perester
\( k_{obs} \) The observed rate constant for the rate of perester disappearance in the sulfide-perester reaction
\( D_{rel} \) The relative rate of acceleration of perester disappearance in the presence of sulfide, \( k'_S/k_H \)
\( \frac{dG}{dt}_{obs} \) The observed rate of galvinoxyl disappearance in a sulfide-perester solution
\( \frac{dG}{dt}_H \) The rate of disappearance of galvinoxyl due to perester homolysis
\( \frac{dG}{dt}_B \) The rate of galvinoxyl disappearance in the absence of perester
R  The rate of radical production by perester homolysis
R' The rate of radical production by a sulfide-perester solution
### ABBREVIATIONS AND SYMBOLS -- Continued

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_S$</td>
<td>The rate of radical production by the perester-sulfide reaction</td>
</tr>
<tr>
<td>$f_H$</td>
<td>The fraction of perester homolysis that products scavengeable free radicals</td>
</tr>
<tr>
<td>$H$</td>
<td>The fraction of the radicals produced by perester homolysis that react with the scavenger</td>
</tr>
<tr>
<td>$f_S$</td>
<td>The fraction of the perester-sulfide reaction that produces scavengeable free radicals</td>
</tr>
<tr>
<td>$S$</td>
<td>The fraction of the free radicals produced by the perester-sulfide reaction that react with the scavenger</td>
</tr>
<tr>
<td>$R_i$</td>
<td>The rate of initiation of polymerization by perester homolysis</td>
</tr>
<tr>
<td>$R'_i$</td>
<td>The rate of initiation of polymerization by a perester-sulfide solution</td>
</tr>
<tr>
<td>$k_p$</td>
<td>The rate of propagation of polymerization</td>
</tr>
<tr>
<td>$k_t$</td>
<td>The rate of termination of polymerization</td>
</tr>
</tbody>
</table>
ABSTRACT

Organic sulfides accelerate the decomposition of ring-substituted tert-butyl peroxybenzoates (TBP). For example, 1 M methyl sulfide increases the rate of decomposition of TBP by a factor of 17 at 80°. We have found that approximately 2% of this bimolecular reaction produces scavangeable free radicals (galvinoxyl, in limiting and excess amounts, and styrene were used as radical scavengers). Since electron-withdrawing substituents in the phenyl rings of TBP's slow the unimolecular homolysis of the perester (\( \rho = -0.33 \pm 0.03 \)) but speed the bimolecular reactions of TBP's with sulfides (\( \rho = +1.34 \pm 0.03 \)), peresters containing electron-withdrawing substituents decompose almost entirely by a bimolecular mechanism in the presence of 1 M methyl sulfide; thus, the percent radical production from the reaction of negatively substituted peresters with sulfide, although small, can be obtained relatively accurately. The average yield of free radicals from the reaction of 1 M methyl sulfide with substituted TBP's is 2.3±1.5%. We postulate that this radical-producing bimolecular reaction involves an electron transfer (ET). The mechanism of the ET reaction is discussed.

Nucleophiles and peroxides can react by an S\( _N \)2 or ET mechanism. We propose that the production of free
radicals by the bimolecular reaction is a clue to the occurrence of an ET mechanism. A review of the literature reveals several nucleophile-peroxide reactions that produce radicals and can be postulated to react by an ET mechanism. We have developed a kinetic isotope effect method as an additional means for distinguishing $S_N2$ from ET reactions. If the rate constants for reaction of a nucleophile and a $\beta$-deuterated nucleophile are compared (e.g., $CH_3SCH_3$ and $CD_3SCD_3$), $k_H/k_D$ is inverse (i.e., <1) for an $S_N2$ reaction and normal (i.e., >1) for an ET reaction.
I. INTRODUCTION

Much confusion exists over the reactions of nucleophiles with peroxides in that some of these reactions are typical nucleophilic displacements while others produce free radicals at an accelerated rate.\(^1\) For example, the reactions between benzoyl peroxide (BPO) and sulfides follow an \(S_N^2\) mechanism and produce no free radicals;\(^2\) in contrast, a sulfide substituent in the ortho-position of the phenyl ring of tert-butyl peroxybenzoate (TBP) accelerates the perester decomposition by a mechanism that produces mostly free radicals.\(^3\) Both of these reactions can be considered to be nucleophile-peroxide interactions, and it is not clear how the decomposition of the ring-substituted peroxybenzoate leads to radicals while the reaction of BPO with external sulfide produces only ions.\(^4\) We have sought to elucidate this dichotomy by investigating the reactions of TBP with sulfides. The fact that the TBP-methyl sulfide reaction produces scavengable free radicals in low yield led us to examine the possibility that this reaction, as well as other nucleophile-peroxide reactions that also produce free radicals, may be electron transfer reactions.
A. Electron Transfer Reactions

Many apparent nucleophilic displacements involve electron transfer from the nucleophile to the donor. Perhaps the best studied reaction of this type is the reaction of carbanions with halo-substituted nitro alkanes or arenes. A generalized mechanism presented in Eqs. 1-4 shows that this is a chain reaction in which the initiation (Eq. 1) and propagation (Eq. 4) steps are electron transfer reactions. Notice that the products of this reaction (R'R and X⁻) are identical to the products that would have been produced by an SN₂ reaction between RX and R⁻. This illustrates the fact that electron transfer reactions and SN₂ reactions have much in common, and many times, electron transfer reactions can be distinguished from SN₂ reactions only by the observation of free radicals from the electron transfer step.

\[
\text{Electron Donor} + R'X \rightarrow [R'X]^- + \text{Residue} \quad (1)
\]

\[
[R'X]^- + R'^\cdot + X^- \quad (2)
\]

\[
R'^\cdot + R^- \rightarrow [R'R]^-. \quad (3)
\]

\[
[R'R]^-. + R'X \quad R'R + [R'X]^-. \quad (4)
\]
Nucleophiles other than carbanions can also act as electron donors; amines, for example, enter into electron transfer reactions with many acceptors, two of which are carbon tetrachloride and chlorine dioxide. In fact, any nucleophile that has an unshared electron pair is a potential electron donor. Recently, an electron transfer reaction has even been postulated for a typical $S_N2$ displacement between a nucleophile and a carbon substrate. Bank and Noyd observed 2-butyl and thiyl radicals from the reaction of thiophenoxide ion with 2-butyl nosylate. The authors suggest that these radicals come either from a one electron transfer from thiophenoxide to nosylate (Eqs. 5-8) or from an intermediate that contains a one electron transfer structure (Eq. 9).

\[
\begin{align*}
\text{PhS}^- + \text{RONs} + \text{PhS}^+ + \text{RONs}^- & \quad \text{(5)} \\
\text{PhS}^+ + \text{RONs}^- & \rightarrow \text{PhSR} + \text{ONs} & \quad \text{(6)} \\
\text{RONs}^- & \rightarrow \text{R}^- + \text{ONs} & \quad \text{(7)} \\
\text{R}^- + \text{PhS}^+ & \rightarrow \text{RPh} & \quad \text{(8)}
\end{align*}
\]

electron transfer structure (4) among its resonance hybrids (Eq. 9).

\[
\begin{align*}
\text{N}^- & \text{Cl}^+ \leftrightarrow \text{N}^- & \text{C}^+ & \text{L}^- \leftrightarrow \text{N}^- & \text{C}^+ & \text{L}^- \leftrightarrow \text{N}^- & \text{C}^+ & \text{L}^- \\
1 & 2 & 3 & 4
\end{align*}
\]
The above examples indicate that one electron transfer contributions to nucleophilic displacement reactions may be more common than has been realized. In fact, all nucleophile-substrate reactions could have a contribution from structure 4 of Eq. 9. The magnitude of the contribution of 4 should depend on the balance between the ionization potential and nucleophilicity of the nucleophile as well as the electron affinity of the substrate.

B. Peroxide-Nucleophile Interactions

Because of a low lying vacant anti-bonding orbital around their oxygen-oxygen bond, peroxides have relatively high electron affinities. In fact, Tokumaru and Simamura suggested in 1963 that many peroxide-nucleophile reactions involve electron transfer intermediates. Therefore, peroxide-nucleophile reactions may be either a nucleophilic displacement reaction (Eq. 10) or an electron transfer reaction (Eq. 11).

\[ \text{S}_\text{N}^\text{2} \]
\[ D + XOOY \rightarrow [D^+ - \text{OX} + \cdot \text{OX}] \rightarrow \text{Ultimate products} \quad (10) \]

\[ \text{ET} \]
\[ D + XOOY \rightarrow [D^+ + \cdot \text{OX} + \cdot \text{OX}] \rightarrow \text{Similar or identical products} \quad (11) \]

The major observable difference between these two reaction types is the leakage of free radicals from the ET intermediate. Thus the most informative method of studying
these reactions is to investigate their free radical chemistry; peroxides are useful substrates for study in this context because their radical chemistry is well characterized. Furthermore, because much is known about nucleophilic displacements on peroxides, peroxidic substrates provide a rich source for investigations on the dichotomy of $S_N^2$ and ET reactions.

In addition to our study of the TBP-sulfide reaction, which we believe to be an ET reaction, we have reviewed the literature of peroxide-nucleophile reactions and have found several other examples of electron transfer reactions. In general, $S_N^2$ and ET reactions respond in similar ways to changes in reaction variables; however, ET reactions can be identified by an accelerated rate of radical production. Also, to substantiate our results and to aid future research on nucleophile-peroxide reactions, we have developed a kinetic isotope effect method that can distinguish $S_N^2$ from ET reactions.
C. References Chapter I

1. For a review see:


4. See footnote 12, ref. 2.

5. For a review see:


II. RESULTS

A. Kinetic Studies

The rate of tert-butyl peroxybenzoate (TBP) disappearance in the presence of a nucleophile is the sum of the rate of TBP homolysis and the rate of the nucleophile assisted reaction. If the nucleophile is sulfide, abbreviated S, then the rate can be written as in Eq. 1, where $k_H$ is the rate of unimolecular homolysis, $k_S$ is the bimolecular rate of the sulfide-perester reaction,

$$-\frac{d[TBP]}{dt} = k_H[TBP] + k_S[S][TBP]$$

where $[TBP]$ is the concentration of TBP, and $[S]$ is the concentration of sulfide (the brackets indicate concentration in moles/liter). At 80°, methyl sulfide ($\text{Me}_2\text{S}$) accelerates the decomposition of TBP by so slight an amount that in 0.05 M $\text{Me}_2\text{S}$ the rate of the bimolecular perester-sulfide reaction is only slightly less than the rate of the perester homolysis. Therefore, in order to study the sulfide accelerated reaction, a high sulfide concentration must be used in order that $k_S[S]$ is significantly greater than $k_H$. For this reason we used 1.0 M sulfide in most of our experiments; at this sulfide concentration, the bimolecular reaction accounts for 94% of TBP disappearance.
The use of high sulfide concentration results in pseudo-unimolecular perester disappearance; i.e., the sulfide concentration remains constant and $k_S[S]$ in Eq. 1 can be replaced by $k_S'$ to yield Eq. 2, where $k_S'$ is the pseudo-unimolecular rate constant for the perester-sulfide reaction. Since the observed rate constant ($k_{obs}$)

$$\frac{d[TBP]}{dt} = k_H[TBP] + k_S'[TBP]$$

(2)

obtained from the rate of pseudo-unimolecular perester disappearance in the presence of sulfide in the sum of $k_S'$ and $k_H$ (Eq. 3), $k_S'$ is calculated from Eq. 4.

$$\frac{d[TBP]}{dt} = (k_H + k_S')[TBP] = k_{obs}[TBP]$$

(3)

$$k_S' = k_{obs} - k_H$$

(4)

1. Reaction Order. The perester disappearance was followed by observation of the decrease in the infra-red absorbance of the carbonyl perester bond at 1758 cm$^{-1}$, and $k_{obs}$ was obtained from Eq. 5. $^1$ Iodometric titration

$$\ln(A-A_\infty) = -k_{obs}t + \ln(A_0-A_\infty)$$

(5)
of the perester was also used to calculate $k_{\text{obs}}$. We determined that the rate constants were independent of the method of determination by showing that both methods give the same $k_{\text{obs}}$ in carbon tetrachloride.

In the infra-red analysis the plots of $\ln(A-A_0)$ versus $t$ are linear to at least 80% conversion indicating that the perester disappearance is pseudo-unimolecular as predicted by Eq. 3. Further proof of unimolecularity was obtained by the initial rate method. A plot of $\log$ (initial rate of perester disappearance) versus $\log$ (perester concentration) is linear over a ten-fold range in perester concentration (Appendix I-1). The slope of this line which is the reaction order in perester is 1.00.

Since $k_{\text{obs}}$ is the rate constant for pseudo-unimolecular perester decomposition, Eq. 4 can be used to determine the reaction order in sulfide. Substitution of $k_S[S]$ for $k'_S$ into Eq. 4 yields Eqs. 6 and 7.

$$k_S[S] = k_{\text{obs}} - k_H$$

(6)

The reaction order in sulfide is obtained from

$$\log(k_{\text{obs}} - k_H) = \log k_S + \log[S]$$

(7)

measuring $k_{\text{obs}}$ at different sulfide concentrations; Eq. 7 predicts that a graph of $\log(k_{\text{obs}} - k_H)$ vs. $\log[S]$ should
be a straight line with a slope equal to the order of the reaction in sulfide. The experimental plot yields a straight line with a slope of 1.10 (Appendix I-2). These results show that the sulfide-perester reaction is first order in both sulfide and perester.

2. **Induced Decomposition.** TBP is known to be subject to induced decompositions. For example, Bentrude and Martin reported that the rate of decomposition of tert-butyl o-(methylthio)-peroxybenzoate decreased by 22% when 0.2 M styrene was added to the reaction mixture. They attributed this decrease to inhibition of the induced decomposition of the perester by styrene. Similarly, when we added styrene to methyl sulfide-perester reaction mixtures, the rate decreased by 28% (Table II-1). A decrease was also noted when styrene was used with the perester alone. Therefore, all of the rate constants were determined with 0.2 M styrene added to eliminate induced decomposition. In addition, the reactions were carried out in ampoules which were sealed under vacuum after thorough degassing.

The use of styrene as an inhibitor had little effect on the reaction order. The pseudo-unimolecular plots of perester disappearance remained linear, and the calculated orders of perester and sulfide were 0.79 and 0.94 respectively (Appendix I-3,4).
TABLE II-1

Styrene Inhibition of Perester Decomposition\textsuperscript{a}

<table>
<thead>
<tr>
<th>[Me\textsubscript{2}S]</th>
<th>[Styrene]</th>
<th>T °C</th>
<th>(k_{\text{obs}}\times10^5) sec(^{-1})</th>
<th>(k_s\times10^5) b M(^{-1}) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.970</td>
<td>--</td>
<td>80</td>
<td>2.05</td>
<td>2.03</td>
</tr>
<tr>
<td>1.04</td>
<td>--</td>
<td>80</td>
<td>2.24</td>
<td>2.07</td>
</tr>
<tr>
<td>0.996</td>
<td>0.2</td>
<td>80</td>
<td>1.51</td>
<td>1.44</td>
</tr>
<tr>
<td>1.00</td>
<td>0.2</td>
<td>80</td>
<td>1.61</td>
<td>1.53</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>130</td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>0.2</td>
<td>130</td>
<td>29.8</td>
<td></td>
</tr>
</tbody>
</table>

a. 0.01 M TBP in carbon tetrachloride.

b. \(k_s = \frac{k_{\text{obs}}-k_H}{[\text{Me}_2\text{S}]}\)
B. Solvent Effect on Reaction Rate

The rate of the methyl sulfide-TBP reaction was followed in six solvents by iodometric titration of the perester. The effect of solvent on reaction rate is given in Table II-2. Only acetic acid caused any appreciable increase in the reaction rate. Some peroxide-nucleophile reactions are acid catalyzed: the reaction of tert-butyl hydroperoxide and methyl sulfide is dependent on the proton donating ability of the solvent.\(^5\) Probably the rate increase in acetic acid is due to a similar acid catalysis. With the exception of acetic acid, the reaction rates increase linearly with the polarity of solvents as measured by Kosower \(E_T\) values\(^6\) (Figure II-1). The effect of solvent polarity on the reaction rate will be discussed in a later section after the solvent effects on other peroxide-nucleophile reactions have been presented.

C. Substituent Effect on Reaction Rate

One of the most widely used mechanistic probes is the Hammett equation, Eq. 8.

\[
\log \frac{k}{k_0} = \rho \sigma
\]  

As originally determined by Hammett,\(^7\) \(\sigma\) is a measure of the electron donating or withdrawing effect of a substituent in benzoic acid ionization. The \(\rho\)-value measures
TABLE II-2

Solvent Effect on the Reaction Rate$^a$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_{obs} \times 10^5$ $^b$</th>
<th>$E_T$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>1.5</td>
<td>32.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.7</td>
<td>34.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>tert-Butyl alcohol</td>
<td>2.2</td>
<td>43.9</td>
</tr>
<tr>
<td>Methanol</td>
<td>2.5</td>
<td>55.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 0.05 M TBP, 1.0 M Me$_2$S, 0.2 M styrene, 80°C.

$^b$ By iodometric titration.

$^c$ The transition energy for charge-transfer absorption band for pyridinium N-phenolbetaine in the given solvent, ref. 6.
Figure II-1. The Effect of Solvent Polarity on the TBP-Me₂S Reaction Rate: 0.01 M TBP, 1.0 M Me₂S at 80°.
the sensitivity of the reaction to electron supply or withdrawal.

Four phenyl-substituted peresters were synthesized to examine the substituent effect on reaction rate of both the sulfide assisted decomposition and the thermal decomposition of TBP. In addition, five phenyl-substituted methyl phenyl sulfides were synthesized and the substituent effects in the nucleophile were determined.

1. The Substituent Effect on the Rate of Perester Homolysis. Since the observed rate constant for the methyl sulfide-TBP reaction is the sum of perester homolysis and the sulfide accelerated decomposition, both $k'_H$ and $k_{obs}$ must be determined to calculate $k'_S$. At 80°, the temperature at which the sulfide-perester reactions were run, the rate of perester homolysis is slow and $k'_H$ for each perester was extrapolated from higher temperatures, using the Arrhenius equation (Eq. 9). Table II-3 shows that the rate constants and the activation energies

$$\log k'_H = \frac{E_a}{2.303R} \frac{1}{T}$$

(9)
determined by previous workers are not in agreement; therefore, we repeated the experiments. For comparison with the data of the other workers, our rate constants at 120° and activation energies are also included in Table II-3. Since our
## TABLE II-3

Homolysis of tert-Butyl Peroxybenzoates

<table>
<thead>
<tr>
<th>Perester</th>
<th>$k_H \times 10^5$ sec$^{-1}$, 120°</th>
<th></th>
<th>$E_a$ kcal/mole</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref. 9 $^a$</td>
<td>This Work $^b$</td>
<td>Ref. 10 $^c$</td>
<td>Ref. 9</td>
</tr>
<tr>
<td>$p$-CH$_3$O-TBP</td>
<td>10.6</td>
<td>19.2</td>
<td>--</td>
<td>36.1</td>
</tr>
<tr>
<td>TBP</td>
<td>8.99</td>
<td>10.3</td>
<td>13.0</td>
<td>37.5</td>
</tr>
<tr>
<td>$p$-Cl-TBP</td>
<td>6.40</td>
<td>7.93</td>
<td>11.0</td>
<td>39.3</td>
</tr>
<tr>
<td>$p$-NO$_2$-TBP</td>
<td>3.19</td>
<td>5.03</td>
<td>6.72</td>
<td>41.3</td>
</tr>
<tr>
<td>3,5-(NO$_2$)$_2$-TBP</td>
<td>--</td>
<td>3.98</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

---

*a.* In diphenyl ether.
*b.* 0.01 M perester, 0.2 M styrene in carbon tetrachloride.
*c.* 0.04 M perester in undecane.
*d.* Calculated from Eq. 9 using data at 110°, 120°, 130°.
*e.* Plots in Appendix I-5.
results are between the other results and were obtained in carbon tetrachloride as were the results for the sulfide-perester reactions, we employed our data to calculate $k_H$ at 80°. Table II-4 gives the results of these calculations. The Arrhenius plots for all five peresters are in Figure AI-5 of Appendix I.

The data in Table II-3 has also been used to study substituent effects on perester homolysis. Blomquist and Berstein reported a $\rho$-value of -0.9 for perester decomposition in diphenyl ether\textsuperscript{9}; Antonovskii et al. obtained a $\rho$-value of -0.34 in undecane.\textsuperscript{10b} Antonovskii's group attributed their smaller $\rho$-value to a decrease in polarity of undecane compared to diphenyl ether. The negative $\rho$-value indicates that electron donating groups weaken the 0-0 bond by increasing the electron density at this bond thereby increasing the rate of bond breaking.

A plot of our results of log $k_H$ at 120° versus $\sigma$ gave $\rho = -0.38\pm0.08$, with a correlation coefficient, $r$, of 0.934 (Figure II-2). A better correlation was obtained with $\sigma^+$ values (Figure II-3, $\rho = -0.33\pm0.03$, $r = 0.985$). Thus, our results agree well with those of Antonovskii,\textsuperscript{10b} but do not agree with the better known values reported by Blomquist and Berstein.\textsuperscript{9}

2. The Perester Substituent Effect on the Perester-Sulfide Reaction Rate. For the perester-sulfide reaction a good Hammett correlation was obtained with phenyl
Figure II-2. A Plot of the Hammett Equation, Using $\sigma$, for the Homolysis of Phenyl-Substituted tert-Butyl Peroxybenzoates; 0.01 M Perester in CCl$_4$ at 120°.
Figure II-3. A Plot of the Hammett Equation, Using $\sigma^+$, for the Homolysis of Phenyl-Substituted tert-Butyl Peroxybenzoates; 0.01 M Perester in CC$_4$ at 120°. 

$\rho = -0.33 \pm 0.03$
substituted peresters. The results in Table II-4 are plotted in Figure II-4. The \( p \)-value, +1.34\( \pm \)0.03 \( (r = 0.999) \), is very near to the \( p \)-value obtained from similar reactions. Denny, Goodyear, and Goldstein found a \( p \)-value of +1.24 for triphenyl phosphine attack on substituted tert-butyl perbenzoates.\(^{11}\) The \( p \)-value for the reaction of dimethyl aniline with disubstituted benzoyl peroxides is +1.6.\(^{12}\)

The \( p \)-value for the sulfide-perester reaction has the opposite sign from the \( p \)-value for perester homolysis. Thus, while electron-withdrawing groups slow down perester homolysis, they accelerate the sulfide-perester reaction. The methoxy-substituted compound reacts with 1.0 M methyl sulfide only 9 times faster than it undergoes homolysis, while the dinitro-substituted perester reacts with methyl sulfide 12,000 times faster than it homolyzes \((D_{rel}', Table\ II-4)\). The increase in relative reactivity means that the homolysis reaction becomes a smaller component of the total reaction when electron-withdrawing groups are attached to the perester. For example, when \( p-\text{CH}_3\text{O}-\text{TBP} \) reacts in 1 M methyl sulfide, 10% of the perester disappears by homolysis; however, when \( 3,5-\left(\text{NO}_2\right)_2-\text{TBP} \) reacts in 1 M methyl sulfide, only 0.008% of the perester disappears by homolysis. When the free radical character of the perester-sulfide reaction is discussed in Section
TABLE II-4

The Sulfide-Assisted Decomposition of tert-Butyl Peroxybenzoates\textsuperscript{a}

<table>
<thead>
<tr>
<th>Perester</th>
<th>( k'_s \times 10^5 ) \text{sec}^{-1}</th>
<th>( k'_h \times 10^5 ) \text{sec}^{-1}</th>
<th>( D_{rel} )</th>
<th>( \frac{k_h}{k_{obs}} \times 100 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CH(_3)O-TBP</td>
<td>0.89</td>
<td>0.10</td>
<td>8.9</td>
<td>10</td>
</tr>
<tr>
<td>TBP</td>
<td>1.46</td>
<td>0.088</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>2-Cl-TBP</td>
<td>3.34</td>
<td>0.042</td>
<td>80</td>
<td>1.2</td>
</tr>
<tr>
<td>2-NO(_2)-TBP</td>
<td>15.5</td>
<td>0.029</td>
<td>535</td>
<td>0.19</td>
</tr>
<tr>
<td>3,5-(NO(_2))(_2)-TBP</td>
<td>134</td>
<td>0.011</td>
<td>12000</td>
<td>0.008</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 0.01 M perester, 1.0 M methyl sulfide, 0.2 M styrene in carbon tetrachloride at 80°.

\textsuperscript{b} Calculated from data in Table II-3.

\textsuperscript{c} \( k'_s/k'_h \).
Figure II-4. A Plot of the Hammett Equation for the Reaction of Phenyl-Substituted tert-Butyl Peroxybenzoates with $\text{Me}_2\text{S}$; 0.01 M Peroester, 1.0 M $\text{Me}_2\text{S}$ in $\text{CCl}_4$ at 80°.
E, the fraction of the reaction that occurs by homolysis will be very important.

3. **The Sulfide Substituent Effect on the Perester-Sulfide Reaction Rate.** A series of aryl methyl sulfides were chosen to study the sulfide substituent effects. The low reactivity of TBP prevented its use as the substrate (Table II-7). Methyl phenyl sulfide decomposes TBP only 1.4 times faster than TBP homolyzes, and $k_S^i$ is only 60% of $k_{obs}$. For some substituted phenyl methyl sulfides, $k_S^i$ would be much smaller and could not be accurately measured as it would be a small fraction of the total reaction. Therefore, the more reactive tert-butyl p-chloroperbenzoate (p-Cl-TBP) was used as the substrate. Not only is this perester more reactive but it also homolyzes more slowly so that it reacts with methyl phenyl sulfide 9 times faster than it homolyzes; perester homolysis is 10% of the total reaction and can be corrected for without losing accuracy.

The data for substituted methyl phenyl sulfides reacting with p-Cl-TBP is in Table II-5. The Hammett plot (Figure II-5) has a slope of $-1.68 \pm 0.05$ ($r = 0.999$). The methoxy-substituted sulfide reacts too fast and was omitted in the calculation of the $\rho$-value. This $\rho$-value is similar to that for other peroxide-nucleophile reactions. Martin et al. found a $\rho$-value of -1.8 for
\begin{table}
\begin{center}
\caption{The Reaction of \textit{tert}-Butyl \textit{p}-Chloroperoxybenzoate with \textit{p}-C<sub>6</sub>H<sub>5</sub>SCH<sub>3</sub> \textsuperscript{a}}
\begin{tabular}{lcc}
\textbf{X} & \textbf{\(k_{\text{obs}} \times 10^5\)} & \textbf{\(k'_s \times 10^5\)} \\
& \text{sec}^{-1} & \text{sec}^{-1} \\
\hline
\textit{p}-CH\textsubscript{3}O- & 1.86 & 1.82 \\
\textit{p}-\text{CH}<sub>3</sub>\textsubscript{3}C- & 0.914 & 0.87 \\
\textit{p}-CH\textsubscript{3}- & 0.820 & 0.78 \\
H- & 0.420 & 0.38 \\
\textit{p}-Cl- & 0.208 & 0.17 \\
\end{tabular}
\end{center}
\textsuperscript{a} 0.01 M perester, 1.0 M sulfide, 0.2 M styrene, carbon tetrachloride, 80°C.
\end{table}
Figure II-5. A Plot of the Hammett Equation for the Reaction of $p$-Cl-TBP with $X-C_6H_4SCH_3$; 0.01 M $p$-Cl-TBP, 1.0 M $X-C_6H_4SCH_3$ in $CCl_4$ at 80°.
substituted peresters of type 1. O'Driscoll and Ricchezza measured a \( p \)-value of -2.7 for the reaction of substituted dimethylaniline with benzoyl peroxide.

To compare the effect of substitutions in the sulfide moiety in the perester reaction with that in the benzoyl peroxide reaction, the \( p \)-value for the reaction of methyl aryl sulfides with benzoyl peroxide was measured. The results are given in Table II-6 and Figure II-6. Again the methoxy-substituent reacted faster than predicted and was omitted in the calculation of the slope. The \( p \)-value is \(-1.30 \pm 0.13\) \((r = 0.985)\).

D. The Effect of Sulfide Structure on the Reaction Rate

A limited study was done on the effect of sulfide structure on the perester-sulfide reaction rate (Table II-7). Methyl sulfide, the least sterically hindered sulfide, has the fastest reaction rate. Because 1.0 M solutions of tert-butyl sulfide and phenyl sulfide have no
TABLE II-6
The Reaction of Benzoyl Peroxide with X-C₆H₅SCH₃

<table>
<thead>
<tr>
<th>X</th>
<th>kₛ×10³ M⁻¹ sec⁻¹ a,b</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CH₃O⁻</td>
<td>3.39</td>
</tr>
<tr>
<td>p-CH₃⁻</td>
<td>1.69</td>
</tr>
<tr>
<td>p-(CH₃)₃C⁻</td>
<td>1.65</td>
</tr>
<tr>
<td>H⁻</td>
<td>0.83</td>
</tr>
<tr>
<td>p-Cl⁻</td>
<td>0.54</td>
</tr>
<tr>
<td>p-Br⁻</td>
<td>0.43</td>
</tr>
</tbody>
</table>

a. 0.01 M benzoyl peroxide, 0.1 M sulfide, carbon tetrachloride, 40°C.

b. kₛ = kₜobs/[S].
Figure II-6. A Plot of the Hammett Equation for the Reaction of BPO with $X-C_6H_4SCH_3$; 0.01 M BPO, 0.1 M $X-C_6H_4SCH_3$ in CCl$_4$ at 40°.
measurable effect on the decomposition rate of TBP, the more reactive tert-butyl 3,5-dinitroperoxy-benzoate [3,5-(NO₂)₂-TBP] was studied. Methyl sulfide reacts 47 times faster with this perester than does tert-butyl sulfide. The weaker nucleophile, dimethyl disulfide, reacts about as fast as the sterically hindered tert-butyl sulfide.

E. Radical Production

The most important difference between the decomposition of tert-butyl-o-(methylthiyl)-peroxybenzoate and the decomposition of benzoyl peroxide induced by sulfide is the lack of radical production by the BPO-sulfide reaction. When BPO reacts with methyl sulfide, no radicals are detected. However, when slower reacting disulfides are used, radicals are produced. Pryor and Bickley, however, were able to show that these radicals are produced from a concurrent unimolecular homolysis of BPO by measuring the relative rates of radical production in the presence and absence of sulfide. They observed that the rate of radical production decreased in the presence of sulfide. On the other hand, Martin and Bentrude found that the rate of radical production by the sulfide substituted perester, 1, is much faster than by the unsubstituted perester. 4b

Before discussing the perester-sulfide system, it is necessary to derive the equations for radical production.
<table>
<thead>
<tr>
<th>Perester</th>
<th>Sulfide</th>
<th>$k_{obs} \times 10^5$</th>
<th>$k'_{S} \times 10^5$</th>
<th>$D_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>$\text{Me}_2S$</td>
<td>1.55</td>
<td>1.47</td>
<td>17</td>
</tr>
<tr>
<td>TBP</td>
<td>$\text{t-Bu}_2S$</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TBP</td>
<td>PhSPh</td>
<td>2.98$^b$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TBP</td>
<td>PhSCH$_3$</td>
<td>0.22</td>
<td>0.13</td>
<td>1.4</td>
</tr>
<tr>
<td>$\text{P-Cl-TBP}$</td>
<td>PhSCH$_3$</td>
<td>0.42</td>
<td>0.38</td>
<td>9</td>
</tr>
<tr>
<td>3,5-(NO$_2$)$_2$-TBP</td>
<td>$\text{Me}_2S$</td>
<td>134</td>
<td>134</td>
<td>12000</td>
</tr>
<tr>
<td>3,5-(NO$_2$)$_2$-TBP</td>
<td>$\text{t-Bu}_2S$</td>
<td>2.5</td>
<td>2.5</td>
<td>210</td>
</tr>
<tr>
<td>3,5-(NO$_2$)$_2$-TBP</td>
<td>MeSSMe</td>
<td>2.7</td>
<td>2.7</td>
<td>250</td>
</tr>
</tbody>
</table>

a. In carbon tetrachloride and 2.0 M styrene at 80°.

b. 110°.

c. $k'_{S}/k_{H}$. 
In these equations provision is made for radical production from the perester-sulfide reaction in excess of that which would be expected from perester homolysis alone.

The rate of radical production can be measured using scavengers. Perester homolysis produces radicals at a rate \( R \) (Eq. 10), where \( f_H \) is the fraction of the homolysis that produces scavengeable radicals and \( \varepsilon_H \) is the efficiency of the scavenger in trapping free radicals. It is very difficult to separate \( f_H \) and \( \varepsilon_H \). In earlier work in determining radical production by nucleophile-peroxide reactions, \( \varepsilon_H \) was assumed to be unity and the product \( f_H \varepsilon_H \) was reported as radical efficiency. However, both of these parameters govern the amount of radicals that are scavenged, and it will be useful in our work to separate them. One, \( f_H \), is concerned with the efficiency of the initiator in producing radicals, the other, \( \varepsilon_H \), with the efficiency of the scavenger in trapping radicals.

Our derivation will assume that scavenger efficiency remains the same in the presence and absence of sulfide.

If \( \varepsilon_H \) is unity, then \( f_H \varepsilon_H \) should be independent of scavenger. Table II-8 lists \( f_H \varepsilon_H \) for substituted peresters determined with three scavengers. For each perester, \( f_H \)
TABLE II-8
The Efficiency of Several Radical Scavengers for the Homolysis of Substituted Peroxybenzoates

<table>
<thead>
<tr>
<th>Perester</th>
<th>Galvinoxyl&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Styrene&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Amine&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;O-TBP</td>
<td>0.69</td>
<td>0.90</td>
<td>--</td>
</tr>
<tr>
<td>TBP</td>
<td>0.52</td>
<td>0.49</td>
<td>0.80</td>
</tr>
<tr>
<td>Cl-TBP</td>
<td>0.68</td>
<td>0.82</td>
<td>0.60</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;-TBP</td>
<td>0.54</td>
<td>0.05</td>
<td>0.95&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>(NO&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;-TBP</td>
<td>0.28</td>
<td>0</td>
<td>--</td>
</tr>
</tbody>
</table>

<sup>a</sup> Galvinoxyl scavenger in CCl<sub>4</sub> at 80° calculated by Eq. 17.

<sup>b</sup> Styrene scavenger in neat styrene at 80°, calculated from Eq. A11-2 using R<sub>p</sub> reported in Table II-12.

<sup>c</sup> α-Naphthyl amine scavenger in undecane at 90°, ref. 10b.

<sup>d</sup> 110°.
is independent of the scavenger used and the difference in $f_H\epsilon_H$ for the same perester determined with different scavengers is due to a different $\epsilon_H$ for each scavenger. Clearly the radical production by perester homolysis is dependent on scavenger, and $\epsilon_H$ should be included in Eq. 10 and in the following equations. The use of $\epsilon_H$ makes it possible to compare $f_H$ values determined with different scavengers.

In 1.0 M methyl sulfide the sulfide-perester reaction produces radicals at a rate $R_S$ (Eq. 11); $f_S$ is the fraction

$$R_S = 2f_S\epsilon_S k'_S [I]_0$$  \hspace{1cm} (11)

of the reaction that produces scavengeable free radicals and $\epsilon_S$ is the efficiency of the scavenger in capturing those radicals. The observed initial rate of radical production by a sulfide-perester solution ($R'$) is the sum of radical production by homolysis and by the sulfide-perester reaction (Eq. 12).

$$R' = 2(f_H\epsilon_H k_H + f_S\epsilon_S k'_S) [I]_0$$  \hspace{1cm} (12)

The rate of radical production by sulfide displacement relative to the rate of radical production by perester homolysis is expressed in Eq. 13.
The experimentally observable rate of radical production in the presence of sulfide is $R'$ not $R_S$, and the ratio $R'/R$ is an easily measured experimental value. Eq. 14 relates $R'/R$ to $R_S/R$.

\[
\frac{R'}{R} = \frac{(f_{S}^S k_S^0[I]_0 + f_{S}^S k_S^I[I]_0)}{f_{H}^H k_H^I[I]_0} = 1 + \frac{R_S}{R}
\]

If $R'/R$ is greater than unity, then the perester-sulfide reaction produces radicals. It is necessary to again point out that the above equations apply only to initial rates of radical production during which the perester concentration is constant. If other than initial rates are used, then $[I]_0$ must be replaced by $[I]_0 \exp(-k/t)$ which is the concentration of perester at any time $t$.

Three methods were used to measure $R'/R$: limiting scavenger, excess scavenger, and styrene polymerization. Each method has advantages and disadvantages which are discussed in the following sections.

1. **Limiting scavenger.** The easiest way to measure rates of radical production is by following the disappearance of a colored free radical scavenger. Galvinoxyl is a good scavenger to use with peresters since it reacts
quantitatively with carbon or oxygen radicals.\textsuperscript{15} The rate of radical production by perester homolysis is equal to the rate of scavenger disappearance (Eq. 15).

\[ R = -(\frac{dG}{dt}) = 2f_{\text{H}} k_{\text{H}} [I]_0 \exp - (k_{\text{H}} t) \]  \hspace{1cm} (15)

The decrease in scavenger concentration \(- (dG/dt)\) is observed spectrometrically by measuring the decrease in the absorbance of the scavenger as it reacts. An important property of the scavenger is that it reacts with radicals to form products which do not absorb light in the same region as the scavenger.

In the limiting scavenger method the initial concentration of perester is much higher than the initial concentration of scavenger so that all of the scavenger disappears before any change in perester concentration occurs. Thus, the scavenger should disappear by zero order kinetics. That is the rate of disappearance of scavenger is constant with time; because the perester concentration is constant, Eq. 15 is replaced by Eq. 16.

\[ -(\frac{dG}{dt}) = 2f_{\text{H}} k_{\text{H}} [I]_0 \]  \hspace{1cm} (16)

To measure \((dG/dt)\) for perester homolysis, carbon tetrachloride solutions of galvinoxyl and perester ([perester]/[galvinoxyl] = 20) were degassed and sealed in
spectrometer cells. The cells were placed in a heated cell compartment and the decrease in galvinoxyl absorbance with time was plotted by a recorder. The plot was a straight line with a slope proportional to the rate of galvinoxyl disappearance. Control experiments demonstrated that galvinoxyl in carbon tetrachloride is stable at 80°, and that the rate of disappearance is independent of galvinoxyl concentration. Thus the galvinoxyl disappearance was caused only by reaction with radicals produced by perester homolysis. Since the rate of perester decomposition at 80° is known, the value of $f_{H^\epsilon H}$ for each perester was calculated using Eq. 17.

$$f_{H^\epsilon H} = \frac{-(dG/dt)}{2[I]_0}$$ (17)

To eliminate any error which might arise in a single run, the value of $(dG/dt)$ used to calculate $f_{H^\epsilon H}$ was obtained from a graph of $\log (dG/dt)$ versus $\log [I]_0$. This graph was constructed by measuring $(dG/dt)$ at three or more perester concentrations (Appendix I, Figure AI-6). Since these graphs are linear and have a slope of near unity, the rate of disappearance of galvinoxyl is first order in perester and the efficiency of galvinoxyl at scavenging radicals is independent of rate of radical production.
The perester efficiencies determined by limiting galvinoxyl are reported in Table II-8 along with the efficiencies determined by Antonovskii et al. who used α-naphthylamine as a free radical scavenger. The fair agreement between these two methods indicates that the galvinoxyl system is valid. The efficiency of tert-butyl 3,5-dinitroperoxybenzoate is much smaller than the efficiency of the other peresters. This low efficiency is due either to poor trapping efficiency of 3,5-dinitrobenzoate radicals by galvinoxyl or to an ionic decomposition of the perester. Ionic decompositions of this sort have been well documented for substituted 2-propyl nitroperoxybenzoates by Winstein. However, Winstein did not look for ionic decomposition of tert-butyl nitroperoxybenzoate. It is possible that the dinitro-substituted tert-butyl peroxybenzoate decomposes at least partly by an ionic mechanism. Without an extensive product analysis it is difficult to ascertain the importance of the ionic decomposition. If any ionic decomposition is occurring in this perester, then the efficiency in Table II-8 represents a minimum value.

The measurement of R for perester homolysis by galvinoxyl disappearance is simple and accurate; however, the addition of methyl sulfide to the reaction mixture greatly complicates the determination of (dG/dt). The plots of (dG/dt) versus time remain linear for the initial part of
the reaction, but galvinoxyl disappearance is not due to the perester-sulfide reaction alone. Control experiments demonstrated that galvinoxyl is not stable at 80° in 1.0 M methyl sulfide solutions in carbon tetrachloride. A 6x10^-4 M galvinoxyl solution decolorized at a rate of 0.6x10^-8 M/sec. The rate of radical production is not fast enough to over shadow this blank reaction. Furthermore, for the slower reacting peresters, homolysis amounts to a measurable fraction of the total perester disappearance (k_H/k_observ, Table II-4). The observed rate of galvinoxyl disappearance is due to a combination of a blank reaction, perester homolysis, and sulfide assisted decomposition. The observed rate of radical production in the sulfide-perester reaction is greater than the sum of the blank reaction and perester homolysis. Therefore, the sulfide assisted reaction produces radicals in excess of perester homolysis. The rate of radical formation is expressed in Eq. 18 where (dG/dt)_observ is the total observed rate of galvinoxyl disappearance, (dG/dt)_S is the rate of galvinoxyl disappearance due to the sulfide assisted perester decomposition, (dG/dt)_H is the rate of galvinoxyl disappearance due to perester homolysis, and (dG/dt)_B is
the rate of galvinoxyl disappearance due to the blank reaction.

The observed rate of galvinoxyl disappearance is the sum of three separate reaction rates each of which is independent of time as long as the perester concentration is constant. Since \((dG/dt)_H\) is known from perester homolysis studies and \((dG/dt)_B\) can be measured in the absence of perester, \((dG/dt)_S\) can be found from Eq. 19. Since \(R_S\) is proportional to \((dG/dt)_S\) and \(R\) is

\[
(dG/dt)_S = (dG/dt)_\text{obs} - (dG/dt)_H - (dG/dt)_B
\]  

proportional to \((dG/dt)_H\), the ratio of these two rates at the same perester concentration is then equal to \(R_S/R\) which is the amount of radical production of the sulfide-perester reaction relative to the radical production by perester homolysis.

The validity of Eq. 19 must be carefully investigated. If it is correct, then the ratio of \((dG/dt)_S\) to \((dG/dt)_H\) will be independent of perester concentration. Table II-9 list experimental values of \((dG/dt)_\text{obs}\), \((dG/dt)_H\), and \((dG/dt)_S\) at several perester concentrations for four peresters. The dinitro-substituted perester was not investigated by this method because at 80° this perester decomposes too fast to allow for the measurement of initial rate of radical production. Also listed in Table
II-9 are the ratios of \((dG/dt)_S\) to \((dG/dt)_H\) for each perester concentration. This ratio is independent of perester concentration only for the nitro-substituted perester; for the other peresters, this ratio decreases as perester concentration increases. This anomaly can be explained by the occurrence of an increased blank reaction caused by the presence of perester and sulfide in the same reaction mixture.

Equation 19 predicts that at zero perester concentration, \((dG/dt)_S\) is equal to \((dG/dt)_{obs} - (dG/dt)_B\). If the correct blank reaction has been used to calculate \((dG/dt)_S\), then a graph of \((dG/dt)_S\) vs. [perester] should extrapolate to zero at zero perester concentration. Figure II-7, which presents this graph for each perester, shows that this condition is met only for tert-butyl p-nitroperoxybenzoate; for the other peresters, \((dG/dt)_S\) extrapolated to zero perester concentration is greater than zero. This indicates that a larger blank reaction than had been expected is occurring. The size of this additional blank is equal to \((dG/dt)_S\) extrapolated to zero perester concentration. Figure II-7 shows that the increased blank reaction is dependent on perester substitution. The increase in the blank is \(3.0 \times 10^{-8}\) M/sec for methoxy substituent, \(1.9 \times 10^{-8}\) M/sec for chloro substituent, and \(1.3 \times 10^{-8}\) M/sec for unsubstituted perester. When the increased blank reaction is used to recalculate \((dG/dt)_S\), then the ratio of
## TABLE II-9

The Rate of Galvinoxyl Disappearance in the Methyl Sulfide-Perester Reaction

### tert-Butyl p-methoxyperoxybenzoate

<table>
<thead>
<tr>
<th>[Perester]</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} )</th>
<th>( \frac{dG}{dt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
</tr>
<tr>
<td>0.001</td>
<td>1.8</td>
<td>0.14</td>
<td>1.1</td>
<td>7.8</td>
</tr>
<tr>
<td>0.0025</td>
<td>3.6</td>
<td>0.35</td>
<td>3.1</td>
<td>8.8</td>
</tr>
<tr>
<td>0.01</td>
<td>5.4</td>
<td>1.3</td>
<td>3.5</td>
<td>2.7</td>
</tr>
<tr>
<td>0.025</td>
<td>7.7</td>
<td>3.5</td>
<td>3.6</td>
<td>1.0</td>
</tr>
<tr>
<td>0.05</td>
<td>11.2</td>
<td>7.0</td>
<td>4.6</td>
<td>0.66</td>
</tr>
</tbody>
</table>

### tert-Butyl Peroxybenzoate

<table>
<thead>
<tr>
<th>[Perester]</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} )</th>
<th>( \frac{dG}{dt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
</tr>
<tr>
<td>0.0025</td>
<td>2.2</td>
<td>0.25</td>
<td>1.4</td>
<td>5.6</td>
</tr>
<tr>
<td>0.01</td>
<td>3.0</td>
<td>1.0</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>0.025</td>
<td>4.7</td>
<td>2.5</td>
<td>1.6</td>
<td>0.64</td>
</tr>
<tr>
<td>0.05</td>
<td>7.3</td>
<td>4.6</td>
<td>2.1</td>
<td>0.46</td>
</tr>
<tr>
<td>0.10</td>
<td>12.4</td>
<td>9.4</td>
<td>2.4</td>
<td>0.26</td>
</tr>
<tr>
<td>0.20</td>
<td>20.7</td>
<td>18.8</td>
<td>1.9</td>
<td>0.10</td>
</tr>
</tbody>
</table>

### tert-Butyl p-chlorperoxybenzoate

<table>
<thead>
<tr>
<th>[Perester]</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} )</th>
<th>( \frac{dG}{dt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
</tr>
<tr>
<td>0.001</td>
<td>2.6</td>
<td>0.05</td>
<td>1.9</td>
<td>32</td>
</tr>
<tr>
<td>0.0025</td>
<td>1.6</td>
<td>0.15</td>
<td>1.2</td>
<td>8.0</td>
</tr>
<tr>
<td>0.01</td>
<td>3.1</td>
<td>0.60</td>
<td>1.9</td>
<td>3.2</td>
</tr>
<tr>
<td>0.025</td>
<td>4.4</td>
<td>1.5</td>
<td>2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>0.05</td>
<td>7.0</td>
<td>3.0</td>
<td>3.4</td>
<td>1.1</td>
</tr>
<tr>
<td>0.10</td>
<td>11.1</td>
<td>6.0</td>
<td>4.5</td>
<td>0.75</td>
</tr>
</tbody>
</table>

### tert-Butyl p-nitroperoxybenzoate

<table>
<thead>
<tr>
<th>[Perester]</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} ) ( \times 10^8 )</th>
<th>( \frac{dG}{dt} )</th>
<th>( \frac{dG}{dt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
<td>( M/sec )</td>
</tr>
<tr>
<td>0.001</td>
<td>1.1</td>
<td>0.03</td>
<td>0.5</td>
<td>17</td>
</tr>
<tr>
<td>0.0025</td>
<td>1.1</td>
<td>0.08</td>
<td>0.4</td>
<td>5</td>
</tr>
<tr>
<td>0.01</td>
<td>2.8</td>
<td>0.40</td>
<td>1.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.25</td>
<td>4.4</td>
<td>0.70</td>
<td>3.1</td>
<td>4.4</td>
</tr>
<tr>
<td>0.05</td>
<td>9.4</td>
<td>1.5</td>
<td>7.3</td>
<td>4.8</td>
</tr>
<tr>
<td>0.10</td>
<td>21.8</td>
<td>3.3</td>
<td>17.9</td>
<td>5.4</td>
</tr>
</tbody>
</table>

\( \frac{4.8+0.4}{3} \)
<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.0x10^{-4} M galvinoxyl in carbon tetrachloride at 80°.</td>
</tr>
<tr>
<td>b</td>
<td>Total rate of galvinoxyl disappearance in 1.0 M methyl sulfide.</td>
</tr>
<tr>
<td>c</td>
<td>Rate of galvinoxyl disappearance due to perester homolysis (Figure AI-6).</td>
</tr>
<tr>
<td>c</td>
<td>Rate of galvinoxyl disappearance due to sulfide-perester reaction; calculated from Eq. 19 with [(dG/dt)_B = 0.6x10^{-8} \text{ M/sec.}]</td>
</tr>
</tbody>
</table>
Figure II-7. The Rate of Disappearance of Galvinoxyl as a Function of Perester Concentration in the Perester-Me₂S Reaction; 6x10⁻⁴ M Galvinoxyl, 1.0 M Me₂S in CCl₄ at 80°C.
(dG/dt)_S to (dG/dt)_H is independent of perester concentration. Table II-10 presents these data. Although we have no explanation for the excess blank reaction, the data in Table II-10 indicate that the use of the increased blank does produce consistent results; i.e., (dG/dt)_S/(dG/dt)_H is independent of perester concentration. However, because of unexpected complication with the blank reaction, the data are suspect and can be proven correct only by agreement with other methods. Even so the data do show that the sulfide assisted decomposition of tert-butyl peroxynbenzoates does produce radicals at an accelerated rate.

2. **Excess Scavenger.** In the excess scavenger method, the perester-sulfide reaction is monitored until all of the perester has reacted; excess scavenger is used so that some remains at the end of the reaction period. The efficiency of radical production by the bimolecular reaction is calculated from the amount of scavenger consumed (Eq. 20), and the rate of reaction is calculated from the first order plot of scavenger disappearance (Eq. 21). Here [G] is the concentration of galvinoxyl at time t, [G]_0 is the initial concentration of galvinoxyl,

\[
\epsilon_c = \frac{[G]_0 - [G]_\infty}{2[G]_0} \quad (20)
\]

\[
\ln \frac{[G] - [G]_\infty}{[G]_0 - [G]_\infty} = -k_{\text{obs}}t \quad (21)
\]
TABLE II-10

The Application of the Increased Blank Reaction to the Rate of Galvinoxyl Disappearance in the Methyl Sulfide-Perester Reaction\(^a\)

<table>
<thead>
<tr>
<th>[Perester]</th>
<th>( \frac{dG}{dt} \times 10^8 ) ( \frac{dG}{dt} ) ( \frac{dG}{dt} )</th>
<th>( \frac{dG}{dt} ) ( \frac{dG}{dt} ) ( \frac{dG}{dt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{Perester}] )</td>
<td>( \times 10^8 )</td>
<td>( \times 10^8 )</td>
</tr>
<tr>
<td>tert-Butyl p-Methoxyperoxybenzoate(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0025</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>0.01</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>0.025</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>0.05</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td>( 0.28 \pm 0.1 )</td>
<td>0.28</td>
<td>0.1</td>
</tr>
<tr>
<td>tert-Butyl Peroxybenzoate(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>0.3</td>
<td>0.12</td>
</tr>
<tr>
<td>0.05</td>
<td>0.8</td>
<td>0.17</td>
</tr>
<tr>
<td>0.10</td>
<td>1.1</td>
<td>0.14</td>
</tr>
<tr>
<td>( 0.14 \pm 0.03 )</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>tert-Butyl p-Chloroperoxybenzoate(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.025</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>0.05</td>
<td>1.7</td>
<td>0.6</td>
</tr>
<tr>
<td>0.10</td>
<td>2.8</td>
<td>0.5</td>
</tr>
<tr>
<td>( 0.5 \pm 0.1 )</td>
<td>0.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

a. 6x10\(^{-4}\) M galvinoxyl in carbon tetrachloride at 80\(^\circ\).  
b. Corrected for calculated blank reaction.  
c. \( (dG/dt)_B = 3.6x10^{-8} \) M/sec.  
d. \( (dG/dt)_B = 1.9x10^{-8} \) M/sec.  
e. \( (dG/dt)_B = 2.5x10^{-8} \) M/sec.
and \([G]_\infty\) is the concentration of galvinoxyl after all of the perester has reacted.

The excess scavenger technique is superior to the limiting scavenger method in that both the rate of disappearance of perester and efficiency of radical production can be calculated from the same experiment. Actually this method is not needed for determining \(R_g/R\) because only the product of the rate of decomposition and efficiency is necessary to calculate this ratio. However, because of the unusual occurrence of the excess blank reaction in the limiting scavenger method, the data from this method may not be correct and another method is needed to establish the accuracy of the data. The independent determination of efficiency and rate of perester disappearance makes the excess scavenger method ideal for use as a second system. The value of \(k_{obs}\) serves as an internal reference because it is dependent of the radical-scavenger reaction. If, for any reason, the scavenger is unsuitable and gives erroneous results, \(f_{H}c_{H}\) as well as \(k_{obs}\) will be in error. The value of \(k_{obs}\) is known from infra-red analysis and can be compared to the value of \(k_{obs}\) determined by the excess scavenger method. If the two rate constants agree, then the experimental value of \(f_{H}c_{H}\) is probably correct.

In order for the excess scavenger method to be accurate, the disappearance of galvinoxyl should be due
to the sulfide-perester reaction alone. Any additional reaction of galvinoxyl must be corrected for when Eqs. 20 and 21 are used. For the peresters that react slower than tert-butyl p-nitroperoxybenzoate, a large fraction of radical production is due to perester homolysis. While it is possible to correct galvinoxyl destroyed by homolysis, it is difficult and not very accurate. In addition, because these reactions are so slow and have to be followed to completion, all of the galvinoxyl would be used up by the galvinoxyl-sulfide reaction before all of the perester had reacted.

Only the nitro-substituted peresters react fast enough so that the blank reaction and perester homolysis are unimportant. For these peresters, homolysis amounts to less than 1% of the total reaction and the production of radicals is fast enough so that the blank reaction accounts for only a small fraction of galvinoxyl disappearance. Since the blank reaction is nearly independent of galvinoxyl concentration and can be determined independently, the disappearance of galvinoxyl due to the blank can be corrected for. This correction is made for each data point used in Eq. 20 and for the final concentration of galvinoxyl. The corrected value of [G] is obtained by adding the concentration of galvinoxyl decolorized in time t in the blank reaction to the observed value of [G] at the same time t. This correction was
minimized by increasing the perester concentration or by lowering the reaction temperature.

The results of the excess scavenger method are presented in Table II-11. R was calculated from Eq. 15 and R' was calculated from Eq. 22, where εSfS and kobs are the experimentally determined values of efficiency of radical production and rate of sulfide-perester reaction determined from Eqs. 20 and 21.

\[
R' = 2\varepsilon S f S k_{\text{obs}} [I]_0
\]  

A correction factor, \([G]_B/[G]_0-[G]_\infty\), is also included in Table II-11. It represents the fraction of the total disappearance of galvinoxyl that was caused by the blank reaction. When this fraction is small, the agreement between kobs and kS' is good. Since there is no competition from perester homolysis and very little blank reaction, the value of R'/R measured for these peresters is probably more accurate than that found by limiting scavenger. Unfortunately though, this method could be used for only two of the five peresters and the nitro-substituted perester is the only perester investigated by both methods. The agreement of the two methods is poor (R'/R is 6, measured by limiting scavenger, and 19, measured by excess scavenger) and a third method of measuring radical production had to be used.
TABLE II-11
Excess Galvinoxyl Scavenger

<table>
<thead>
<tr>
<th>Perester</th>
<th>$f_S$</th>
<th>$k_{obs} \times 10^5$</th>
<th>$k_{IR} \times 10^5$</th>
<th>$\frac{G_B}{G-G_0}$</th>
<th>$\frac{R'}{R}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-NO$_2$-TBP$^f$</td>
<td>0.016</td>
<td>10.9</td>
<td>15.5</td>
<td>0.61</td>
<td>12</td>
</tr>
<tr>
<td>$p$-NO$_2$-TBP$^g$</td>
<td>0.020</td>
<td>14.5</td>
<td>15.5</td>
<td>0.21</td>
<td>20</td>
</tr>
<tr>
<td>3,5-$(NO_2)_2$TBP$^h$</td>
<td>0.013</td>
<td>24.1</td>
<td>24.5</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>3,5-$(NO_2)_2$TBP$^i$</td>
<td>0.014</td>
<td>160</td>
<td>137</td>
<td>0</td>
<td>730</td>
</tr>
<tr>
<td>3,5-$(NO_2)_2$TBP$^j$</td>
<td>0.016</td>
<td>119$^k$</td>
<td>137</td>
<td>0</td>
<td>620</td>
</tr>
</tbody>
</table>

a. 1.0 M methyl sulfide, 1.0x10$^{-3}$ M galvinoxyl in carbon tetrachloride at 80°.
b. Calculated from Eq. 20.
c. Calculated from Eq. 21.
d. Fraction of total galvinoxyl disappearance due to blank reaction.
e. Calculated from Eq. 15 and Eq. 22.
f. 0.010 M perester.
g. 0.022 M perester.
h. 60°, 0.026 M perester.
i. 0.027 M perester.
j. 0.5 M methyl sulfide-$d_6$, 0.025 M perester.
k. $k'_S$. 
3. **Styrene polymerization.** In view of the problems encountered in galvinoxyl studies, styrene polymerization was used as a third method of measuring $R'/R$. This method has been used extensively in the investigation of the amine-benzoyl peroxide reaction.\(^{18}\) Dilatometric techniques are required for accurate results; however, reasonably accurate data can be obtained by gravimetric analysis if errors are minimized by using initial reaction rates, low polymer conversion, and the ratio of polymerization rates.

A simple method of determining $R'/R$ is to allow two tubes of styrene of the same perester concentration to react for identical time periods.\(^{1a}\) One tube contains only perester and styrene and the other tube contains perester, styrene, and methyl sulfide. The reaction time is chosen so that the polymer conversion is low (usually 3-4\%) and the concentration of perester remains nearly constant. The polymer in each tube is then precipitated, filtered and weighed. $R'/R$ is calculated from Eq. 23.

This equation

$$
\frac{R'}{R} = \left[ \frac{\frac{k_H}{(k_H + k_S')}}{\frac{\ln \left( \frac{[M]_0}{[M]_t} \right)}{-k_H t/2}} \right]^{2} = \left[ \frac{\ln \left( \frac{[M]_0}{[M]_t} \right)}{-\left( k_H + k_S \right) t/2} \right]^{2} \tag{23}
$$

is derived in Appendix II; $[M]_0$ and $[M]_t$ are the initial and final concentrations of styrene in the absence of sulfide, and $[M]'_0$ and $[M]'_t$ are the initial and final
concentrations of styrene in the presence of sulfide. The results obtained from styrene polymerization are presented in Table II-12.

Styrene polymerization has two important limitations. First, because of inhibition of styrene polymerization by nitro groups (a styrene-TBP solution did not polymerize when 0.05 M m-dinitrobenzene was added as an inhibitor) the efficiency of polymerization of tert-butyl p-nitroperoxybenzoate (p-NO₂-TBP) was very low and tert-butyl 3,5-dinitroperoxybenzoate [3,5-(NO₂)₂-TBP] did not initiate styrene polymerization. In fact the dinitro perester actually inhibited the thermal styrene polymerization. Therefore, data were not obtained for 3,5-(NO₂)₂-TBP and the results for p-NO₂-TBP were not precise because the low efficiency of polymerization reduced the rate of polymerization to a very low level. At this level, the second interference of styrene polymerization, the thermal polymerization of styrene (1.1x10⁻⁵ M/sec at 80°C) becomes important. Equation 24 is used to correct the rate of polymerization for thermal polymerization. For most of the reactions studied the rate of polymerization was approximately ten times faster than thermal polymerization and Eq. 24 is not a large correction.

\[ R_P, \text{corrected} = \left[ (R_{P, \text{obs}})^2 - (R_{P, \text{thermal}})^2 \right]^{1/2} \]

(24)
### TABLE II-12

Radical Production in the Methyl Sulfide-Perester Reaction

Measured by Styrene Polymerization\textsuperscript{a}

<table>
<thead>
<tr>
<th>Perester</th>
<th>$R_p \times 10^4$\textsuperscript{b} M/sec</th>
<th>$R_p' \times 10^4$\textsuperscript{c} M/sec</th>
<th>$\frac{R_p'}{R}$\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{O-} \text{TBP}$</td>
<td>1.4</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TBP</td>
<td>1.0</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>$\text{Cl-} \text{TBP}$</td>
<td>0.98</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{NO}_2\text{-} \text{TBP}$</td>
<td>0.17\textsuperscript{e}</td>
<td>0.44\textsuperscript{e}</td>
<td>12.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 0.05 M perester, 80°, reaction time is 1 hr.

\textsuperscript{b} Corrected for styrene thermal polymerization, $R_p,\text{thermal} \approx 1.2 \times 10^{-5}$ M/sec.

\textsuperscript{c} 1.0 M methyl sulfide, corrected for styrene thermal polymerization in presence of 1.0 M methyl sulfide, $R_p,\text{thermal} \approx 2 \times 10^{-5}$ M/sec.

\textsuperscript{d} Calculated by Eq. 23.

\textsuperscript{e} Reaction time is 1.5 hr., corrected for styrene thermal polymerization in presence of 0.05 M nitrobenzene, $R_p,\text{thermal} \approx 0.9 \times 10^{-5}$ M/sec.
However, $R_p$ for $p$-NO$_2$-TBP initiated styrene polymerization was only twice the rate of thermal polymerization and Eq. 24 was used. Furthermore, additional error was introduced because the low efficiency of the nitro-substituted perester resulted in smaller polymer weights. Since $R'/R$ is related to the ratio of polymer squared, a small error in the determination of $R_p$, thermal or $R_p$ is magnified in the calculation of $R'/R$. An error of 0.01 g in polymer weight can change $R'/R$ by 25%. Thus $R'/R$ for $p$-NO$_2$-TBP is only an approximate value. The rate of initiation of the other perester reactions are fast enough so that styrene thermal polymerization is relatively unimportant and enough polymer is formed so that errors in work up are unimportant.

4. Percent Radical. The values of $R_s/R$ for all three methods are collected in Table II-13. The sulfide assisted decomposition of 3,5-(NO$_2$)$_2$-TBP produces radicals at a much greater rate than the other perester-sulfide reactions. However, these values are ratios of the rate of radical production by the assisted reaction to rate of radical production by perester homolysis. The relative rate of radical production by the 3,5-(NO$_2$)$_2$-TBP-sulfide reaction is much faster than that of the other perester-sulfide reactions because the rate of perester homolysis is slower and the rate of sulfide assisted decomposition
### TABLE II-13
Radical Production in the Methyl Sulfide-Perester Reaction\(^a\)

<table>
<thead>
<tr>
<th>Perester</th>
<th>(D_{rel})</th>
<th>(R_S/R) (^c)</th>
<th>Limiting (^d)</th>
<th>Excess (^d)</th>
<th>Styrene (^e)</th>
<th>Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-\text{CH}_3\text{O}-\text{TBP})</td>
<td>8.9</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>TBP</td>
<td>17</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>(p-\text{Cl}-\text{TBP})</td>
<td>81</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>(p-\text{NO}_2\text{-TBP})</td>
<td>535</td>
<td>5</td>
<td>19</td>
<td>675</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>3,5-(\text{NO}_2)^2\text{-TBP})</td>
<td>12000</td>
<td>-</td>
<td>675</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) 1.0 M methyl sulfide, 80°.

\(^b\) \(k_S'/k_H\).

\(^c\) \(R_S/R = (R'/R) - 1\).

\(^d\) Limiting galvinoxyl scavenger in \(\text{CCl}_4\).

\(^e\) Excess galvinoxyl scavenger in \(\text{CCl}_4\).

\(^f\) Styrene polymerization in styrene solution.
is faster. A better understanding of radical production by the bimolecular reaction is obtained from $f_S$, the fraction of the bimolecular reaction that produces scavengable free radicals.

Solving Eq. 13 for $f_S$ yields Eq. 25. In Eq. 25, $f_H e_H / e_S$ is a correction factor that allows us to compare $f_S$ values measured with different scavengers.

Let us consider the actual problems encountered in calculating $f_S$ from Eq. 25. In the sulfide-perester reaction, radicals are formed in the solvent cage. The fraction of the radicals that escape the cage is $f_S$; depending on the scavenger used, some fraction, $e_S$, is captured by the scavenger. This fraction is the efficiency of the scavenger. Our data permits us to calculate only the product of $f_S e_S$ and not either one separately. Previous workers have implicitly assumed that $e_S$ is unity (by incorporating the scavenger efficiency into the term $f_H$), and the efficiency of radical production is then given by $f_S$. However, as the data in Table II-8 indicate, different scavengers have different efficiencies in trapping radicals from the same reaction; thus, $e_S$ is not unity. Therefore, to measure an $f_S$ which is
independent of scavenger a method must be employed to evaluate \( \varepsilon_s \) for each scavenger.

We chose to calculate scavenger efficiency from a standard reaction and to assume that the efficiency of the scavenger in the standard reaction is the same as the scavenger efficiency in the perester sulfide reaction. This is the same technique that was used by Antonovskii et al. to evaluate \( f_H \) for perester homolysis.\(^\text{10}\) They chose homolysis of \( \alpha, \alpha' \)-azo-bis (iso-butyronitrile) (AIBN) as a standard reaction; we chose perester homolysis. From the rate of scavenger disappearance during perester homolysis we can calculate \( f_H \varepsilon_H ^{\text{H}} \) (Eq. 10). Again we are faced with the problem of separating \( f_H \) and \( \varepsilon_H \). In order to calculate \( \varepsilon_H \) we must assign a value to \( f_H \), but what should this value be? Antonovskii et al. observed a value of 0.95 for \( f_H \varepsilon_H ^{\text{H}} \) for the homolysis of \( \text{P}-\text{NO}_2\text{-TBP} \) determined using \( \alpha \)-napthyl amine scavenger.\(^\text{10b} \) Since they had evaluated \( \varepsilon_H \) for this scavenger to be near unity\(^\text{10a} \) (the evaluation was done by determining \( f_H \varepsilon_H ^{\text{H}} \) for the homolysis of AIBN, which has a known value of \( f_H \)), \( f_H \) for the homolysis of \( \text{P}-\text{NO}_2\text{-TBP} \) must also be near unity. We will assume that \( f_H \) for the remaining peresters is also unity. Therefore, \( \varepsilon_H \) is given by \( f_H \varepsilon_H ^{\text{H}} \) in Table II-8. Certainly for some of the peresters investigated, \( f_H \) may be less than unity and in these cases the calculated value of \( \varepsilon_H \) will appear to be larger than it actually is, and \( f_s \) calculated from Eq. 25
will also be too large. The advantage of assuming \( f_H = 1 \) is that the calculated \( f_S \) will always be a maximum value. This is an acceptable assumption as long as we remember its source and accompanying limitations.

Now that we have assigned a value to \( f_H \), \( \epsilon_H \) can be calculated for each scavenger-perester system. However, one additional assumption is needed to calculate \( f_S \). As mentioned earlier, this assumption is that the scavenger efficiency is the same in trapping radicals formed from perester homolysis as it is in trapping radicals formed from the perester-sulfide reaction. It is difficult to evaluate the effect of this assumption on the accuracy of \( f_S \). Some of the radicals in the sulfide-perester reaction probably are formed from the sulfide and we cannot determine how the efficiency of trapping these radicals compares to the efficiency of trapping radicals from perester homolysis. One possible clue is provided by the dimethylaniline-benzoyl peroxide reaction. This reaction initiates styrene polymerization, but the polystyrene isolated contains no nitrogen (see p. 84). Many of the radicals formed in the BPO-amine reaction contain nitrogen (see p. 105), but evidently they are not trapped by styrene. If sulfur containing radicals formed in the TBP-sulfide reaction are similarly not reactive with scavenger, then \( \epsilon_S \) will be less than \( \epsilon_H \) and \( f_S \) calculated using the assumption \( \epsilon_H = \epsilon_S \) will be too small. We must
remember the presence of this assumption and realize that \( f_S \) calculated with this assumption represents a minimum value.

After applying the assumptions \( f_H = 1 \) and \( e_H = e_S \) to Eq. 25, we obtain Eq. 26.

\[
\frac{R_S}{R} = \frac{k_S}{k_H} \quad (26)
\]

In using Eq. 26 \( R_S \) and \( R \) must be measured using the same scavenger. Thus \( f_S \) is the relative acceleration of radical production divided by the acceleration of perester decomposition or, in other words, the ratio of the rate of scavenger disappearance in methyl sulfide containing solutions (corrected for scavenger loss due to first order perester homolysis and blank reactions) to scavenger disappearance in non-sulfide solutions divided by the ratio of the rates of perester disappearance in sulfide solutions to non-sulfide solutions. Table II-14 lists \( f_S \times 100 \) determined by the applicable methods for each perester-sulfide reaction. It is convenient to think of \( f_S \times 100 \) as the percent of the bimolecular reaction that yields scavenger radicals. Considering the problems involved, the agreement in \( f_S \) between the three methods is quite good. It appears that \( f_S \) is independent of perester substitution, and if all of the data are averaged, \( 2.3 \pm 1.5\% \) of the sulfide-perester reaction produces scavenger radicals.
TABLE II-14

Percent Radical Production
by the Methyl Sulfide-Perester Reaction$^a$

<table>
<thead>
<tr>
<th>Perester</th>
<th>Limiting$^b$</th>
<th>Excess$^c$</th>
<th>Styrene$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{-CH}_3$-TBP</td>
<td>0.5</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>TBP</td>
<td>0.6</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>$\text{-Cl}$-TBP</td>
<td>0.6</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>$\text{-NO}_2$-TBP</td>
<td>0.9</td>
<td>3.5</td>
<td>2.3</td>
</tr>
<tr>
<td>3,5-$(\text{NO}_2)_2$-TBP</td>
<td>-</td>
<td>4.7</td>
<td>-</td>
</tr>
</tbody>
</table>

Average = 2.3±1.5

a. 1.0 M Me$_2$S, 80°.
b. $f_s/100$, given by $(R_s/R)/D_{rel}$ in Table II-13.
c. Limiting galvinoxyl scavenger in CCl$_4$.
d. Excess galvinoxyl scavenger in CCl$_4$.
e. Styrene polymerization in styrene solution.
Even though this is a small fraction, the use of three methods of radical scavenging proves that this reaction does produce radicals in addition to those produced by perester homolysis.

F. Product Studies

The major products from the reaction of methyl sulfide and tert-butyl peroxybenzoate were analyzed by gas chromatography (glpc) with carbon tetrachloride and chlorobenzene as solvents both in the presence and absence of styrene. The results are in Table II-15. At least six minor products were formed, but each comprised less than one percent of the total products and was not identified.

In carbon tetrachloride containing 0.02 M styrene, the major products are tert-butyl alcohol (90%) and benzoyloxymethyl methyl sulfide (BOMS, 98%), which was identified by isolation from a large scale reaction. No benzoic acid could be detected; however, the glpc sensitivity to this compound is small and 1-2% of benzoic acid would not have been detected. Infra-red analysis was not useful because the benzoic acid carbonyl absorption at 1687 cm\(^{-1}\) is obscured by the broad BOMS absorption near 1705 cm\(^{-1}\).

In the absence of styrene, the yield benzoic acid was 40-50% and the yield of BOMS decreased accordingly, while the tert-butyl alcohol yield remained unchanged.
<table>
<thead>
<tr>
<th>Major Products</th>
<th>No Styrene</th>
<th>0.2 M Styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆H₅Cl</td>
<td>CCl₄</td>
</tr>
<tr>
<td>tert-butyl alcohol</td>
<td>0.88</td>
<td>0.91</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>--</td>
<td>0.4</td>
</tr>
<tr>
<td>BOMS</td>
<td>0.47</td>
<td>0.6</td>
</tr>
</tbody>
</table>

a. Determined by gas chromatography after reaction at 80° for at least five half-lives; product yield is mole product/mole perester.

b. Limit of glpc sensitivity.
The increased yield of benzoic acid may be due to induced decomposition. Although this hypothesis was not pursued, the products formed in the presence of styrene were assumed to be representative of the perester-sulfide reaction. Equation 27 accounts for 90% of the reaction products.

\[ C_6H_5COOC(CH_3)_3 + CH_3SCH_3 \rightarrow (CH_3)_3COH + CH_3SCH_2OCC_6H_5 \] (27)

The absence of some possible products is also important. No dimethyl sulfoxide, tert-butyl benzoate, or acetone were detected. The absence of a detectable amount of acetone does not exclude the occurrence of tert-butoxy radicals. Control experiments on the homolysis of tert-butyl peroxide demonstrated that in chlorobenzene at 120° in the absence of methyl sulfide, 73% of the tert-butoxy radicals forms acetone. When 1 M methyl sulfide is added, the yield of acetone is reduced to 20%. Since the radical fraction of the perester-sulfide reaction is only 2%, the maximum concentration of acetone that can be formed is only about 0.4% of the total products. This amount is too small to be detected.

Dimethyl sulfoxide and benzoic anhydride are initial products in the benzoyl peroxide-methyl sulfide reaction. These products further react to produce benzoic acid and BOMS as final products. To prove that a similar reaction
between dimethyl sulfoxide and tert-butyl benzoate does not occur in perester-sulfide reactions, a carbon tetrachloride solution of dimethyl sulfoxide and tert-butyl benzoate was heated at 80°. After 115 hr no BOMS had been formed and the dimethyl sulfoxide concentration had remained constant. Thus, absence of dimethyl sulfoxide as a reaction produce is not due to subsequent reactions.

Two other related product analysis were done. One experiment indicated that methyl sulfide-d₆ has no effect on the yield of BOMS. A second experiment showed that no tert-butyl sulfoxide is formed in the reaction of tert-butyl p-nitroperbenzoate with tert-butyl sulfide.

G. Isotope Effects

The influence of deuterium substitution on reaction rates have long been used to elucidate reaction mechanisms. Therefore, we synthesized dimethyl sulfide-d₆ and measured the isotope effect \( \frac{k_H}{k_D} \) for the reaction of methyl sulfide with several peroxidic compounds. The results in Table II-16 show that the isotope effects for perester reactions are normal \( \frac{k_H}{k_D} \) while isotope effects for tert-butyl hydroperoxide and benzoyl peroxide reactions are inverse \( \frac{k_H}{k_D} \). This separation into inverse and normal isotope effects is very important and is discussed further in Section VI.
<table>
<thead>
<tr>
<th>Peroxide</th>
<th>$k_H \text{ sec}^{-1} \text{ M}^{-1}$</th>
<th>$k_D \text{ sec}^{-1} \text{ M}^{-1}$</th>
<th>$k_H/k_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzoyl Peroxide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(9.81 \pm 0.18) \times 10^{-2}$</td>
<td>$(11.8 \pm 0.1) \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(9.76 \pm 0.19) \times 10^{-2}$</td>
<td>$(10.8 \pm 0.2) \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Average</strong></td>
<td>$(9.78 \pm 0.3) \times 10^{-2}$</td>
<td><strong>0.88 \pm 0.5</strong></td>
</tr>
<tr>
<td><strong>tert-butyl Hydroperoxide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(14.6 \pm 0.7) \times 10^{-5}$</td>
<td>$(16.8 \pm 0.3) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(17.1 \pm 0.4) \times 10^{-5}$</td>
<td>$(17.5 \pm 0.5) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(15.9 \pm 0.4) \times 10^{-5}$</td>
<td>$(15.3 \pm 0.5) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(16.6 \pm 0.4) \times 10^{-5}$</td>
<td>$(16.6 \pm 0.4) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Average</strong></td>
<td>$(15.9 \pm 0.9) \times 10^{-5}$</td>
<td><strong>0.93 \pm 0.3</strong></td>
</tr>
<tr>
<td><strong>tert-Butyl Peroxybenzoate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(1.60 \pm 0.04) \times 10^{-5}$</td>
<td>$(1.56 \pm 0.01) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(1.68 \pm 0.03) \times 10^{-5}$</td>
<td>$(1.57 \pm 0.06) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(1.63 \pm 0.01) \times 10^{-5}$</td>
<td>$(1.42 \pm 0.06) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Average</strong></td>
<td>$(1.64 \pm 0.04) \times 10^{-5}$</td>
<td><strong>1.08 \pm 0.08</strong></td>
</tr>
<tr>
<td><strong>tert-Butyl 3,5-dinitroperoxybenzoate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(136 \pm 1.6) \times 10^{-5}$</td>
<td>$(126 \pm 2.6) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(132 \pm 3.8) \times 10^{-5}$</td>
<td>$(126 \pm 3.1) \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Average</strong></td>
<td>$(134 \pm 2.8) \times 10^{-5}$</td>
<td><strong>1.06 \pm 0.03</strong></td>
</tr>
</tbody>
</table>

**a.** Second order rate constant for reaction of substrate with methyl sulfide.

**b.** Second order rate constant for reaction of substrate with methyl sulfide-d$_6$.

**c.** In CCl$_4$, 40°.

**d.** In tert-butyl alcohol, 80°.

**e.** In CCl$_4$, 80°.
H. Temperature Effects

The effect of temperature on the reaction of tert-butyl 3,5-dinitroperoxybenzoate was studied. This perester was chosen because it reacts fast enough so that the reaction rate can be measured over a wide temperature range without correcting for perester homolysis. Figure II-8 presents the Arrhenius graph of the data in Table II-17. A least squares treatment of this line yields Eq. 28.

\[ \ln k = 3.72 \times 10^8 \exp\left(-18.5 \pm 0.6 \times 10^3 / RT \right) \] (28)

An activation energy of -18.5 kcal/mole and an entropy of activation of -19.7 e.u. is compatible with either an \( S_N^2 \) or an electron transfer reaction. The linearity of the Arrhenius graph over a 40\( ^\circ \) temperature range may indicate that the decomposition of peresters by methyl sulfide is not a combination of two mechanisms, but the temperature range is much too small to be certain of this.

The effect of temperature on radical production by the 3,5-(NO\(_2\))-TBP sulfide reaction was also investigated. The results II-11 indicate that there is a small decrease in radical production at lower temperatures. However, the effect is so small that it is insignificant.
TABLE II-17

The Reaction Rate of tert-Butyl 3,5-Dinitroperoxybenzoate with Methyl Sulfide at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>k_s x 10^5 sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>137</td>
</tr>
<tr>
<td>60.3</td>
<td>59.0</td>
</tr>
<tr>
<td>70.0</td>
<td>24.5</td>
</tr>
<tr>
<td>80.0</td>
<td>4.64</td>
</tr>
</tbody>
</table>

a. 0.01 M perester, 0.0 M methyl sulfide, 0.2 M styrene in carbon tetrachloride.
Figure II-8. A Plot of the Arrhenius Equation for the Reaction of 3,5-(NO₂)₂-TBP with Me₂S; 0.01 M 3,5-(NO₂)₂-TBP, 1.0 M Me₂S in CCl₄.
I. References Chapter II


3. Ref. 1a, p 45.

   (b) W. G. Bentrude and J. C. Martin, ibid., 84, 1561 (1962).


8. Ref. 1a, pp 22-25.


III. EXPERIMENTAL

A. Materials

Sulfides: Methyl sulfide (Me₂S) was purchased from Matheson Coleman and Bell; tert-butyl sulfide and methyl phenyl sulfide were purchased from Eastman Chemical Company. The sulfides were distilled from sodium hydroxide.

tert-Butyl peroxybenzoate (TBP): This material was purchased from Lucidol (98%). One sample of TBP was purified by dissolving in pentane and passing the pentane solution through a florisil column. The TBP was recovered by removing the pentane under vacuum. Since the rate of reaction with Me₂S and the rate of decoloration of galvinoxyl was the same for both the florisil treated and untreated TBP, subsequent samples of TBP were used without purification.

Benzoyl peroxide (BPO): This material was purchased from Matheson Coleman and Bell. Before use, it was re-crystallized several times from carbon tetrachloride-methanol solution.

Galvinoxyl: This material was synthesized by Dr. H. T. Bickley by the method of Khrasch and Joshi.¹

Styrene: This material was purchased from Aldrich Chemical Company. It was washed with a 10% sodium hydroxide solution to remove inhibitors, washed with water, dried over calcium sulfate, and distilled at reduced
pressure. The center fraction (~70%) was retained for polymerization studies.

Solvents: All solvents used in kinetic runs were purified according to accepted literature procedures.²

B. Syntheses

1. Aryl-Substituted tert-Butyl Peroxybenzoates. All the substituted peresters were synthesized from tert-butyl hydroperoxide and the corresponding acid chloride by the method of Blomquist and Berstein.³ The p-methoxy derivative, which was obtained as a liquid (lit. mp 18.5-19°),³ was purified by passing through a florisil column. The other peresters, which are solids, were purified by two recrystallizations from hexane. The melting points are tert-butyl p-chloroperoxybenzoate, 47-47.5° (lit., 49°)³; tert-butyl p-nitroperoxybenzoate, 75-77° (lit., 79°)³; tert-butyl 3,5-dinitroperoxybenzoate, 86-87°. Iodometric titration indicated that the peresters were 98-100% pure, and the IR spectra of the peresters showed no absorption bands due to hydroperoxide, acid, or ester.

2. Aryl-Substituted Aryl Methyl Sulfides. Each sulfide was synthesized by methylation of the corresponding thiophenol with dimethyl sulfate.⁴ The thiophenols were distilled before use, and the sulfides were distilled from sodium hydroxide or recrystallized from pentane.
3. *tert-Butyl Benzoate*. This compound, which was used as a GLPC standard, was synthesized by the reduction of TBP with triphenyl phosphine.\(^5\) It was purified by distillation at reduced pressure (bp 59-60°, 0.5 mm) and its structure confirmed by NMR and IR.

4. **Dimethyl sulfide-d\(_6\)**. This compound was synthesized by refluxing dimethyl sulfoxide-d\(_6\) (Aldrich Chemical Company, 99\(^\%\)) with ammonium bromide.\(^6\) The deuterated sulfide was distilled from sodium hydroxide; the NMR spectrum of the distillate showed <1\% hydrogen impurity.

5. **Dimethylmethoxysulfonium Tetraphenylborate**. This salt was prepared by the method of Torssell.\(^7\) The sulfonium ion formed in the reaction of dimethyl sulfoxide with dimethyl sulfate was precipitated by the addition of sodium tetraphenylborate to the reaction solution. Recrystallization from acetonitrile yielded white crystals which melt at 175-190°, solidify, and then sublime above 260° (lit. mp 190°, solidify and melt again at -290°).\(^7\)

C. Kinetic Methods

Reaction samples were made by the following procedure. The perester and sulfide were weighed out in a 10-ml volumetric flask and diluted to volume with solvent. One ml aliquots were transferred to Pyrex tubes (9 mm o.d. x 10 in. long) which had previously been sealed off at one
end. The tubes were attached to an "8-titted cow" equipped with a threeway stop-cock which was connected to the system, a nitrogen source, and a vacuum pump. The samples were frozen with liquid nitrogen and the system was then evacuated. Next the system was opened to the nitrogen source and allowed to warm to room temperature. This procedure was repeated two more times; after the fourth evacuation, the frozen samples were sealed off with a torch. The volume above the surface of the sample was made as small as possible to minimize the vaporization of the methyl sulfide within the tube.

The samples were placed in a constant temperature bath and at predetermined times were removed, cooled, and stored in the refrigerator. Because of the importance of the infinity points in the kinetic plot, two infinity points were taken after about 10 perester half-lives. After all samples had been removed, the perester concentration of each sample was determined by either IR or by iodometric analysis.

1. **Infra-Red Method.** The absorbance of the perester carbonyl band at approximately 1758 cm\(^{-1}\) was measured with a Perkin Elmer 621 grating spectrophotometer.\(^9\) When the cell width was 2 mm, we could conveniently analyze perester concentrations between 0.001 and 0.01 M. The rate constant for perester decomposition was calculated from Eq. II-5.
The data were analyzed by a computer program using formulas given by G. W. Snedecor ["Statistical Methods", 4th ed., Iowa State College Press, Ames, Iowa, 1946, pp 118, 137, 139].

2. **Iodometric Method.** Because of interference from the absorption bands of some solvents, we were unable to use the IR method with some solvents. Therefore, for the solvent studies we determined the perester concentration by iodometric titration using a procedure similar to that reported by Wagner, Smith, and Peters. The method we used is as follows: One ml of the reaction solution is dissolved in 15 ml of freshly distilled 2-propanol. Glacial acetic acid (2 ml) and sodium iodide (~0.5 g) are added and the solution refluxed for 3-5 minutes. After cooling in ice water, the solution is diluted with approximately 20 ml of water and titrated with a sodium thiosulfate solution to a yellow-to-colorless end point (iodine serves as its own indicator). We obtained satisfactory results with an initial perester concentration of 0.05 M and a thiosulfate concentration of 0.01 M. At these concentrations, 1-10 ml of titrant is required to titrate the initial and final kinetic points. Rate constants for perester decomposition were calculated from Eq. II-5 using ml of titrant instead of absorbance.
This iodometric method is superior to other iodometric methods that have been used to determine perester concentration because the reaction time is fast, no special precautions are needed to exclude oxygen, and the blank reaction is small (~0.03 ml of 0.01 M Na$_2$S$_2$O$_4$).

D. Scavenger Methods

1. Limiting and Excess Scavenger. The disappearance of the free radical scavenger galvinoxyl was followed by monitoring the decrease in absorption at 570 nm ($\varepsilon = 760$). The samples containing galvinoxyl were degassed and sealed in pyrex cuvettes that were constructed with pyrex tubing attached to the cuvette tops so that the seal was made on the tubing and the cuvettes could be reused. The sealed cuvettes were placed in a Beckman DB spectrometer which was equipped with a water heated cell block so that the reaction could be run in the spectrometer. The instrument was also equipped with a Gilford Automatic Cuvette Positioner, Gilford Model 222 Photometer, and a recorder. With this instrument the rate of change of absorbance of four samples can be recorded consecutively so that four kinetic runs can be carried out simultaneously, making this a very useful instrument for scavenger studies. For fast runs the absorbance could be recorded continuously; for slow runs the absorbance of four samples could be recorded overnight.
In some runs the initial disappearance of galvinoxyl was extremely fast; however, this anomaly could be corrected by careful purification of the perester, sulfide, and solvent. We attempted to use two other free radical scavengers, 1,1-diphenyl-2-picrylhydrazyl (DPPH) and γ,γ-bis-(diphenylene)-β-phenyl-allyl (BDPA), but we were unable to obtain linear plots of scavenger absorbance vs. time.

2. Styrene Polymerization. In all styrene polymerization experiments we used 5 ml styrene solutions and usually 0.05 M perester. Under these conditions, sufficient polymer to be weighed accurately (~0.1-0.2 g) was formed at low polymer conversion (<2%). The solutions were placed in 10-ml round bottom ampoules, degassed under helium, and placed in a constant temperature bath for the allotted time interval. The polymer was precipitated by dropwise addition of the reaction solution to 300-400 ml of methanol with constant stirring. The polymer was filtered, dried overnight in a vacuum oven, and weighed. The rate of the thermal polymerization of styrene was measured by heating samples of styrene for long time intervals (~5 hr.) and then precipitating and weighing the polymer.

E. Product Analysis

Benzoic acid, tert-butyl alcohol, and α-benzoyloxy-methyl methyl sulfide (BOMS) were analyzed with a Glowall
gas chromatograph equipped with a flame ionization detector. An SE-30 column was used to separate the high boiling components, and a DIDP-Bentone column was used to separate the low boiling components. In addition to the identified components at least six high boiling components and two low boiling components were detected; however, none of these unknown components amounted to more than 1% of the total reaction products.

The fact that BOMS is a major reaction product was shown by its isolation from a large scale reaction. After the solvent was removed, BOMS was distilled (bp 101-103, 0.5 mm). The NMR and IR spectra of the isolated compound were identical to the spectra of BOMS reported by Pryor and Bickley. The isolated compound was used as a GLPC standard.

Dimethyl sulfoxide and tert-butyl benzoate were shown not to be reaction products; the addition of a small amount of each compound to a reaction sample produced two new GLPC peaks which had the retention times of the added compounds. In order to show that these compounds are stable under the reaction conditions, a reaction solution was made up with known amounts of dimethyl sulfoxide and tert-butyl benzoate, allowed to react for five perester half-lives, and was then analyzed; the ester and dimethyl sulfoxide concentrations were unchanged from the initial concentrations.
F. References Chapter III


8. The volume of gas above the sample was approximately one ml. Since the vapor pressure of Me₂S at 80° is about 1250 mm (Ref. 2, p 34) and since the mole fraction of Me₂S in a 1.0 M Me₂S solution in carbon tetrachloride is 0.1, the partial pressure of Me₂S is only 125 mm. The amount of Me₂S vapor at this pressure, temperature, and volume amounts to only 0.3% of the Me₂S in solution.


(b) R. C. Lamb, F. F. Rogers, G. D. Dean, Jr., and F. W. Voight, Jr., *ibid.*, 84, 2635 (1962).


IV. THE DIMETHYLANILINE-BENZYL Peroxide Reaction

A. Early Investigations

The reaction of dimethylaniline (DMA) with benzoyl peroxide (BPO) has many similarities to the reaction of dimethyl sulfide with tert-butyl peroxybenzoate; for example, the solvent effects, $P$-values, products, and most important, extent of radical production are similar. The radical production by the BPO-DMA reaction at low temperatures has been the subject of many papers over the last twenty years. A review of this work with particular attention given to the source of radicals will lead to a better understanding of the TBP-sulfide reaction.

The BPO-DMA reaction might appear to be a typical nucleophilic displacement since it involves a nucleophile reacting with a compound with a good leaving group (benzoate ion); however, it has an unexpected characteristic—it produces radicals as proven, for example, by the fact that this mixture can be used to initiate the polymerization of styrene at 0°. This reaction has fascinated researchers over two decades; however, the publications on this system have been confusing because the products arise both from a free radical and an ionic pathway and the kinetics are complicated by an induced decomposition which introduces a radical chain reaction.
1. **Horner's Electron Transfer Mechanism.** Some of the earliest investigations of the BPO-DMA reaction were carried out by Horner and co-workers. In 1955 Horner presented the mechanism shown in Scheme IV-1 in which he considered the reaction to be an electron transfer and not a nucleophilic displacement.²

**Scheme IV-1**

*Horner's Mechanism for the DMA-BPO Reaction*

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{N} & \quad \text{CH}_3 \\
\text{N} & \quad \text{CH}_3 \\
\text{C}_6\text{H}_4 & \quad \text{OC}_6\text{H}_4
\end{align*}
\]

(1)

(2)
The above mechanism was suggested to rationalize the isolation (after aqueous workup) of a 38% yield of methylaniline and a 15% yield of $p$-benzoyloxydimethylaniline along with benzoic acid and formaldehyde. When the
reaction was run in styrene, the polystyrene formed contained no nitrogen and thus the benzoyloxy radical was assumed to be the initiating radical, as shown in Eq. 6.\(^3\) This mechanism suggests that the low yield of polymer is due to cage recombination of \(3c\) and \(3d\) (Eqs. 4 and 5).

2. Walling's Nucleophilic Displacement Mechanism

In 1958, Walling and Indicator published a paper in which they supported the earlier work of Imoto and co-workers who had postulated an \(S_N^2\) mechanism for the BPO-DMA reaction. Walling and Indicator reported an extensive kinetic study of the reaction of BPO with DMA by following the disappearance of BPO and by also measuring the rate of styrene polymerization.\(^4\) From the rate of polymerization, they calculated the efficiency of initiation of polymerization. Their data (some of which are shown in Table IV-1) point out several important facts about this reaction:

1. The reaction rate and polymerization efficiency are nearly independent of the nature of the solvent.
2. The efficiency of radical production is fairly low. Table IV-1 shows that in methyl methacrylate at \(80^\circ\) the BPO-DMA reaction initiates polymerization with an efficiency of 0.10, and BPO homolysis has an efficiency of 0.58. Thus the ratio of efficiency of the BPO-DMA reaction to the efficiency of BPO homolysis is 0.176 (0.10/0.58). Therefore, only about 1/5 of the BPO molecules undergoing
TABLE IV-1
Solvent Effect on the Rate and Efficiency
of the DMA-BPO Reaction\(^a\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp °C</th>
<th>(k_2 \times 10^4) (^b)</th>
<th>(\varepsilon) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0</td>
<td>2.8(^d)</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>0</td>
<td>5.2(^d)</td>
<td></td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>0</td>
<td>1.8(^d)</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>0</td>
<td>9.4(^d)</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>0</td>
<td>2.1(^d)</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>1.0(^e)</td>
<td>0.08</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0</td>
<td>1.4(^e)</td>
<td>0.29</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>0</td>
<td>1.1(^e)</td>
<td>0.07</td>
</tr>
<tr>
<td>Acetone</td>
<td>0</td>
<td>1.6(^e)</td>
<td>0.11</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0</td>
<td>1.8(^e)</td>
<td>0.05</td>
</tr>
<tr>
<td>Styrene</td>
<td>0</td>
<td>2.4(^f)</td>
<td>0.20</td>
</tr>
<tr>
<td>Styrene</td>
<td>20</td>
<td>5.0(^f)</td>
<td>0.22</td>
</tr>
<tr>
<td>Styrene</td>
<td>30</td>
<td>11.7(^f)</td>
<td>0.24</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>40</td>
<td>57(^f)</td>
<td>0.16</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>80</td>
<td>130(^f)</td>
<td>0.10</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>80</td>
<td>0.31(^g)</td>
<td>0.58(^h)</td>
</tr>
</tbody>
</table>

\(a\). Data of Walling and Indicator, ref 4.
\(b\). Bimolecular rate constant for BPO-DMA reaction.
\(c\). Efficiency of the system in initiating polymerization.
\(d\). \(k_2\) measured by iodometric titration of BPO.
\(e\). In 4.46 M styrene, \(k_2\) obtained from rate of polymerization.
\(f\). In neat monomer, \(k_2\) obtained from rate of polymerization.
\(g\). First order rate constant in sec\(^{-1}\) for thermal decomposition of BPO with no added DMA.
\(h\). Efficiency of BPO homolysis in initiating polymerization.
reaction with DMA produce scavengerable free radicals.

In spite of the absence of solvent effect, Walling assumed that the first step in the reaction is displacement of DMA on BPO to yield a quaternary hydroxyl amine derivative (4, Eq. 7).

\[
\begin{align*}
\text{Ph-N:} + & \quad \text{Ph} \\
\text{CH}_3 & \quad \text{C}=0 \\
\text{Ph} & \quad \text{O} \\
\text{CH}_3 & \quad \text{C}=0 \\
\text{Ph} & 
\end{align*}
\rightarrow
\begin{align*}
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{Ph-N-O-C-Ph} \\
\text{CH}_3
\end{array} \right] + \\
\text{PhCO}_2
\end{align*}
\tag{7}
\]

Walling suggested that free radicals are formed by the homolysis of intermediate 4 (Eq. 8). The low efficiency of polymerization was accounted for by the ionic decomposition of 4 to form the quaternary imine 5 (Eq. 9).

\[
\begin{align*}
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{Ph-N-O-C-Ph} \\
\text{CH}_3
\end{array} \right] + & \quad \text{Ph-N}^+ + \quad '\text{O-C-Ph} \\
& \quad \text{Ph-N-O-C-Ph} \\
& \quad \text{CH}_3
\end{align*}
\tag{8}
\]

\[
\begin{align*}
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{Ph-N} \\
\text{CH}_2
\end{array} \right] + & \quad \text{Ph} \quad \text{H} \\
& \quad '\text{O-C-Ph} \\
& \quad \text{HO-C-Ph}
\end{align*}
\tag{9}
\]

Walling admitted that 5 could be formed by disproportionation of the homolysis products of 4 (Eq. 10) or from intermediate II in Horner's mechanism (Eq. 11). The
quaternary imine has been shown

\[
\begin{align*}
\text{CH}_3 & \quad \text{Ph-N}^+ \\
\text{CH}_3 & \quad \text{CH} & \quad \text{OCPh} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph-N}^+ & + \cdot \text{OCPh} \rightarrow \left[ \begin{array}{c}
\text{CH}_3 \\
\text{Ph-N}^+ \\
\text{CH}_2 \\
\end{array} \right] + \text{HOCPh} \\
\end{align*}
\]

(10)

\[
\begin{align*}
\text{CH}_3 & \quad \text{Ph-N}^+ \\
\text{CH}_3 & \quad \text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph-N}^+ & + \cdot \text{OCPh} \rightarrow \left[ \begin{array}{c}
\text{CH}_3 \\
\text{Ph-N}^+ \\
\text{CH}_2 \\
\end{array} \right] + \text{PhCO}^- + \text{PhCOH} \\
\end{align*}
\]

(11)

to be present in systems that bear similarity to the BPO-DMA reaction; for example, in the reaction of ethylene-triamine with BPO the enamine formed from the imine in Eq. 12 can be trapped using 2,5-dichloro-3,6-dimethoxybenzoquinone (Eq. 13).5

\[
\begin{align*}
\text{Et}_3\text{N} & + \text{BPO} \rightarrow \text{Et}_2\text{N}^+=\text{CH-CH}_3 \\
& \xrightarrow{\text{Bi}} \text{Et}_2\text{N}-\text{CH=CH}_2 + \text{BH} \\
\end{align*}
\]

(12)

\[
\begin{align*}
\text{Et}_2\text{N}-\text{CH=CH}_2 & + \text{CH}_3\text{O} & \text{C1} \\
\text{OCH}_3 & \text{C1} & \text{CH}_3 \\
\end{align*}
\]

(13)
Walling's and Horner's mechanisms are quite different. Walling envisioned the reaction as a direct $S_N^2$ displacement with radicals being produced by homolysis of an intermediate. According to Horner, the reaction goes by an electron transfer from amine to peroxide in which radical ions are the initial intermediates. In 1960 the key question was does $4$ produce radicals or do radicals produce $4$? This question stimulated further investigation during the following decade.

3. Kinetics and Substituent Effects. Other investigators who have worked on this reaction have reported rate constants that are in good agreement with those reported by Walling (Table IV-2). O'Driscoll, who has done the most work on the kinetics, used dead-end polymerization techniques in order to obtain rate constants and efficiencies. He has studied substituent effects on the rate and on efficiencies for substitution in both the amine and peroxide. The $\rho$-values, which are typical for an $S_N^2$ displacement, are $+1.6$ for peroxide substituents and $-2.6$ for amine substituents. The substituent effect on efficiency of radical production, illustrated in Figure IV-1, is complex and not well understood.

In a later paper O'Driscoll observed the formation of a complex between DMA and BPO and measured the equilibrium constant for complex formation by spectroscopic observations. O'Driscoll suggests that the BPO-DMA reaction
### TABLE IV-2
Comparitive Rates of the DMA-BPO Reaction

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp °C</th>
<th>$k_2 \times 10^4$ a</th>
<th>$\epsilon$ b</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0</td>
<td>2.8 c</td>
<td>--</td>
<td>Walling 4</td>
</tr>
<tr>
<td>Styrene</td>
<td>0</td>
<td>2.4 d</td>
<td>0.20</td>
<td>&quot;</td>
</tr>
<tr>
<td>Styrene</td>
<td>30</td>
<td>11.7 d</td>
<td>0.24</td>
<td>&quot;</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0</td>
<td>5.2 c</td>
<td>--</td>
<td>&quot;</td>
</tr>
<tr>
<td>Benzene</td>
<td>30</td>
<td>30 c</td>
<td>0.10</td>
<td>O'Driscoll 8 a</td>
</tr>
<tr>
<td>Benzene</td>
<td>25</td>
<td>23 c</td>
<td></td>
<td>Hrabak 6</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0</td>
<td>1.4</td>
<td></td>
<td>Mesrobian 7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>30</td>
<td>23</td>
<td></td>
<td>&quot;</td>
</tr>
</tbody>
</table>

a. Bimolecular rate constant.

b. Efficiency of the system in initiating polymerization.

c. $k_2$ obtained by iodometric titration of BPO.

d. $k_2$ obtained from rate of polymerization.

e. With 4.46 M styrene.

f. In presence of free radical scavenger $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl (DPPH).
Figure IV-1. The Substituent Effect on the Efficiency of Radical Production in the DMA-BPO Reaction; $f$ vs. $2\sigma_X$ for Reaction of $X,X'$-Substituted BPO with DMA ●, $f$ vs. $\sigma_Y$ for Reaction of BPO with Y-Substituted DMA ▲, $f$ vs. $2\sigma_X$ for Reaction of $X-X'$-Substituted BPO with p-Cl-DMA ■.
proceeds through a complex that is in equilibrium with starting materials (Eq. 14). This complex may be the precursor to an electron transfer intermediate.

\[
\text{DMA} + \text{BPO} \xrightarrow{\text{[DMA,BPO]}} \text{radicals (14)}
\]

B. The Amine Oxide-Benzoyl Peroxide Reaction

In order to determine if Walling's mechanism is correct, it is necessary to show that the homolysis of \( 4 \) can account for all of the radical production. The reaction of dimethylaniline N-oxide (DMAO) with benzoic anhydride (\( \text{Bz}_2\text{O} \)) forms an intermediate which is identical to the intermediate postulated by Walling for the \( S_N^2 \) displacement of DMA on BPO (Eq. 15). If both reactions proceed through

\[
\begin{align*}
\text{Ph-N=O + PhCOCPh} & \xrightarrow{\text{[Ph-N-O-CPh]}} \text{Ph-N-O-CPh} + \text{PhCO}_2^- \\
\end{align*}
\]

this intermediate, then both the efficiency of radical production and the products must be the same for each reaction; Sato and Imoto have measured the efficiency of the DMAO-BPO reaction,\(^9,10\) and Huisgen et al. have determined the products from both reactions.\(^11,12\)
1. **Efficiency of Radical Production.** The DMAO-Bz₂O reaction in benzene initiates the polymerization of methyl methacrylate only in the presence of ethanol. In fact, the rate of polymerization is first order in ethanol; Sato *et al.* suggested that the ethanol helps the free radicals to escape from the solvent cage since ethanol does not appear to increase the rate of the reaction.⁹ It is true that this reaction will initiate polymerization; however, the efficiency is very low when compared to the efficiency of the BPO-DMA reaction. Walling found that the efficiency of the BPO-DMA reaction in initiating the polymerization of neat methyl methacrylate at 40° was 0.16.⁴ For the Bz₂O-DMAO reaction in 4.46 M methyl methacrylate containing 0.886 M ethanol, the efficiency was only 0.0008.¹⁰ In this example, the BPO-DMA reaction produces radicals 200 times more efficiently than the Bz₂O-DMAO reaction. Thus, while the homolysis of 4 formed in the Bz₂O-DMAO reaction may produce radicals at low efficiencies in ethanolic solutions, it cannot account for the much higher efficiency of radical production by the BPO-DMA reaction in styrene. In fact, the anhydride reaction will not initiate the polymerization of neat styrene⁹ as does the BPO-DMA reaction.⁴

Sato and co-workers synthesized an analogue of 4 as shown in Eq. 16. The rate of polymerization of 3.0 M acrylonitrile in dimethyl formamide initiated by the homolysis of salt 6 is
four times slower than the rate of acrylonitrile polymerization initiated by homolysis of BPO. Calculations, using Eq. AII-4 and the data in the last two lines of Table IV-1, show that at 80° the rate of polymerization of methyl methacrylate initiated by the DMA-BPO reaction is approximately 8 times the rate of polymerization initiated by BPO homolysis. Thus the rate of polymerization of methyl methacrylate initiated by the DMA-BPO reaction is 32 times the rate of polymerization of acrylonitrile initiated by homolysis of 6. In the homolysis of anilinium ions, the counter ion should have little effect; and, therefore, homolysis of the anilinium ion, 6, or the similar ion, 4, cannot account for the rate of polymerization initiated by the DMA-BPO reaction. It should be noted that in the above example 6 was homolyzed in acrylonitrile and the DMA-BPO reaction was run in methyl methacrylate. Since in the DMAO-Bz₂O reaction the rate of polymerization varied with monomer in the order acrylonitrile>>methyl methacrylate>vinyl chloride>styrene, the use of methyl methacrylate in the homolysis reaction
would result in an even greater increase in the difference in polymerization rates. The above examples clearly show that Walling's suggestion that homolysis of 4 is responsible for the radical production in the DMA-BPO reaction is not likely.

2. The Effect of Scavengers on Products. Huisgen used product studies to determine that branching between radicals and ions in the BPO-DMA reaction must occur before the formation of 4\textsuperscript{12}. The major reaction products of the DMAO-BPO reaction are shown in Eq. 17; 7 is a rearrangement product of 4 (Eq. 17a), and 9 which leads to a demethylation product (10) is formed from 5. In the
DMA-BPO reaction product 10 can be produced from 4 (Eq. 17b), if the reaction follows an $S_N^2$ mechanism, or by an additional radical path directly from 2 (Eq. 18a), if the reaction follows an electron transfer mechanism. According to Walling's mechanism, 2 comes from homolysis of 4. If

$$\begin{align*}
\text{CH}_3 & \quad \text{RCO}_2 \quad \text{CH}_3 \quad \text{O} \\
\text{Ph-N}=\text{CH}_2 & + + \quad \rightarrow \quad \text{Ph-N-CH}_2\text{OCR} \quad \rightarrow 10
\end{align*}$$

Walling is correct, 11 is produced from 4 and products of both the DMA-O-Bz$_2$O reaction and the DMA-BPO reaction should be affected in the same way by radical scavengers. If Horner is correct, radical production precedes the formation of 4 and the BPO-DMA reaction would produce 10 by way of 2 without forming 4 and thus would be influenced by radical scavengers more than the DMAO-Bz$_2$O reaction would be. However, 4 can also be formed from 2 by a cage combination of the radicals (Eq. 18b); 4 formed in this way will be independent of added scavenger. Thus, if Eq. 18b represents the major pathway for decomposition of
2, product studies will not be able to distinguish an ET reaction from an $S_N^2$ reaction.

In summary, product 10 can be formed by an ionic or radical pathway. If 4 is the first intermediate of the BPO-DMA reaction, this reaction as well as the $\text{Bz}_2\text{O-DMAO}$ reaction should show similar scavenger effects on products. On the other hand, if 2 is the first intermediate of the BPO-DMA reaction and 4 is only a minor subsequent product formed by radical combination of 2, then the scavenger effect on products will be different from the scavenger effects on the $\text{Bz}_2\text{O-DMAO}$ products.

Huisgen compared the products from the reaction of acetyl peroxide ($\text{Ac}_2\text{O}_2$) and $p$-chlorodimethylaniline to the products from the reaction of acetic anhydride ($\text{Ac}_2\text{O}$) and $p$-chlorodimethylaniline N-oxide (Table IV-3).\(^{12}\) The arguments concerning the comparison of products from the BPO-DMA reaction and from the $\text{Bz}_2\text{O-DMAO}$ reaction still apply to these reactions even though the compounds are slightly different. When scavengers are added to the reaction mixture, the yield of 10 in the $\text{Ac}_2\text{O}_2$-DMA reaction decreases by 50% while the yield of 10 in the $\text{Ac}_2\text{O}$-DMAO reaction remains nearly unchanged. Thus the formation of 10 in the peroxide reaction must include a radical path while the formation of 10 in the anhydride reaction must be ionic. Also, the yield of 8 is much less in the peroxide reaction than in the anhydride reaction. Since
TABLE IV-3

The Effect of Radical Scavengers on Products<sup>a</sup>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>% Yield&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% Yield&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;N-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>9, 10</td>
<td>64, 65</td>
</tr>
<tr>
<td>Styrene + Acetic Acid</td>
<td>7, 8</td>
<td>57, 55</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;N&lt;sup&gt;+&lt;/sup&gt; + CH&lt;sub&gt;3&lt;/sub&gt;COCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>36, 30</td>
<td>8, 6</td>
</tr>
<tr>
<td>Cumene</td>
<td>15, 16</td>
<td>10, 11</td>
</tr>
<tr>
<td>Styrene</td>
<td>19, 18</td>
<td>8, 9</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data from ref 12.

<sup>b</sup> Data for two separate runs.
8 is a rearrangement product of 4, Eq. 17a, the smaller yield of 8 in the peroxide reaction indicates that the relative yield of 4 must also be smaller in this reaction than in the anhydride reaction. In the peroxide reaction, the smaller yield of 8 and the decrease in formation of 10 in the presence of radical scavengers are very good evidence that the peroxide reaction and anhydride reaction do not share 4 as a common initial intermediate and thus follow different reaction mechanisms. A further indication of the occurrence of two different mechanisms in these reactions is that in the study of the Ac₂O-DMAO reaction Huisgen did not detect any p-hydroxydimethylaniline after basic workup;¹¹ the corresponding product, p-benzoyloxydimethylaniline, was isolated by Horner from the reaction of BPO with DMA and attributed to a radical path.²

C. Evidence for an Electron Transfer Mechanism

1. Observation of the Amine Cation-Radical. The above discussion suggests that Walling's mechanism is incorrect, but does not explicitly prove that Horner's mechanism is correct. In 1963 Graham and Mesrobian presented a mechanism involving an electron transfer intermediate.⁷ In the absence of radical scavengers they found that the DMA-BPO reaction was 3/2 order in peroxide. They interpreted this to be due to an induced decomposition of peroxide, which is not unexpected since BPO is very
susceptible to induced decomposition. An odd result of their work was the isolation in 38% yield of the cation-radical tetramethylbenzidine (\textsuperscript{13}, Eq. 22). Graham and Mesrobian also suggest a mechanism involving electron transfer, but because of the induced decomposition which they assume is occurring, and because of their isolation of the product \textsuperscript{13}, they suggest the mechanism shown below in Scheme IV-2, Eqs. 19-24. Their mechanism is very similar to Horner's in that it involves an electron transfer as the first step.

**Scheme IV-2**

Graham and Mesrobian's Mechanism for the DMA-BPO Reaction

\[
\text{PhCO}_2^+ + \text{PhN} + \text{PhCO}_2^- + \text{PhN}^+ + 2\text{H}^+.
\]
Reactions 23 and 24 are responsible for the induced decomposition, and they explain the large yield of the cation-radical which is obtained. The low efficiency of the system results both from the induced decomposition (Eqs. 22, 24) and from electron transfer (Eq. 20).

The reactions postulated by Graham and Mesrobian are similar to some reactions that occur in the electrochemical oxidation of DMA (Eqs. 25-27). Support for

\[
\text{Ph-N} \xrightleftharpoons{1e} \left[ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \right]^+ \quad \text{Ph-N} \xrightleftharpoons{1e} \left[ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \right]^+ 
\]
the presence of the cation-radical of DMA, 12, in these reactions comes from work by Margaritova and co-workers who observed the broad amine cation-radical absorption band at 4600-4700 Å in the DMA-BPO reaction mixture. Hand also observed this band during the electrochemical oxidation of DMA. Thus, the involvement of 12 in the reaction of BPO with DMA is established from electrochemical and spectroscopic studies.

2. Dependence of the Reaction Rate on Amine Ionization Potential. The presence of the cation radical of DMA does not alone prove an electron transfer intermediate because the cation-radical could be formed in a secondary reaction of benzoyloxy radicals and DMA (Eq. 20 in Mesrobian's mechanism). However, explicit evidence for an electron transfer was published by two groups of Russian workers who demonstrated a relationship between ionization potential of the amine and activation energy for reactions of amines with BPO.
Margaritova and Rusakova measured the activation energies for reactions of BPO with DMA, triethylamine, and aniline. The activation energies for the reactions investigated by Margaritova and Rusakova are dependent on the ionization potentials of the amines and not the base strengths of the amines (Table IV-4). Aniline and DMA have about the same basicity constant yet the activation energies for their reactions with BPO are substantially different. However, this difference does correspond to a difference in amine ionization potential as shown by the results in Table IV-4 and the results of Melik-Ogandzhanyan et al. who found that a linear relationship is obtained when the ionization potential of an aliphatic amine is plotted versus the log of the reaction rate of the amine with BPO. The results of both groups show that as the ionization potential of the amine increases, the rate of reaction decreases, and the activation energy increases. This indicates that the rate determining step in the reaction is electron transfer from amine to BPO, and the lack of correlation of basicity constant with reaction rate, observed by Margaritova and Rusakova, indicates that the rate determining step is not an $S_N^2$ displacement.

D. An Electron Transfer Mechanism

It is now apparent that the production of radicals in the BPO-DMA reaction cannot result from homolysis of 4.
<table>
<thead>
<tr>
<th>Amine</th>
<th>$E_a^a$ kcal/mole</th>
<th>ionization$^b$ eV</th>
<th>$K_b^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylaniline</td>
<td>11.2, 10.8</td>
<td>7.14, 7.3</td>
<td>1.1x10^{-10}</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>11.4, 11.3</td>
<td>7.5</td>
<td>5.5x10^{-4}</td>
</tr>
<tr>
<td>Aniline</td>
<td>13.8, 14.4</td>
<td>7.7, 7.95</td>
<td>4.2x10^{-10}</td>
</tr>
</tbody>
</table>

\( a, b, c \) Data from ref 16, $E_a$ measured in benzene and in benzene-water emulsion. Ionization potentials reported by different workers. Basicity constant, ref 17.
It also appears unlikely that radicals result from the homolysis of any radical pair intermediate or other type intermediate which is produced by an $S_N^2$ displacement. It seems more likely that radicals arise, as Horner originally suggested, by an electron transfer (ET) from amine to peroxide. The evidence for an ET reaction rather than an $S_N^2$ reaction can be summarized as follows: (1) The efficiency of the DMAO-Bz$_2$O reaction is much less than the efficiency of the BPO-DMA reaction. (2) The product composition of the DMA-BPO reaction is altered by radical scavengers. (3) Products analogous to electrochemical oxidation of DMA have been isolated from the reaction. (4) The reactivity of the amine is determined by ionization potential and not basicity.

1. **Product Analysis.** Swan et al. have reported a detailed product analysis of the BPO-DMA reaction.$^{18,19,20}$ In addition to the major products, they have isolated several minor products under varying reaction conditions. Most of the products are dimers formed from reaction of 5 and/or 11 with DMA (Eq. 28).

\[
\begin{align*}
\text{5} & \quad \text{DMA} \\
\text{11} & \quad \text{DMA} \\
\end{align*}
\]
As shown in Eq. 28, the isolation of the above combination products in the BPO-DMA reaction does not indicate whether 5, 11, or both are present in the reaction system. Both 5 and 11 could be formed from 2; 5 by disproportionation (Eq. 29) or by combination to 4 followed by elimination (Eq. 31) and 11 by proton abstraction by benzoate ion (Eq. 30).

\[
\begin{align*}
\text{Ph} & \quad \text{C}=\text{O} \\
\text{CH}_3 & \quad \text{Ph-N}^+ \quad \text{I}^-
\end{align*}
\]

\[\xrightarrow{2} \]

\[
\begin{align*}
\text{Ph-N-O} & \quad \text{OCPh} \\
\text{CH}_3 & \quad \text{Ph-N=CH}_2
\end{align*}
\]

\[\xrightarrow{4} \]

\[
\begin{align*}
\text{CH}_3 & \quad \text{Ph-N=CH}_2 \\
\text{Ph-CO}_2^- & \quad \text{Ph-CO}_2^-
\end{align*}
\]

\[\xrightarrow{5} \]

Swan et al. found that when 5 and 11 are generated independently, 11 reacts with N-phenylmaleimide but 5 does not; they therefore used N-phenylmaleimide as a trapping agent to show that 11 is present in the BPO-DMA reaction system. When BPO reacts with DMA in the presence of N-phenylmaleimide, a 40% yield of trapped 11 is obtained.
This result along with earlier results in trapping products from $\text{Eq}$. (Eqs. 12-13)\textsuperscript{5} indicates that both free radical and ionic intermediates are present during the reaction. Thus the original confusion over the presence of both radical and ionic products can be explained by subsequent reactions of an ET intermediate.

2. Reaction Scheme. We wish to suggest that all of the experimental facts on the BPO-DMA reaction can be accounted for by an ET mechanism and not by the nucleophilic displacement mechanism that is usually written.\textsuperscript{1a,1b,8d} Our mechanism is quite similar to that originally suggested by Horner\textsuperscript{2}; an electron transfer from the amine donor to the peroxide acceptor forms an unstable intermediate, $2^+$, which decomposes by ionic and radical paths as shown in Scheme IV-2. The experimental results do not exclude the possibility of a minor contribution from a nucleophilic displacement, but for simplicity, we have assumed that only an electron transfer mechanism occurs in this reaction.\textsuperscript{Eq. 32.} The weak complex $1^-$, observed by O'Driscoll,\textsuperscript{9} represents some sort of association prior to ET. The $\rho$-values observed, +1.6 for substituents in the BPO ring and -2.6 for substituents in the phenyl-group of DMA, are consistent with ET being the rate determining step. Further support for ET is the linear free energy correlation of reaction rate with ionization potential of amines.
Scheme IV-3

An Electron Transfer Mechanism for the DMA-BPO Reaction

\[ \text{PhNMe}_2 + \text{BPO} \rightleftharpoons [\text{PhNMe}_2, \text{BPO}] \xrightarrow{\text{Rate step}} [\text{PhNMe}_2^+, \text{PhCO}_2^-, \text{PhCO}_2^-] \]

\[ \xrightarrow{1} \quad \xrightarrow{2} \]

(32)

\[ \xrightarrow{2} \text{Ph-N}^+ \quad \text{PhCO}_2^- + \text{PhCO}_2^- \]

(33)

\[ \xrightarrow{12} \]

\[ \xrightarrow{2} \left[ \begin{array}{c} \text{CH}_3 \\ \text{Ph-N-CH}_2 \end{array} \right]^* + \text{PhCO}_2 \overset{\text{CH}_3}{\xrightarrow{11}} \overset{\text{O}}{\xrightarrow{13}} \text{Ph-N-CH}_2\text{OCPh} \]

(34)

\[ \xrightarrow{5} \left[ \begin{array}{c} \text{CH}_3 \\ \text{Ph-N=CH}_2 \end{array} \right]^+ + \text{PhCO}_2 \overset{\text{CH}_3}{\xrightarrow{14}} \overset{\text{O}}{\xrightarrow{15}} \text{Ph-N-CH}_2\text{OCPh} \]

(35)
I

\[ \text{Ph-N}^+ + \text{PhCO}_2^- + \text{PhCO}_2\text{H} \quad (36\text{a}) \]

\[ \text{Ph-N}^- + \text{PhCO}^- + \text{PhCO}_2\text{H} \quad (36\text{b}) \]

\[ \text{Ph-N}^- \rightarrow \text{Ph-N}^- \text{CH}_2^- \text{Ph-N} \quad (38) \]

\[ \text{Ph-N}^+ + \text{Ph-N} \rightarrow \text{Ph-N-CH}_2^-\text{Ph-N} \quad (39) \]

\[ 2 \text{Ph-N}^+ \rightarrow \text{N-Ph-Ph-N} + 2\text{H}^+ \quad (39) \]

\[ \text{Ph-N^-} \rightarrow \text{N-Ph-CH}_2^-\text{Ph-N} \rightarrow \text{dimer} \quad (40) \]
The lack of solvent effect on reaction rate indicates that the transition state occurs very early before much charge separation is actually developed (the transition state more closely resembles a charge transfer complex rather than complete electron transfer to form charged intermediates). Scavangeable free radicals are produced by diffusive separation of the radical pairs in 2. The amine cation-radical has been identified in this system by observation of its absorption band at 4600-4700 Å. Eq. 33. Benzoate ion can abstract a proton from the cation-radical to form 11 which has been trapped in 40% yield. Benzoyloxy radicals and 11 combine to form product 13. On aqueous work up, 13 would yield N-methyl aniline, formaldehyde, and benzoic acid, all of which are observed as products.  Eq. 34. Disproportionation of 2 would lead to 5 which in turn can combine with benzoate ion to form 14. In some cases 5 has been trapped. Eq. 35. Compound 4 can be formed by a radical combination of the components of 2. Both radical scavenger experiments and product studies indicate that 4 is a product of 2 and not the initial reaction product formed by an $S_N2$ displacement of DMA on BPO. Intermediate 4 is very unstable and decomposes by homolysis, Eq. 36a, which is known to be a minor pathway; by rearrangement to 7, Eq. 36b (subsequent products from 7 have been isolated); by an elimination reaction, Eq. 36c; or in some cases, by a
displacement to yield amine oxide and acid anhydride, Eq. 36d, which can rapidly react together. The amine oxide in Eq. 36d has not been observed; however, in a similar reaction, Huisgen has isolated the amine oxide in 80% yield from the reaction of BPO with 16 (Eq. 41). 22 Also during the reaction of BPO with triethyl amine the IR absorbance of the anhydride has been observed. 15 Eq. 37. Product 15 can be formed by a cage combination followed by rearrangement; Horner isolated 15 in 15% yield. 2 Eqs. 38-40. These are reaction pathways that produce the minor products observed by Swann. 18, 19

The similarities of the BPO-DMA reaction and the TBP-methyl sulfide reaction strongly suggests that the latter reaction is also an electron transfer. However, it is necessary to examine other reactions of nucleophiles with peroxides so that they too can be considered in determining the mechanism of the TBP-sulfide reaction.

\[
\begin{align*}
\text{PhCO} \quad \text{C} = \text{O} \\
\text{O} \quad \text{O} \\
\text{Ph}
\end{align*}
\]

\[
\text{BPO} \rightarrow \text{PhCOCPh}
\]
E. References Chapter IV


21. For discussion see pp 167-168.

V. NUCLEOPHILIC DISPLACEMENTS ON PEROXIDES

The reactions of nucleophiles with peroxidic compounds have been vigorously investigated during the last twenty years. Many examples of these reactions such as the reactions of sulfides with hydroperoxides or acyl peroxides, and phosphines with hydroperoxides, acyl peroxides, or peroxyesters are now understood to be bimolecular nucleophilic displacements. Sulfide displacement on BPO and phosphine displacement on TBP may be closely related to the TBP-methyl sulfide (Me₂S) reaction, and a detailed discussion of these SN₂ reactions will help us characterize the SN₂ mechanism in the sulfide-TBP case should that reaction occur by an SN₂ mechanism. Once we understand the expectations of an SN₂ mechanism in the sulfide-peroxide case, we can compare our results to those expected if the reaction were a nucleophilic displacement.

A. The Sulfide-Benzoyl Peroxide Reaction

1. Mechanism. This reaction was first studied by Horner and more recently by Pryor and Bickley. It is a typical bimolecular displacement of sulfide on peroxidic oxygen. Since sulfide greatly accelerates the rate of BPO disappearance by an ionic pathway, Pryor refers to this reaction as an assisted heterolysis. Also disulfides accelerate the rate of BPO disappearance but to a lesser degree. Table V-1 lists some relative rate
**TABLE V-1**

The Reaction of BPO with Sulfides and Disulfides

<table>
<thead>
<tr>
<th>Sulfide or Disulfide</th>
<th>$k'_S/k'_H$</th>
<th>Rel. Rate$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Sulfide</td>
<td>5.0$\times$10$^4$</td>
<td>260</td>
</tr>
<tr>
<td>Propyl Sulfide</td>
<td>4.5$\times$10$^4$</td>
<td>240</td>
</tr>
<tr>
<td>iso-Butyl Sulfide</td>
<td>3.1$\times$10$^4$</td>
<td>160</td>
</tr>
<tr>
<td>tert-Butyl Sulfide</td>
<td>2.0$\times$10$^3$</td>
<td>10</td>
</tr>
<tr>
<td>tert-Butyl Disulfide</td>
<td>3.6$\times$10$^2$</td>
<td>1.9</td>
</tr>
<tr>
<td>Methyl Phenyl Sulfide</td>
<td>3.8$\times$10$^3$</td>
<td>22</td>
</tr>
<tr>
<td>Phenyl Sulfide</td>
<td>1.9$\times$10$^2$</td>
<td>1</td>
</tr>
<tr>
<td>Methyl Disulfide</td>
<td>4.6$\times$10$^2$</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$^a$ In chlorobenzene at 40°, data from Ref 3.

$^b$ $k'_S$ is the pseudo-unimolecular rate of BPO disappearance in 1.0 molar sulfide or disulfide; $k'_H$ is rate of BPO homolysis, 2$\times$10$^{-7}$ sec$^{-1}$ at 40°.

$^c$ Rate of disappearance of BPO in sulfide relative to rate of disappearance in phenyl sulfide.

$^d$ $k'_S$ extrapolated from data at 100° assuming that $E_a$ for phenyl sulfide is the same as $E_a$ for tert-butyl sulfide.

$^e$ This work, in carbon tetrachloride at 40°.
constants for increase in the rate of BPO disappearance \((k'_S/k_H)\) and for the effect of sulfide structure on the reaction rate.

The reaction mechanism given by Pryor and Bickley is shown in Scheme V-1. The exact nature of intermediate 1 is not known. However, a study of the polar solvent effect on the reaction rate of BPO with methyl disulfide (Table V-2) shows that this reaction is much less sensitive to a change in solvent polarity than are some related reactions in which the products are charge separated species. For example, in a paper published after Pryor and Bickley's work was completed, Harpp and Gleason postulated that the reaction of disulfides with aminophosphines follows Eq. 4 in which the intermediate is the phosphonium salt 4. The rate of this reaction shows a similar dependence on

\[
\begin{align*}
\text{(Et}_2\text{N)}_3\text{P} + \text{RSSR} + (\text{Et}_2\text{N})_3\text{P}^+\text{SR} & \rightarrow \text{RSR}^+ (\text{Et}_2\text{N})_3\text{P}^=\text{S} \\
\end{align*}
\]

solvent effect as does other reactions in which charged intermediates have been implicated. For this reaction a plot of \(\log k\) at 30° vs. \(E_T\) is linear and has a slope of 32x10^-2. If the BPO-Me_2S reaction forms charged intermediate 1a, then the reaction rate should show a similar dependence on solvent polarity. A plot of \(\log k\) at 80° vs. \(E_T\) for the Me_2S-BPO reaction is linear; however, the slope
Scheme V-1

Pryor and Bickley's Mechanism for the Methyl Sulfide-BPO Reaction

\[
\text{CH}_3\text{SCH}_3 + \text{PhCOOCPh} \xrightarrow{\text{rate step}} \text{CH}_3\text{S}^+ \xrightarrow{\text{step a}} \text{CH}_3\text{S} \xrightarrow{\text{step b}} \text{CH}_3\text{SCH}_2\text{OCPh}
\]

(1)

(2)

(3)

\[
1 \xrightarrow{\text{slow}} \text{CH}_3\text{S}^=\text{CH}_2 \xrightarrow{\text{slow}} \text{CH}_3\text{S}^=\text{CH}_2^+ \xrightarrow{\text{slow}} \text{CH}_3\text{SCH}_2\text{OCPh}
\]

(3)
<table>
<thead>
<tr>
<th>Solvent</th>
<th>((\text{PhCH}_2)_2\text{S}^a)</th>
<th>(\text{Ph}_3\text{b})</th>
<th>(\text{R}_3\text{N}^c)</th>
<th>(\text{BPO}^d)</th>
<th>((\text{Et}_2\text{N})_3\text{P})</th>
<th>(S_8)</th>
<th>(\text{RBr})</th>
<th>(\text{t-BuSSBu-t})</th>
</tr>
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<tbody>
<tr>
<td>Hexane</td>
<td>0.01</td>
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</tr>
<tr>
<td>Cyclohexane</td>
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<td>0.01</td>
<td></td>
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<td></td>
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<td>(\text{CCL}_4)</td>
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<td></td>
<td></td>
<td>0.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.6</td>
<td>3.5</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(o)-Dichlorobenzene</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzonitrile</td>
<td></td>
<td></td>
<td></td>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
<td>7.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

d. Ref 3.
Figure V-1. The Effect of Solvent Polarity on the Reaction Rate of Several $S_N2$ Reactions; tris(diethylamino)phosphine + Dibenzyl Disulfide ■, Di-tert-Butyl Disulfide + BPO ●, Triphenyl Phosphine + TBP ▲.
of the line is only $4.3 \times 10^{-2}$. Since the rate of the BPO-\( \text{Me}_2\text{S}_2 \) reaction is 7.5 times less sensitive to solvent polarity than is the rate of the aminophosphine-disulfide reaction, \( \text{la} \) alone is not a good representation of the reaction intermediate. Pryor and Bickley suggested that the intermediate is not totally ionic but has some covalent character, and in Scheme 1, the covalent contribution necessary to explain the solvent effect was postulated to be a tetracovalent sulfur compound (\( \text{lb} \)) which was considered to be an important resonance contributor to \( \text{la} \).

Recent investigations of other nucleophile-peroxide reactions have presented new evidence to support a tetracovalent sulfur intermediate. First, in similar reactions in which selenide is the nucleophile, a stable tetracovalent intermediate has been isolated (Eq. 5).\(^9\) Dropwise addition of methyl phenyl selenide to a \( \text{CCl}_4 \) solution at room temperature produces a white precipitate, methylphenyldibenzoyloxyyselenurane \( 5 \), in 92% yield. After

\[
\begin{align*}
\text{PhSeCH}_3 + \text{PhCOOCPH} & \rightarrow \text{Ph} \quad & \text{Reflux} \quad & \text{PhSeCH}_2\text{OCPh} \\
\text{CH}_3 \quad & \text{O} \quad & \text{2 hr} \\
5 & \rightarrow & 6
\end{align*}
\]

refluxing in \( \text{CCl}_4 \) for two hours, the rearrangement product, \( \alpha\)-benzoyloxymethyl phenyl selenide \( 6 \), is isolated in 60% yield. When \( 5 \) is decomposed in alkyl selenides, mixed
substitution products are formed indicating that the rearrangement reaction is an intermolecular reaction (Eq. 6). After the initial heterolysis of 5 to form the ion pair, 7, the decomposition reaction is identical to the well known Pummerer rearrangement (Eq. 7).\textsuperscript{10}

\[
\begin{align*}
5 \rightarrow & \quad \text{Ph} \quad \text{Se}^+ \quad \text{CH}_3 \quad \text{OCPH} \quad \text{-OCPH} \quad \text{PhSe=CH}_2 \quad \text{PhSe-CH}_2^+ \rightarrow 6 \\
\text{CH}_3\text{SCH}_3 + \text{PhCOCPH} \rightarrow & \quad \text{CH}_3\text{S=CH}_2 + \rightarrow 3
\end{align*}
\]

The isolation of 5 in the selenium system indicates that the similar compound, 1b, can be formed in the sulfide system, but, as expected, the sulfur covalent intermediate is less stable than the selenium analogue, 5, and is not detectable under normal reaction conditions. However, in reactions similar to the BPO-Me\textsubscript{2}S reaction, tetracovalent sulfur intermediates have been identified. For example, Johnson and Rigau have shown that a tetracovalent sulfur compound is formed as an unstable intermediate in the reaction of tert-butyl hypochlorite with sulfides at low temperatures (Eq. 8).\textsuperscript{11} They observed that the mnr
spectrum of the product of the reaction of methyl phenyl sulfide with tert-butyl hypochlorite at -46° is similar to the spectrum of methylphenyl tert-butoxysulfonium fluoroborate except the chemical shifts are somewhat different (Table V-3). Since the chemical shift differences cannot be entirely accounted for by ion-pairing phenomena, the data strongly suggest that 8 is a true intermediate.

Martin and Arhart have actually synthesized two stable tetracovalent sulfur compounds 9 and 10. They reported that 10 decomposes slowly in an ether solution at room temperature. However, we expect that both 9 and 10 should be much more stable than 1b because 1b can undergo internal displacement (Eq. 9), or heterolyze to 1a which can also undergo displacement (Eq. 10) or rearrangement (Eq. 11). On the other hand, the alkoxy substituted compounds are stable to internal displacement, and because of the absence of β-hydrogen atoms, the heterolysis products do not easily decompose.
TABLE V-3
NMR Spectra of Intermediates in the Reaction of Methyl Sulfide with tert-Butyl Hypochlorite

δ values, ppm

<table>
<thead>
<tr>
<th>Compound</th>
<th>C₆H₅⁻</th>
<th>-SCH₃</th>
<th>-t-C₄H₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅SCH₃ BF</td>
<td>7.75 (3H, m)</td>
<td>3.42</td>
<td>1.54</td>
</tr>
<tr>
<td>C₆H₅SCH₃ Cl</td>
<td>7.70 (3H, m)</td>
<td>3.78</td>
<td>1.49</td>
</tr>
</tbody>
</table>

a. Table reproduced from Ref 11.
When Martin and Arhart studied the $^{19}$F nmr spectra of 9 and 10, they found that the singlet peak due to free $R_F^+$OH in the system becomes broader as the temperature is increased from $-60^\circ$. The broadening was attributed to rapid exchange between the alkoxy ligands and free alcohol. They also found that a similar exchange occurs with alkoxide ions, but the rate of exchange is much slower than for alcohols.
In view of the above evidence supporting a tetra-covalent sulfur intermediate in similar reactions, \( \sim l_b \) may be an intermediate of the BPO-sulfide reaction and not just a resonance structure. If \( \sim l_b \) is an intermediate, the reaction can be represented by Eq. 12 in which the ionic intermediate \( \sim l_a \) is in equilibrium with the covalent intermediate \( \sim l_b \). This equilibrium can be established in either of two ways; by the initial formation of \( \sim l_a \) which could rapidly form \( \sim l_b \) by cage recombination of the ion pair, or by the formation of \( \sim l_b \) which could rapidly heterolyze to \( \sim l_a \).

\[
\begin{align*}
\text{CH}_3\text{SCH}_3 + \text{PhCO}_2\text{Ph} & \rightleftharpoons \text{CH}_3\text{S}=\text{CH}_2 + \text{PhCO}_2\text{H} \\
l_a & \rightleftharpoons l_b
\end{align*}
\]
The reaction proceeds as follows. As the sulfide begins to bond to the α-oxygen, the β-oxygen acquires a partial negative charge, and the sulfur acquires a partial positive charge (11a). If the reaction follows a normal $S_N2$ pathway, then the charge development would increase; a benzoate ion would be displaced, and the ion pair $\text{la}^{\sim}$ would be formed. However, since the polar solvent effect on reactions that form ionic intermediates is much larger than it is in this reaction (Table V-2 and Figure V-1), we believe that $\text{la}^{\sim}$ may not be the initially formed intermediate. The small polar solvent effect can be explained by the covalent intermediate $\text{lb}^{\sim}$ which can be formed by a path that does not involve free ions. Instead of forming a free ion, the benzoate leaving group can be stabilized by interaction with the vacant d orbitals of the sulfur atom as represented by $\text{lb}^{\sim}$.

If this interaction is strong enough, the benzoate group becomes bonded to the sulfur atom to form the covalent intermediate $\text{lb}^{\sim}$. The path leading to $\text{lb}^{\sim}$ should have a smaller charge separation than the path leading to $\text{la}^{\sim}$, and therefore, should be less sensitive to solvent polarity. At the reaction temperature (40-100°), $\text{lb}^{\sim}$ should be very unstable and probably not detectable; after it is formed, it should rapidly heterolyze (not homolyze). Martin and Arhart observed no CIDNP or decolorization of galvinoxyl during the thermal
decomposition of $10^{12b}$ to $1a$ which then reacts according to Pryor and Bickley's mechanism.

The formation of covalent intermediates similar to $1b$ in $S_N^2$-like reactions is possible only for nucleophiles such as sulfur and phosphorous that can expand their valence shell to interact with the leaving group. Also, the reaction is more likely for leaving groups that may require extra stabilization to aid in O-O bond scission.

In the transformation of $11a$ to $1b$ through $11b$, the formation of the S-O bonds is not synchronous; bond formation to the $\alpha$-oxygen is always more advanced than bond formation to the $\beta$-oxygen. In fact, in some cases the leaving group and substrate may form an intimate ion pair which rapidly combines. The difference between the formation of an intimate ion pair and the formation of $1a$ is that in the intimate ion pair the leaving group is much more closely associated with the cation and does not escape from the solvent cage. We have included a reaction path through $11b$ to indicate that in some reactions the degree of charge separation is small and the leaving group does not become a free ion. The degree of charge separation and the degree of separation between the substrate and leaving group depends on the ability of the nucleophile to stabilize the leaving group and the need of the leaving group for such stabilization. This will be
illustrated in the next section by the reaction of phosphine with BPO and TBP.

The formation of DMSO and Bz₂O in the BPO-Me₂S₃ reaction provides some insight on the decomposition of the sulfonium salt, la. The benzoate counter ion in la can either abstract a proton from the sulfonium ion to form ylide 2 or it can react with the sulfonium ion in an S_N² displacement reaction to form DMSO and Bz₂O. Since the anhydride and DMSO are unstable together, their formation is reversible, and thus an equilibrium is established between la, and DMSO and Bz₂O as shown in Eq. 12. Because the stable reaction products are formed from the ylide, the final reaction products would indicate that the normal sulfide oxidation product, DMSO (normal refers to the oxidation of sulfide by hydrogen peroxide, hydroperoxides, or peroxy acids), la is not formed. However, this is not correct. As the reaction proceeds, la is consumed by ylide formation and the equilibrium in Eq. 12 is shifted towards la. Actually the initial product is the normal oxidation product; because of its instability under the reaction conditions, it is not isolated and the final product is a rearrangement product of the oxidation product.

2. Radical Production. Pryor and Bickley closely examined the BPO-sulfide reaction to discover if
radical production arises from a leakage of free radicals from an electron transfer reaction, or from homolysis of \( \text{lb} \), or from homolysis of the ylide 2. Analysis of data on the polymerization of styrene proves that the sulfide-assisted reaction was totally ionic; the only radicals produced were formed by homolysis of unreacted BPO. Due to possible inaccuracies in styrene polymerization experiments (see Appendix II) we used the free radical scavenger galvinoxyl to test for a radical component of the BPO-Me\(_2\)S reaction. We designed our experiment so that as little as 0.05% radical yield could have been detected; nevertheless, no radicals could be detected from the sulfide-assisted reaction.

B. The Phosphine-Peroxide Reaction

Alkyl- or arylphosphines rapidly reduce hydroperoxides, alkyl peroxides, acyl peroxides, and tert-butyl peroxyesters to the corresponding alcohols, ethers, anhydrides, and tert-butyl esters. In these bimolecular nucleophilic displacements, phosphines are oxidized to phosphine oxide. The reactions of acyl peroxides and tert-butyl peroxyesters appear to be closely related to the TBP-Me\(_2\)S reaction.

1. The Reaction of Phosphine with Benzoyl Peroxide.

Denny and co-workers have studied the reaction of triphenylphosphine with BPO which contained O\(^{18}\)-enriched carbonyl
oxygen atoms. After the reaction was completed, they found that the anhydride contained all of the excess \( ^{18}\text{O} \) with a distribution shown in Eq. 13. The equilibration

\[
\text{Ph}_3\text{P} + \text{PhCO-OCPh} \rightarrow \text{Ph}_3\text{P}-\text{OCPh} \rightarrow \text{Ph}_3\text{P}=\text{O} + \text{PhC-O-CPh}
\]

\[
\text{Ph}_3\text{P} + \text{PhCO-OCPh} \rightarrow \text{Ph}_3\text{P}=\text{O} + \text{PhC-O-CPh}
\]

of 1/2 of the \( ^{18}\text{O} \) between the \( \beta \) and \( \gamma \)-oxygen indicates that the anhydride is formed by the ion pair mechanism shown in Eq. 13. Furthermore, the \( ^{18}\text{O} \) distribution results prove that the anhydride is not formed from a pentacovalent phosphorous intermediate, 12 (see p. 133), because, as shown in Eq. 14, such an intermediate would produce \( ^{18}\text{O} \) enrichment in the \( \alpha \) and \( \gamma \)-oxygen atoms only (Eq. 14a). Also, if 12 could heterolyze, then the

\[
\text{Ph}_3\text{P} + \text{PhCO-OCPh} \rightarrow \text{Ph}_3\text{P}=\text{O} + \text{PhC-O-CPh}
\]

\[
\text{Ph}_3\text{P} + \text{PhCO-OCPh} \rightarrow \text{Ph}_3\text{P}=\text{O} + \text{PhC-O-CPh}
\]
covalent mechanism would predict that the phosphine oxide would contain excess O\textsuperscript{18} (Eq. 14b), which it does not.

Additional O\textsuperscript{18} labeling experiments were done to prove that the phosphine attacks the more electropositive peroxidic oxygen.\textsuperscript{5b} This experiment, involving various substituted BPO's, is presented in Eq. 15. When R is NO\textsubscript{2} and R' is CH\textsubscript{3}O,

\[
\text{R-C}_6\text{H}_4\text{-C-O-O-C-C}_6\text{H}_4\text{-R'} + (\text{C}_4\text{H}_9)_3\text{P} \rightarrow \text{R-C}_6\text{H}_4\text{-C-O-P(}\text{C}_4\text{H}_9)_3 \text{-O-C-C}_6\text{H}_4\text{-R'}
\]

\[
\text{R-C}_6\text{H}_4\text{-C-NH}_2 + \text{other amides} \quad \text{and acids}
\]

100% of the O\textsuperscript{18} is found in the NO\textsubscript{2}-substituted amide; and when R is NO\textsubscript{2} and R' is H, 95% of attack still occurs at the α-position. The results indicate that the anhydride 13 is formed by nucleophilic attack of the benzoate ion bearing the more electropositive group at the carbonyl carbon of the phosphonium intermediate. This implies that the less stable benzoate anion is the one initially displaced; this appears to be true because the more
electronegative group forces phosphine to attack the oxygen nearest it which is the most electrophilic. Thus the leaving group is determined by electronic effects in the ground state which is indicative of an early transition state.

2. The Reaction of Phosphine with tert-Butyl Peroxy-benzoate. Denny has also used O¹⁸ labeling experiments to determine the position of attack of phosphine on TBP.⁵c The results in Eq. 16 indicate that again the poorer leaving group is displaced. In this reaction 79% of the label remained in the carbonyl oxygen; the remaining amount was found in the oxygen of the tert-butoxy group. Because some of the carbonyl label is lost, the reaction mechanism is not exactly as shown in Eq. 16. In fact, other experimental results are not consistent with the production of a free tert-butoxy anion. For example, when the reaction was run in the presence of 1.0 M p-nitrobenzoate ion, tert-butyl p-nitrobenzoate was isolated in 8% yield. Also the polar solvent effect is not consistent with a charged intermediate. The slope of a graph of log k vs. E_T is only 7x10⁻², four times less than for the
reaction of aminophosphines with disulfides (Figure V-2).

To explain the above experimental results, Denny postulated a mechanism that involves displacement on the \( \beta \)-oxygen of the perester to form a pentacovalent phosphorous intermediate, 15. The formation of 15 in the TBP-phosphine reaction is analogous to the formation of 1b in the BPO-Me₂S reaction (Eq. 12). The formation of 15 can be explained as follows:

\[
\begin{align*}
\text{Phosphine attacks the more electropositive oxygen in an } S_N^2 \text{ reaction as shown by the investigation of the BPO-phosphine reaction.}^{5a,5b} \\
\text{However, in the TBP-phosphine reaction, as a partial charge develops on the } \alpha \text{-oxygen, it is stabilized by interaction with vacant } sp^3d \text{ orbital of the phosphorous atom. This interaction leads directly to 15. Pentacovalent phosphorous compounds similar to 15 are well known and have been studied in connection with the Berry pseudo-rotation.}^{15}
\end{align*}
\]

Denny suggested that the \( ^{18}\text{O} \) labeling results indicate that the products are formed by an internal displacement of 15 through a transition state shown in Eq. 17. This transition state involves some charge separation in that
there is partial positive charge development on the tert-butyl carbon and negative charge development on the $\beta$-oxygen. Notice that in Eq. 17 the $\alpha$-oxygen becomes the oxygen in the phosphine oxide.

\[
\begin{align*}
15 & \rightarrow R_3P\overset{\beta}{\beta}C(CH_3)_3 \rightarrow \text{PhCOOC(CH}_3)_3 + R_3P=O \\
\end{align*}
\]  

Denny favored the formation of 15 over the formation of the ion pair 14a for several reasons. First, when the reaction is run in ethanol, no ethyl benzoate is formed. This indicates that no free tert-butoxide is formed because if tert-butoxide were formed, it would rapidly react with ethanol to form ethoxide ions which would react with the phosphonium ion salt 14a to yield ethyl benzoate. Second, if tert-butyl benzoate were formed by tert-butoxide displacement on 14a, then no labeled oxygen would be incorporated into the tert-butoxy oxygen. The enrichment in the tert-butoxy oxygen is explained by the heterolysis of 15 to form the ion pair, 14b. Some scrambling of the labeled oxygen occurs before 14b recombines to 15, and the alkoxy oxygen becomes labeled (Eq. 18). Support for the formation of 14b is provided by the isolation of an 8% yield of tert-butyl p-nitrobenzoate when the reaction is run in a 1.0 M solution of
p-nitrobenzoate anion. Third, the relatively small polar solvent effect (Figure V-1) indicates that charged intermediates are not the initial products as shown in Eq. 16.

If we could synthesize TBP with $^{18}$O enrichment in the $\alpha$-oxygen, we could easily determine whether $^{14}$a or $^{15}$ is the intermediate that forms the ester. As shown in Eq. 19, the covalent intermediate would produce labeled phosphine oxide, and the ionic intermediate would produce labeled ester. Probably Denny has not done this experiment because of the difficulty in synthesizing the necessary labeled TBP.

\[ R_3P-OCPh \rightarrow R_3P=O^{18} + PhCO-Bu-t \]  
\[ R_3P + PhCO^{18}Bu-t \rightarrow R_3P=O + PhCO-Bu-t \]
Covalent products lb and 15 are the initial intermediates in the reaction of BPO with Me₂S and TBP with phosphine, but reactions of this type do not always react through a covalent intermediate. For example, Denny has shown conclusively that the BPO-phosphine reaction decomposes through ion pairs and not through a covalent intermediate (page 130). The ion pair that is formed is not the more stable one that would result from heterolysis of an initially formed covalent intermediate, and therefore, the ion pair must be the initially formed intermediate. It would be very interesting to determine the solvent effect on this reaction. If Denny is right, the effect of solvent on the rate of the BPO-phosphine reaction should be quite large. Another example of a nucleophilic displacement that involves ion pairs is the reaction of sulfide and tert-butyl hypochlorite. Although the data are not exact, this reaction is very sensitive to a change in solvent polarity. For example, the reaction is approximately 240 times faster in acetonitrile than in cyclohexane and is thus only about half as sensitive to change in solvent polarity as is the reaction of aminophosphines with disulfides. However, the sensitivity is more than three times larger than the sensitivity of the disulfide-BPO reaction. Therefore, the displacement on tert-butyl hypochlorite involves more charge separation than does displacement on BPO. This is because chloride
ion is a better leaving group than benzoate ion, and thus
the formation of a covalent intermediate is less important
in its reaction than in the reaction of BPO.

The above discussion demonstrates that some nucleo-
phile-peroxide reactions involve ion pairs while similar
reactions do not. We suggest that a covalent intermediate
is formed when additional stabilization is needed to
assist oxygen-oxygen bond scission. The internal
stabilization by the nucleophile is similar to the
stabilization necessary in the sulfide-hydroperoxide re-
action. This reaction is more dependent on the hydrogen
donating ability of the solvent than the solvent polarity
and in aprotic solvents the reaction is second order in
hydroperoxide. Edwards has suggested that this dependence
on hydrogen bonding is due to hydrogen bonding in the
transition state (Eq. 20). Just as a hydrogen to oxygen

\[
R_2S + ROOH \rightarrow R_2SO + AH + ROH \quad (20)
\]

bond is needed to facilitate this reaction, a nucleophile
to oxygen bond is needed to facilitate some nucleophile-
peroxide reactions. Thus reactions in which insertion
products are formed are closely related to the sulfide-
hydroperoxide reaction; both reactions need extra stabiliza-
tion of the leaving group in order to break the
oxygen-oxygen bond. In one reaction the stabilization is internal and in the other it is external. Therefore, we expect covalent intermediates to occur when the nucleophile is rather weak and/or the leaving group is rather poor. Thus the reaction of phosphine with BPO is ionic while the reaction with TBP, which has the poorer tert-butoxide leaving group, is covalent.

C. A General $S_N2$ Mechanism

Scheme V-2 presents a general mechanism for nucleophilic displacements on peroxides. The usual mechanism that applies to most peroxide-nucleophile reactions is the initial formation of 18 followed by product formation by Eq. 21a. However, for the reactions of acyl peroxides or peresters with nucleophiles that can expand their number of covalent bonds, 18 can undergo ligand exchange via 19 and form mixed products by Eq. 21c. In some cases, the covalent intermediate, 19, may be formed by a covalent pathway through 17 and decompose via transition state 21 to products (Eq. 21b).

Much of Scheme V-2 has already been discussed. For example, the BPO-phosphine reaction forms 18 which decomposes by Eq. 21a (p. 130), and the TBP-phosphine reaction forms 19 which decomposes mostly by Eq. 21b, but does undergo some exchange via Eq. 21c (p. 135).

Actual proof for decomposition of 19 to 20 has not been presented; however, exchange experiments with sulfonium
Scheme V-2

A General Mechanism for the $S_N2$ Reaction of Nucleophiles with Peroxides

\[ \text{Nu} + \text{ROOR} \rightarrow \text{Nu-OR} + \text{Nu} \]

\[ \text{Nu} \rightarrow \text{Nu-OR} + \text{Nu-OR} \]

\[ \text{Nu-OR} + \text{R} \rightarrow \text{Nu-OR} + \text{Nu} \]

\[ \text{Nu} \rightarrow \text{Nu-OR} + \text{Nu-OR} \]

\[ \text{Nu-OR} + \text{HOR}'' \rightarrow \text{Nu-OR} + \text{R'OR}'' \]

\[ \text{R} = \text{RC}-, \text{R}, \text{H} \]

\[ \text{R'} = \text{RC}-, \text{R}, \text{H} \]
salts indicate that compounds similar to \(^\sim 18\) rapidly form compounds similar to \(^\sim 20\).\(^{10b}\) Since \(^\sim 19\) is the probable intermediate in the conversion of \(^\sim 18\) to \(^\sim 20\), the sulfonium salt experiments indicate that the conversion of \(^\sim 19\) to \(^\sim 20\) must be possible. Further evidence for this reaction is presented in the discussion of the TBP-Me\(_2\)S reaction on pages 145-146.

Since Scheme V-2 represents a generalized mechanism, one specialized but very important reaction is not included. It occurs for nucleophiles, such as methyl sulfide, which have \(\beta\)-hydrogen atoms. With these nucleophiles, ylides can be formed from \(^\sim 18\) or \(^\sim 20\), when the \(\beta\)-hydrogen is abstracted by RO\(^-\) or R'O\(^-\) (Eq. 22).\(^{10}\) Equation 22 shows this reaction for \(^\sim 18\).

\[
\begin{align*}
\text{R} & \quad \text{OR} \\
\text{Nu} \quad \rightarrow \quad \text{R-Nu-CH}_2 & + \text{HOR}' \rightarrow \text{R-Nu-CH}_2\text{-OR}'
\end{align*}
\]

We now have a generalized mechanism that can be used to predict what we might expect for the nucleophilic displacement of Me\(_2\)S on TBP. If this hypothetical mechanism agrees with all of the experimental facts, then we can assume that the TBP-Me\(_2\)S reaction is a nucleophilic displacement.
D. An $S_N^2$ Mechanism for the Methyl Sulfide-tert-Butyl Peroxybenzoate Reaction

Scheme V-3 presents the $S_N^2$ mechanism for the TBP-Me$_2$S reaction that is predicted by the general $S_N^2$ mechanism given in Scheme V-2. The following discussion shows that Scheme V-3 can account for nearly all of our experimental results.

Eq. 23. We believe that the TBP-phosphine reaction should be very similar to the TBP-phosphine reaction; i.e., both reactions have poor leaving groups and therefore, should form a covalent intermediate. Just as in nucleophilic displacement by phosphine, methyl sulfide would attack the more electro-positive α-oxygen to yield a covalent intermediate (23a). This is indicated by the effect of substituents in the perester aryl-group which is practically the same for the reaction of TBP with sulfide ($\rho = +1.3$) or with phosphine ($\rho = +1.24$),$^5c$ and by the effect of substituents in the sulfide aryl-group of MeSAr which is nearly the same for the reaction of TBP ($\rho = -1.7$) or BPO ($\rho = -1.3$) with sulfide. The polar solvent effect on the reaction rate of TBP with Me$_2$S (the slope of the plot of log $k$ vs. $E_T$ in Figure II-1 is $0.7 \times 10^{-2}$) is very small. However, this small effect is consistent with other nucleophilic displacements on peroxides in which a covalent intermediate is the initial product (see pp. 116).
Scheme V-3

An $S_N 2$ Mechanism for the Methyl Sulfide-TBP Reaction

\[
\begin{align*}
\text{CH}_3\text{SCH}_3 + \text{PhCOOBu-t} & \rightarrow \text{CH}_3\text{S=CH}_2 + \text{PhCO}_2\text{H} \\
& \quad + \text{HOBu-t} \\
\text{CH}_3\text{SCH}_3 + \text{PhCOOBu-t} & \rightarrow \text{CH}_3\text{SCH}_2\text{OCPh} (26a)
\end{align*}
\]
23b → CH₃SCH₃ + PhCOBu-t

(26b)

23c → CH₃SCH₃ + PhCOBu-t

(26c)
According to Scheme V-2, after the covalent intermediate 19 is formed, it can heterolyze to ion pairs 18 or 20, or decompose through transition state 21 (Eq. 21b). In the TBP-phosphine reaction, the pentacovalent phosphorous intermediate 15 decomposes by Eq. 21b to form phosphine oxide and tert-butyl benzoate. However, in the TBP-Me$_2$S reaction, the analogous products, DMSO and tert-butyl benzoate, are not formed indicating that the tetracovalent sulfur intermediate 23a must be less stable than 15 and must rapidly heterolyze before an internal nucleophilic displacement can occur. A homolytic decomposition of 23a is not considered because the closely related sulfur tetracovalent intermediate, 1b, formed in the BPO-Me$_2$S reaction does not produce radicals. Although the heterolysis product 23c should be more stable than 23b, both ion pairs may be formed as shown by the formation of the corresponding ion pairs 18 and 20 in Scheme V-2. Therefore, we have included the formation of both ion pair 23b and 23c, and since their formation is reversible, they probably exist in equilibrium with each other and with 23a.

Eq. 24. Intermediate 23b can decompose by the Pummerer reaction; the strongly basic tert-butoxide anion would abstract a proton from the sulfonium ion to form the benzoyloxy ylide 24. Once 24 is formed, it heterolyzes to a benzoate ion and a sulfur-stabilized carbonium ion 25 which combine to form BOMS. Because carbon dioxide was
not detected as reaction product from reactions of acyloxy-
sulfonium salts, Johnson and Phillips excluded the possi-
bility of homolysis of 23b.\textsuperscript{10a}

\textbf{Eq. 25.} If 23c is an intermediate, it could be ex-
pected to abstract a proton from the sulfonium ion to form
the \textit{tert}-butoxysulfonium ylide 26. However, this is a
relatively slow reaction as shown by the formation of DMSO
and \textit{Bz}_2O from the reaction of benzoate anion with
benzoyloxysulfonium salt (see p. 120). The proton abstrac-
tion is sluggish and benzoate reacts by another pathway
when feasible. The most likely fate of 23c may well be
ligand exchange to form 23b. The following reactions
illustrate the propensity of sulfonium salts to exchange
ligands. These reactions also provide evidence for the
conversion of 19 to 20 in Scheme V-2.

Eqs. 27-28 show that the exchange between alkoxide
ions and alkoxyxsulfonium salts does occur, and Eqs. 29-30
show that similar exchanges occur between these salts and
acetate anions.\textsuperscript{10b} In Eq. 30 when the sulfonium salt was

\[
\begin{align*}
\text{ArSCH}_2\text{CH}_3\text{BF}_4^- & \quad \text{OCH}_3^- \\
+ Arn'\text{SCH}_2\text{CH}_3\text{BF}_4^- & \quad \text{acetone} \\
\text{2,6-lutidine} & \\
onumber
1389\text{cpm/mol}
\end{align*}
\]

\[
\begin{align*}
\text{ArSCH}_2\text{CH}_3 + Arn'\text{SCH}_2\text{CH}_3 + \text{ArSCHCH}_3 + Arn'\text{SCHCH}_3 \\
999\text{cpm/mol} & \quad 423\text{cpm/mol} \\
\text{Ar} = \text{C}_6\text{H}_5; Arn' = p-\text{CH}_3\text{C}_6\text{H}_4
\end{align*}
\]
less than 1% of original activity in formaldehyde

$$\text{CH}_3\text{SCH}_2\text{BF}_4^- + \text{CH}_3\text{O}^- \rightarrow \text{HCH} + \text{CH}_3\text{SCH}_3$$  \hspace{1cm} (28)

$$\text{OCH}_3^- \text{CH}_3\text{SCH}_2\text{BF}_4^- \xrightarrow{\text{NaOCCCH}_3} \begin{aligned} \text{OCH}_3^- \text{CH}_3\text{SCH}_3 \rightarrow \end{aligned} \text{CH}_3\text{SCH}_2\text{OCCH}_3$$  \hspace{1cm} (29)

$$\begin{aligned} \text{OCH}_3^- \text{(CH}_3)_2\text{CHSCH}_2\text{BF}_4^- \xrightarrow{\text{DMSO}} \text{(CH}_3)_2\text{CHSCH}_2\text{OCCH}_3 \end{aligned}$$

$$\text{(CH}_3)_2\text{CHSCH}_2\text{OCH}_3 + \text{(CH}_3)_2\text{CHSCH}_3 \hspace{1cm} (30)$$

27 20% 6%

treated with a non-exchanging base such as sodium hydride, no rearrangement product 27 was obtained, thus proving that 27 must be formed by displacement on an acyloxy-sulfonium intermediate by free methoxide which is liberated in the exchange reaction.

The preceding reactions indicate that 23b and 23c, which are formed in a solvent cage, can be in an equilibrium mixture. Intermediate 23c either reacts by Eq. 25 or
exchanges to form 23b which reacts via Eq. 24. Johnson and Phillips have shown that ylide 26 reacts by internal proton abstraction to yield isobutylene and DMSO. When dimethylmethoxysulfonium fluoroborate was decomposed in the presence of potassium tert-butoxide, isobutylene and DMSO were isolated (Eq. 31). The absence of DMSO as a product in our reaction excludes the formation of 26. Although 26 is not formed, it is possible that 23c is present, but that it undergoes exchange to form 23b faster than the benzoate anion abstracts a proton from the tert-butoxysulfonium ion.

In summary, 23a is probably the initially formed intermediate but it is very unstable and rapidly heterolyses to 23b and 23c. Because of facile ligand exchange in sulfonium salts, these two intermediates are in equilibrium. Benzoate anion is a weaker base than tert-butoxide and abstracts a proton from the sulfonium salt at a much slower rate than does tert-butoxide, and thus the major decomposition path would be through ylide 24, which is formed by

\[
\begin{align*}
\text{OCH}_3 & \quad \text{OBu-t} \\
\text{CH}_3\text{SCH}_3\text{BF}_4^- + \text{OBu-t} & \rightarrow \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{S}=\text{CH}_2 \\
\text{CH}_3\text{C}=\text{CH}_2 + \text{CH}_3\text{SCH}_3 & \\
\end{align*}
\]  

(31)
proton abstraction by tert-butoxide and not through ylide 26, which is formed by proton abstraction by benzoate.

As 23b decomposes the equilibrium is shifted away from 23c and benzoate exchanges instead of abstracting a proton. Thus all of the product is formed by Eq. 24. Unlike the TBP-phosphine reaction in which Nu-O is formed by an internal nucleophilic displacement (Eq. 17), 23a is not as stable as 15 and heterolyses before a cyclic decomposition can occur.

**Eq. 26.** In the general $S_{N2}$ mechanism (Scheme V-2) a major reaction product is oxygen transfer to nucleophile (Nu-O). The absence of DMSO as a product of the TBP-Me$_2$S reaction is an important discrepancy between what the $S_{N2}$ mechanism predicts and what we actually observe. If the TBP-Me$_2$S reaction follows the same course as the reaction of TBP with triphenyl phosphine, then Eq. 26a should represent the major reaction pathway. Probably Eq. 26a does not occur because 23a is not as stable as 15, and heterolyses before a cyclic decomposition can occur.

Eq. 26b would appear to be a possible reaction. In the BPO-Me$_2$S reaction DMSO is formed by a nucleophilic displacement of a benzoate ion on the sulfonium ion of 23b. Evidently a similar reaction does not occur for a tert-butoxide nucleophile because tert-butoxide is a much stronger base and poorer nucleophile than is benzoate, and therefore, the favored mode of decomposition of 23b
is proton abstraction by tert-butoxide (Eq. 24) rather than nucleophilic displacement by tert-butoxide (Eq. 26b).

Eq. 26c would not be expected to be a facile reaction; the more favored point of attack of the benzoate would be the attack at the sulfur atom to displace tert-butoxide rather than attack at the tert-butyl carbon atom to displace sulfoxide.

Thus the absence of DMSO as a reaction product can be explained, and Scheme V-3 can account for all of the experimental results of the TBP-Me₂S reaction except for radical production. We have found that 2.3±1.5% of this reaction produces scavengeable free radicals. Therefore, we are faced with the same problem that investigators encountered in their work on the BPO-DMA reaction: Are the radicals a subsequent product of a nucleophilic displacement, or are the radicals a product of an entirely different mechanism? We believe that the second case is correct, but to prove this we must say that the reaction mechanism in Scheme 3 cannot possibly account for the radical formation that we observe. In the following section we will discuss the three possible sources of radical production in the nucleophilic displacement reaction and show that they are not responsible for the rate of radical production that we observe.
E. Possible Sources of Radical Production in the $S_{N2}$ Mechanism

1. Ylide Homolysis. Alkylsulfonium ylides decompose by a radical path. Baldwin et al. have used chemically induced dynamic nuclear polarization (CIDNP) to show that free radicals are produced in the decomposition of the stable ylide $28$ (Eq. 32). Isotopic labeling demonstrated that $18\pm6\%$ of the radicals escape from the solvent cage. Similar results have been obtained by Schollkopf et al. at $90^\circ$. Although these results are for alkylsulfonium ylides, they suggest that radical production in our reaction may be due to a homolysis of ylides $24$ or $26$.

Ylide homolysis in our system can be easily discounted. First, ylide $24$ is present in the reaction of BPO with Me$_2$S and in the reaction of Bz$_2$O with DMSO. Since radical production has not been observed in these reactions, $24$ does not homolyze. While it is possible that ylide $26$ may homolyze, the failure to observe reaction products from it excludes its presence in the reaction mixture, and therefore, excludes radical production from its homolysis.
2. **Sulfonium Salt Homolysis.** Perhaps the strongest argument against Horner's electron transfer mechanism for the BPO-DMA reaction is that Walling has suggested that the source of radicals in that reaction is the homolysis of an acyloxyammonium salt (29), which is the expected product of nucleophilic displacement (see p. 86).\(^{20}\) Compounds of this type have been shown to initiate vinyl polymerization; for example, at 80° \(^{30}\) initiates polymerization at a rate four times slower than BPO initiates polymerization.\(^{21}\) While the rate of initiation is too slow to account for the high rate of radical production in the BPO-DMA reaction, the rate of radical production in the TBP-Me\(_2\)S reaction is much slower and perhaps can be explained by the homolysis of a sulfonium salt, formed in an \(S_N^2\) reaction.

\[
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{Ph-N-O-CPh} \\
\text{CH}_3
\end{array} \right] + \begin{array}{c}
\text{CH}_3 \\
\text{N}
\end{array}
\]

The major sulfonium salt present in Scheme V-3 is 23b. Again because of a lack of radical production in the BPO-Me\(_2\)S reaction, which proceeds through the similar sulfonium salt 1a, homolysis of 23b can be excluded as a
radical source. However, 23c may be present and homolysis of this compound cannot be dismissed without further investigation.

Torssell has examined the thermal decomposition of alkoxydimethylsulfonium salts; the decomposition of isobutoxydimethylsulfonium tetraphenylborate (31), shown in Eq. 33, is a representative reaction. Torssell reported that in DMSO 31 is 20% decomposed after two hours at 65° and completely decomposed after 15 minutes at 100°. These data predict that 31 will have a half-life of approximately 50 minutes at 80°; 23c should have a similar half-life were base not present. However, decomposition of alkoxy sulfonium salts is greatly accelerated by bases; for example, the addition of a small amount of triethyl amine to a solution of 31 caused an almost instantaneous disappearance of 31. Since 23c is formed in intimate contact with a base it must have a very short half-life and probably would not have the opportunity to homolyze. However, since the fraction of the TBP-Me₂S reaction that produces radicals is so small, it is possible that a small amount of
homolysis from 23c could account for the radicals which are formed.

To unequivocally rule out radical production by homolysis of 23c, we synthesized methoxydimethylsulfonium tetraphenylborate, 32, and measured the rate at which it initiates styrene polymerization. The sulfonium ion in our system is tert-butoxydimethylsulfonium, but the rate of S-O bond homolysis of this ion and 32 should be similar. At 80° in a 4.3 M styrene solution in acetonitrile, 32 initiates styrene polymerization at a rate 6 times slower than TBP initiates polymerization. In the TBP-Me₂S initiated styrene polymerizations, the reaction is followed to less than 10% conversion, and therefore, even if the tert-butoxysulfonium salt were the only product, it would never amount to more than 10% of the concentration of TBP and would produce radicals at a rate 60 times slower than TBP. Since the rate of radical production by TBP-Me₂S reaction is approximately 3 times slower than production by TBP homolysis (Table II-13), radical production by 33 is extremely slow and makes no contribution to radical production in this reaction.
3. **Electron Transfer from tert-Butoxide to TBP.**

Potassium tert-butoxide reacts with BPO to form free radicals.\(^{23}\) When Shapiro et al. used tert-butyl nitrone to trap the radicals formed in this reaction, they observed a large nitroxyl ESR signal after the addition of tert-butoxide to BPO. They suggested that this signal, which is sharply increased by heat or u.v. irradiation, is due to an electron transfer reaction between tert-butoxide and BPO.

In order to demonstrate that a similar reaction between tert-butoxide and TBP is not the source of radicals in our predicted S\(_N\)\(_2\) mechanism, we measured the rate of radical production in the presence of added benzoic acid. Benzoic acid will neutralize any tert-butoxide that is present and will prevent the occurrence of the possible electron transfer reaction between tert-butoxide and TBP. The benzoate ions formed upon neutralization do not undergo an electron transfer reaction as shown by the fact that radical production is not observed in the BPO-Me\(_2\)S reaction where both BPO and benzoate anions are together. The addition of 0.1 M benzoic acid did not affect the rate of radical production. Thus the source of radicals cannot be attributed to an electron transfer reaction between tert-butoxide ions and TBP.

The S\(_N\)\(_2\) mechanism presented in Scheme V-3 is consistent with reaction products, solvent effect, and \(p\)-values,
but it cannot explain the 2% of the reaction that produces scavengerable free radicals. However, the electron transfer mechanism postulated to explain the results of the BPO-DMA reaction (Scheme IV-3) can also explain all of the experimental results of the TBP-\text{Me}_2\text{S} reaction including radical production.
F. References Chapter V


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VI. AN ELECTRON TRANSFER MECHANISM FOR THE REACTION OF TERT-BUTYL PEROXYBENZOATE WITH METHYL SULFIDE

Chapters IV and V have shown that nucleophiles can react with peroxides by an electron transfer or by a nucleophilic displacement. We propose that a distinguishing characteristic of these reactions is that the radical ion products of the ET reaction form scavengerable neutral free radicals. The observation of free radical production in a peroxide-nucleophile interaction is evidence of an ET reaction. Since we have demonstrated that the radical production by the TBP-Me$_2$S reaction cannot be explained by subsequent reactions of a nucleophilic displacement, we suggest that the TBP-Me$_2$S reaction is an electron transfer reaction, and, therefore, more closely related to the reaction of BPO with DMA than to the reaction of BPO with Me$_2$S. In the following discussion we present an electron transfer mechanism for the TBP-Me$_2$S reaction that is based in a large part on the BPO-DMA reaction mechanism in Scheme IV-2.

A. Examples of Electron Transfer Reactions

Many reactions of good electron donors with good electron acceptors involve electron transfer from the donor to the acceptor. Donors may be anions or neutral species while acceptors may be cations but usually are neutral molecules. Because the products of electron
transfer (ET) reactions often resemble those of nucleophilic displacements, it may be difficult to distinguish the two reactions by product analysis alone. For example, the reaction in Eq. 1 produces normal displacement products:

\[
\text{Ph}_3\text{C}^+\text{ClO}_4^- + \text{t-BuOK} \rightarrow \text{Ph}_3\text{C}^- + \text{t-BuO}^- + \text{KClO}_4 + \text{Ph}_3\text{COBu-t} 
\]

(1)

however, because ESR signals of the triphenyl methyl radical were detected during the reaction, Bilevitch et al. concluded that the reaction follows an ET pathway.\(^2\)

Amines and carbanions, which are isoelectronic, are both nucleophiles and good electron donors. Therefore, many ET reactions have been observed with these compounds.\(^3\) For example, amines enter into ET reactions with carbon tetrachloride\(^4\) and chlorine dioxide.\(^5\)

Peroxides are electron deficient and can be expected to act as acceptors in some reactions. In 1963, Tokumaru and Simamura postulated that induced decomposition of BPO by alkyl radicals involves an ET reaction (Eq. 2).\(^6\)

\[
[P] \quad [R^- \text{O-OP}'] \rightarrow [R^+ \text{O-OP}'] \rightarrow [R^- \text{O-OP}'] 
\]

(2)

Supporting evidence for this mechanism is that radical reactivity correlates with the electron donating ability of
the radical. Additional evidence for Eq. 2 is that the effects of substituents in the phenyl ring of BPO are identical for the reaction of BPO with DMA and for the induced decomposition of BPO by polystyryl radicals. Since the BPO-DMA system probably reacts by an electron transfer, the identical substituent effects for the two reactions strongly suggest that the induced decomposition is also an electron transfer reaction.

Tokumaru and Simamura attributed the electron accepting ability of peroxides to the low-lying vacant antibonding orbital, \( 2p_{\sigma_u} \), around the oxygen-to-oxygen bond. Because amines have relatively low ionization potentials, it is not surprising that they undergo electron transfer reactions with peroxides. However, Tokumaru and Simamura have suggested that in addition to amines, many other peroxide-nucleophile reactions can be thought of as of the electron transfer type.

Recently other ET reactions involving peroxides have been discovered. Chalfont and Perkins have studied the reaction of diphenylhydroxylamine with BPO and have suggested two possible mechanisms, an ET (Eq. 3) and an \( S_{\text{N}2} \) (Eq. 4). The authors point out the difficulties

\[
\text{Ph}_2\text{NOH} + \text{BPO} \rightarrow [\text{Ph}_2\text{NOH} + \text{BPO}^+] \rightarrow \text{PhNO}^- + \text{PhCO}_2\text{H} + \text{PhCO}_2^-. \tag{3}
\]
involved in determining whether Eq. 3 or 4 actually represent the facts; in fact, they are not able to produce hard evidence to support a decision, but rather, based on analogies to other reactions; suggest an ET mechanism.

The reaction between alkyllithium compounds or Grignard reagents and peroxides was once thought to be a nucleophilic displacement reaction, but now Kochi and co-workers have shown that some of these reactions involve free radicals. The effects of scavengers and solvent viscosity on product formation indicate that the electron transfer mechanism shown in Eq. 5 is occurring.

EtLi + BuOOBu → [Et· Li+ BuOOBu·] + [Et·, BuO·] + LiOBu
↓ Products

(5)
B. The Electron Transfer Mechanism

The above examples provide ample precedent for a possible electron transfer from Me₂S to TBP. Although Me₂S is a poorer electron donor than DMA, and TBP is a poorer electron acceptor than BPO, we would expect to observe an electron transfer reaction between Me₂S and TBP if no interfering reaction occurs. Such a reaction would be very similar to the BPO-DMA reaction. Scheme VI-1 presents an electron transfer mechanism for the reaction of TBP with Me₂S.

Eq. 6. Many examples are known of electron transfer reactions that bear similarity to the TBP-Me₂S reaction.¹⁰⁰,¹⁰⁰

Eq. 11 presents a general reaction mechanism for the interaction of an electron donor (D) and an electron acceptor (A). When a good donor and acceptor pair are mixed, a charge transfer (CT) complex is formed almost instantaneously.¹⁰ The formation of the complex is reversible, and the equilibrium constant (Kₐ) depends on the ionization potential of the donor and the electron affinity of the acceptor.¹⁰,³ The CT complex is represented as resonance structure that consists of contributions from a non-bonded ground state and a polar excited state. According to Mulliken, in terms of quantum
Scheme VI-1

An Electron Transfer Mechanism
for the Methyl Sulfide-TBP Reaction

\[ \text{CH}_3\text{SCH}_3 + \text{TBP} \rightarrow \text{CH}_3\text{S}^+ + \text{TBP}^- \]

1. \[ \text{CH}_3\text{S}^+ + \text{PhCO}_2^- \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ \]

2. \[ \text{CH}_3\text{S}^+ + \text{PhCO}_2^- \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuO}^- \]

3. \[ \text{CH}_3\text{S}^+ + \text{PhCO}_2^- \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuO}^- \]

4. \[ \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuOH} \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ \rightarrow \text{BOMS} \]

5. \[ \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuOH} \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ \rightarrow \text{BOMS} \]

6. \[ \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuOH} \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ \rightarrow \text{BOMS} \]

7. \[ \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuOH} \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ \rightarrow \text{BOMS} \]

8. \[ \text{CH}_3\text{S}^-\text{CH}_2^+ + \text{t-BuOH} \rightarrow \text{CH}_3\text{S}^-\text{CH}_2^+ \rightarrow \text{BOMS} \]
\[ \text{CH}_3\text{SCH}_2\text{OCPh} \xrightarrow{\text{+CH}_2\text{HOBu-t}} \text{CH}_3\text{SCH}_2\text{OBu-t} \]

(9)

\[ \text{CH}_3\text{SCH}_2\text{OBu-t} \xrightarrow{\text{HOCPh}} \text{CH}_3\text{SCH}_2\text{OBu-t} \]

(10)
mechanics the ground state, $\psi_0(DA)$, and the excited state, $\psi_1(D^+A^-)$, interact to form a stabilized ground state having a wave function, $\psi'_0$, given by Eq. 12 and an excited state, $\psi'_1$ given by Eq. 13. The coefficients $\lambda$ and $\mu$ generally

$$\psi'_0 = \psi_0(DA) + \lambda \psi_1(D^+A^-)$$ \hspace{1cm} (12)

$$\psi'_1 = \psi_1(D^+A^-) - \mu \psi_0(DA)$$ \hspace{1cm} (13)

are much smaller than unity and thus the excited state makes only a minor contribution to the ground state of the CT complex. Therefore, while the position of the CT absorption band depends on substituents in both the donor and acceptor, it is affected very little by solvent polarity.

The actual formation of radical-anions may be induced by thermal or photochemical excitation. Since $k_d$ is usually slower than the rate of formation of the CT complex, it is the rate determining step, and thus the rate of formation of charged species show very marked dependence on solvent polarity. For example, in CCl$_4$ the tetraphenylenediamine-chloranil system has an optical absorption attributed to the CT complex, but in acetonitrile, it has absorption attributed to radical-ions. The addition of non-polar solvents to the acetonitrile solution causes the CT absorbance to reappear, thus
indicating that the formation of the radical-ions is reversible.\textsuperscript{14} An even more dramatic example of a solvent effect is provided by the effect of solvent polarity on the rate of disappearance of the blue CT complex formed from \( p \)-methoxystyrene and tetracyanoethylene. In cyclohexane more than \( 2.6 \times 10^6 \) sec is required for the disappearance of the blue color, but in formic acid the color is gone after only 12 sec.\textsuperscript{15} In summary, the typical electron transfer reaction in Eq. 11 involves rapid complex formation followed by a slower electron transfer.

In our system, we are concerned with the type of electron transfer reactions that Kosower has categorized as T-class (or thermal) electron transfer reactions.\textsuperscript{1c} Kosower described three types of T-class reactions: slow electron transfer, fast electron transfer, and spontaneous electron transfer. The relative rate of electron transfer depends on the relative energy difference between the CT complex and the radical-ion pair; spontaneous electron transfer can occur when the potential energy of the ion pair is less than the potential energy of the CT complex \( (E_D^+ + A^- < E_{DA}) \). Since the ionization potential of \( \text{Me}_2\text{S} \) is considerably larger than that of DMA (8.68 eV compared to 7.14 eV)\textsuperscript{16} and since TBP is a poorer electron acceptor than tetracyanoethylene or some other commonly used acceptor, the \( \text{Me}_2\text{S}-\text{TBP} \) reaction is not a typical electron transfer reaction in which a CT complex precedes a rate
limiting electron transfer.\textsuperscript{1c} We suggest that due to its lack of stability the Me\textsubscript{2}S-TBP CT complex represents an energy maximum; once formed, the complex undergoes spontaneous electron transfer. Therefore, the transition state of the Me\textsubscript{2}S-TBP reaction resembles a charge transfer complex. This results in a very early transition state with very little charge separation. This lack of charge separation is supported by the insensitivity of this reaction to a change in solvent polarity (Table II-2).

The effect of substituents on the reaction rate supports an early transition state. In the gas phase the substituent effect on the ionization potential of substituted benzyl radicals fits the Hammett equation with a $\rho$-value of $-19.1$.\textsuperscript{17} In solution, $S\textsubscript{N}\textsubscript{1}$ reactions have large negative $\rho$-values; for solvolysis of triphenylmethyl chloride $\rho= -4.5$.\textsuperscript{18} The half-wave potential for substituted BPO's follows the Hammett equation for electron withdrawing groups with $\approx +4.2$.\textsuperscript{19} The smaller $\rho$-value of $+1.31$ observed in the TBP-Me\textsubscript{2}S reaction and in the BPO-DMA reaction ($\rho= +1.6$) indicates little charge separation in the transition state.

The products of the electron transfer reaction are the methyl sulfide cation radical (2a) and the TBP radical-anion (2b). Bond scission of the oxygen-oxygen bond is not synchronous with electron transfer and the bond is not broken until after the transition state has been passed. The radical-anion of tert-butyl peroxide has been observed
at low temperature during radiolysis of tert-butyl peroxide\textsuperscript{20}; however, at 80° the TBP radical-anion is very unstable and rapidly undergoes bond scission to form intermediate 3. From our work it is not possible to determine whether the TBP radical-anion undergoes bond scission by Eq. 14 or by Eq. 15. Since the fraction of the 

\[
\begin{align*}
\text{PhCO}^- + \cdot\text{OBu-t} & \quad \text{(14)} \\
\text{PhCO}^+ + \cdot\text{OBu-t} & \quad \text{(15)}
\end{align*}
\]

reaction which involves radicals is very small, it is not possible to determine which equation is operating. The results of Martin for the decomposition of \(\alpha\)-sulfide-substituted TBP (12) indicates that the predominately formed radical is the \textit{tert}-butoxy radical.\textsuperscript{21} \textit{A priori}, based on energetic arguments, we would expect benzoate ion to be formed in preference to \textit{tert}-butoxide ion. For this reason and to be consistent with Martin, we have chosen to use Eq. 14; however, Appendix 3 shows that the use of Eq. 15 will produce identical results.
In summary, we believe that the electron transfer reaction between \( \text{Me}_2\text{S} \) and TBP is similar to other electron transfer reactions except that the \( \text{Me}_2\text{S}-\text{TBP} \) CT complex, (1) due to its lack of stability, serves as the transition state of rather than the precursor to the electron transfer. After the transition state, the TBP radical-anion (2b) immediately decomposes to a benzoate anion and a tert-butoxy radical which along with the methyl sulfide cation-radical are contained in a solvent cage in close proximity to one another (3). The first reaction intermediate is then represented by 3.

Eq. 7. The components of 3 may diffuse apart to form radicals and ions, or they may combine or react with each other as shown in Eqs. 8-10. The relative importance of the subsequent paths will be solvent dependent, but as the discussion of solvent effects on radical production in Chapter VII points out, the effects are not well understood and depend on many variables other than solvent polarity.

Eq. 8. The ionic components of intermediate 3 can combine to form 4 or the radical components of 3 can combine to form 5. In either case, further combinations within 4 and 5 can lead to the tetracovalent sulfur compound 6. Intermediate 6 is identical to intermediate V-23 which we postulated to be formed in the hypothetical nucleophilic displacement reaction (Scheme V-3). Since the electron transfer reaction and the postulated \( \text{S}_2\text{N}^2 \)
reaction share a common intermediate, further decomposition of 6 should occur as shown in Scheme V-3 and as discussed on pages 144-148. Briefly, 5, 6, and 7 are in equilibrium. Further reaction occurs only through ylide 8 and thus the equilibrium is constantly shifted in that direction.

The only difference between Eq. 8 and Scheme V-3 is the presence of 4, which can be formed by combination of ions within 3. The radical components of 4 can diffuse apart, combine with each other to form 6, or undergo disproportionation to form 8; the low yield of radicals in this system may be the result of the radical destroying reactions that produce 6 and 8. Since the relative rate of formation of 4 to 5 depends on many solvent parameters and the relative stability of the radicals and ions, it is not possible to predict the relative contributions of 4 and 5 to the reaction mechanism. Nevertheless, Eq. 8 can account for the production of radicals and the reaction products, tert-butyl alcohol and BOMS.

Eqs. 9-10. Rather than combining with the sulfide cation-radical to form 5, the tert-butoxy radical in 3 can abstract a proton from the cation-radical to form the sulfur stabilized carbonium ion 9 (Eq. 9). The carbonium ion would rapidly react with benzoate anion to form BOMS. Thus Eq. 9 can explain the experimental results as well as Eq. 8 can; the only difference in the two equations is the sequence of abstraction and combination.
It is possible that the benzoate anion in 3 could abstract a proton from the sulfide cation-radical (Eq. 10) rather than combining with it to form 4. If this were to occur, benzoic acid and a sulfur stabilized radical 10 would be produced. This radical would then combine with the tert-butoxyl radical to form tert-butoxymethyl methyl sulfide (11). This could be a minor pathway that accounts for radical production. The corresponding reaction in the DMA-BPO reaction (Eq. V-34) accounts for 40% of the reaction path; however, it is unlikely that Eq. 10 is that important in this system because radical production by this reaction should depend on the base strength of the benzoate anion; (Eq. 10 should be more favorable for a stronger base, and thus the radical yield from p-MeO-TBP should be higher than from p-NO\textsubscript{2}-TBP.); our results in Table II-14 show that the radical yield is not related to the TBP substituent.

The fact that BPO reacts with Me\textsubscript{2}S by an S\textsubscript{N}2 reaction rather than by an electron transfer reaction, although BPO is more easily reduced than is TBP, can be explained in the following way. The slight increase in the electron affinity of BPO compared to TBP is not as significant as the increase in leaving group ability of benzoate compared to tert-butoxide. Since benzoate is a much better leaving group than tert-butoxide (DMSO reacts rapidly with benzoic anhydride but not at all with
tert-butyl benzoate), the $S_N^2$ reaction is so much more faster than the corresponding $S_N^2$ displacement on TBP that it completely overshadows the small increase that would have been expected for the electron transfer reaction. This can be shown by a comparison of reaction rates.

A very rough estimation of the expected rate of the electron transfer reaction between BPO and Me$_2$S can be obtained from an evaluation of the effect that the change in the ionization potentials of amines has on the activation energies for the reaction of amines with BPO. We can use this evaluation to predict how the difference in ionization potential between DMA and Me$_2$S will effect the rate of electron transfer from each of these donors to BPO. From Table IV-4 we find that the activation energy of the aniline-BPO reaction is 2.6 kcal/M higher than the activation energy of the DMA-BPO reaction, and that the ionization potential of aniline is 0.6 eV higher than the ionization potential of DMA. Thus an increase of 4.3 kcal/M in activation energy would be expected for an increase of 1.0 eV in donor ionization potential. If we assume that this relationship applies to donors other than amines (i.e., assume that donor reactivity depends only on ionization potential), then since the ionization potential of Me$_2$S is 1.54 eV greater than the ionization potential of DMA (see p. 167), the activation energy of the
electron transfer reaction between Me₂S and BPO should be 6.7 kcal/M greater than the activation energy for the DMA-BPO reaction. Using this difference in activation energies and the data of Graham and Mesrobian, using this difference in activation energies and the data of Graham and Mesrobian, for the reaction rate of the BPO-DMA reaction, we calculate that at 40° the second order rate constant for an electron transfer reaction from Me₂S to BPO should be about 6x10⁻⁶ M⁻¹ sec⁻¹. This reaction rate is approximately 2x10³ times slower than that actually observed by Pryor and Bickley. Therefore, while an electron transfer reaction between BPO and Me₂S may occur, it is completely overshadowed by the much faster nucleophilic displacement reaction. Conversely, an electron transfer reaction can be observed for the TBP-Me₂S reaction, which is 1x10⁵ times slower than the BPO-Me₂S reaction, because an S₆² reaction is unfavorable due to the poor tert-butoxide leaving group.

We believe that the experimental results provide adequate evidence to support the electron transfer mechanism proposed in Scheme VI-1. Most of the experimental data such as solvent effects, substituent effects and product analysis are consistent with either an S₂ or an ET mechanism; however, the 2.3±1.5% yield of scavengable free radicals cannot be explained by an S₂ reaction or by any feasible side reaction. We suggest that the radical production must be due to radical leakage from an electron
transfer intermediate such as 3. The low yield of free radicals is not necessarily indicative that the ET reaction is a minor reaction; we believe that it is due to combination and disproportionation reactions of 3 that occur in the solvent cage and decrease the efficiency of radical production. In fact, in the next chapter we will present a kinetic isotope effect technique for distinguishing ET from \( S_N^2 \) reactions. The results of this technique indicate that the electron transfer reaction is the major reaction, but we cannot exclude the possibility that an \( S_N^2 \) reaction is a minor reaction path.

We have written Scheme VI-1 for the reaction of \( \text{Me}_2\text{S} \) with TBP, but we do not wish to imply that this reaction is the only example of a TBP-sulfide electron transfer reaction. Most of our research has been with \( \text{Me}_2\text{S} \); however, other sulfides should also undergo an ET reaction with peresters. For example, we have investigated radical production by the tert-butyl \( p \)-nitroperoxybenzoate with tert-butyl sulfide. The excess galvinoxyl technique shows that approximately 18% of this reaction produces scavengable free radicals, which indicates that this reaction is an electron transfer reaction. Perhaps the larger yield of free radicals is due to less cage combination and disproportionation in the electron transfer intermediate \( \sim \) than in 3. However, to ascertain the exact cause of the higher yield, many more sulfide-perester
reactions would have to be investigated. This reaction demonstrates that electron transfer can be a general reaction for sulfide-perester reactions and is not just a unique property of the Me₂S-TBP reaction.
C. References Chapter VI


25. At 80° in 1.0 M tert-butyl sulfide a 0.00974 M $\text{P-NO}_2$-TBP solution decolorized a $1.0\times10^{-3}$ M galvinoxyl solution at a rate of $1.88\times10^{-8}$ M/sec, and a 0.0475 M perester-sulfide solution decolorized galvinoxyl at a rate of $5.07\times10^{-8}$ M/sec. The sulfide-galvinoxyl blank decoloration was $0.35\times10^{-8}$ M/sec. Using this data and Eq. II-25, we obtain an average value of 18% for the fraction of the perester-sulfide reaction that produces radicals.
VII. NUCLEOPHILE-PEROXIDE REACTIONS: ET OR $S_N^2$

In the previous chapters we have shown that nucleophiles can react with peroxides by a nucleophilic displacement or by an electron transfer. In this chapter we will discuss other examples of peroxide-nucleophile reactions that we believe involve an electron transfer and show how an electron transfer mechanism can explain some of the puzzling results of these reactions. Also we will postulate two methods for distinguishing an ET reaction from an $S_N^2$ reaction.

A. A Survey of Nucleophile-Peroxide Reactions

Table VII-1 presents experimental data for several nucleophile-peroxide reactions. As the data show, these reactions all respond in similar ways to changes in reaction variables; reactions in which scavangeable free radicals are produced cannot be distinguished from other reactions by an examination of the reaction products, Hammett $\rho$-values, the magnitude of the acceleration of the peroxide decomposition produced by the nucleophile, or by the effect of solvent polarity. However, we believe that radical production is a distinguishing characteristic of an electron transfer reaction, and thus those reactions that produce free radicals are electron transfer reactions while those that do not are nucleophilic displacement reactions.
TABLE VII-1
Reactions of Peroxides with Nucleophiles (Donors)

<table>
<thead>
<tr>
<th>No.</th>
<th>Peroxide</th>
<th>Donor</th>
<th>Acceleration</th>
<th>Rho\textsuperscript{b} Peroxide</th>
<th>Rho\textsuperscript{c} Donor</th>
<th>Percent Radical</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BPO\textsuperscript{e}</td>
<td>PhNMe\textsubscript{2}</td>
<td>3\times10\textsuperscript{4} (40°)</td>
<td>+1.6\textsuperscript{f}</td>
<td>-2.7\textsuperscript{g}</td>
<td>18\textsuperscript{h}</td>
<td>1a</td>
</tr>
<tr>
<td>2</td>
<td>BPO</td>
<td>Ph\textsubscript{2}NOH</td>
<td>6\times10\textsuperscript{5} (40°)</td>
<td>+0.8</td>
<td>-</td>
<td>100</td>
<td>1e</td>
</tr>
<tr>
<td>3</td>
<td>BPO</td>
<td>Me\textsubscript{2}S</td>
<td>5\times10\textsuperscript{4} (40°)</td>
<td>-</td>
<td>-1.3\textsuperscript{i}</td>
<td>0</td>
<td>1f</td>
</tr>
<tr>
<td>4</td>
<td>BPO</td>
<td>ArCH=CHAr</td>
<td>4\times10\textsuperscript{3} (45°)\textsuperscript{j}</td>
<td>+1.2</td>
<td>-1.0\textsuperscript{k}</td>
<td>10\textsuperscript{l}</td>
<td>1g</td>
</tr>
<tr>
<td>5</td>
<td>BPO</td>
<td>Me\textsubscript{2}C=Me\textsubscript{2}</td>
<td>1\times10\textsuperscript{2} (45°)</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>1h</td>
</tr>
<tr>
<td>6</td>
<td>TBP\textsuperscript{l}</td>
<td>Me\textsubscript{2}S</td>
<td>17 (80°)</td>
<td>+1.3</td>
<td>-1.7\textsuperscript{i,m}</td>
<td>3</td>
<td>1i</td>
</tr>
<tr>
<td>7</td>
<td>TBP</td>
<td>Ph\textsubscript{3}P</td>
<td>2\times10\textsuperscript{3} (80°)</td>
<td>+1.2</td>
<td>-</td>
<td>0</td>
<td>1j</td>
</tr>
<tr>
<td>8</td>
<td>o-MeS-TBP</td>
<td></td>
<td>5\times10\textsuperscript{3} (80°)\textsuperscript{n}</td>
<td>-</td>
<td>-1.3\textsuperscript{o}</td>
<td>50</td>
<td>1k</td>
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<tr>
<td>9</td>
<td>2-MeS-3-t-BuOO-CO-TBP</td>
<td></td>
<td>1\times10\textsuperscript{5} (80°)\textsuperscript{n}</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>1o</td>
</tr>
<tr>
<td>10</td>
<td>o-Ph\textsubscript{2}C=CH-TBP</td>
<td></td>
<td>42 (80°)\textsuperscript{n}</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>1m</td>
</tr>
<tr>
<td>11</td>
<td>o-Ph\textsubscript{2}C=CH-BPO</td>
<td></td>
<td>387 (70°)\textsuperscript{n}</td>
<td>+0.7</td>
<td>-1.8</td>
<td>11</td>
<td>1m</td>
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<td>Table VII-1 -- continued</td>
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<tr>
<td>a. The acceleration of the rate of peroxide disappearance in a 1.0 M solution of the nucleophile relative to the rate in the same solvent without nucleophile.</td>
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<tr>
<td>b. Hammett equation rho when substituents are in the Ar-group of the peroxide.</td>
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<tr>
<td>c. Substituents in the Ar-group of the nucleophile.</td>
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<td>d. Percent of the total reaction that produces scavengeable free radicals.</td>
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<td>e. Benzoyl Peroxide.</td>
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<td>f. Ref lb.</td>
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<td>g. Ref lc.</td>
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<td>h. Ref ld.</td>
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<tr>
<td>i. This work; nucleophile is Ar-substituted ArSCH$_3$.</td>
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<tr>
<td>j. For reaction of m,m'-Br$_2$-BPO with trans-p,p'-(MeO)$_2$-stilbene.</td>
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<td>k. With $\sigma^+$.</td>
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<td>l. tert-butyl peroxybenzoate.</td>
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<td>m. For reaction with tert-butyl p-chloroperoxybenzoate.</td>
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<tr>
<td>n. Relative to unsubstituted peroxide.</td>
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<tr>
<td>o. Ref lk.</td>
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</table>
Reaction products can give an indication to the reaction type since the general mechanism for $S_N^2$ reactions of nucleophiles and peroxides (Scheme V-2) predicts that oxygen transfer to the nucleophile should be a reaction product; i.e., phosphine oxide, sulfoxide, or epoxide are the products of nucleophilic displacement on peroxides by phosphine, sulfide, or olefin. Such products may indicate an $S_N^2$ reaction, but they do not prove it. Likewise, the occurrence of an ET reaction is not proved by the absence of these products. For example, the reaction of Me$_2$S with TBP or with BPO produces the same sulfide oxidation product (BOMS).! The Me$_2$S-TBP reaction is an electron transfer and the Me$_2$S-BPO reaction is a nucleophilic displacement and both reactions give similar products; therefore, product analysis does not always distinguish the two reaction types.

Table VII-1 shows that radical production is independent of substituent effects. This is expected because both reaction types should be accelerated by electron rich nucleophiles (donors) or electron deficient substrates (acceptors). Therefore, the reaction rates of both ET and $S_N^2$ reactions are increased by electron donating groups in the nucleophile and electron withdrawing groups in the peroxide. The similarity of substituent effects is illustrated by the fact that the ionic reaction of triphenyl phosphine with aryl-substituted TBP (Table VII-1,
reaction 7) has nearly the same \( p \)-value as does the ET reaction of aryl-substituted TBP with \( \text{Me}_2\text{S} \) (Table VII-1, reaction 6). Thus substituent effects are useless for distinguishing nucleophilic displacement reactions from electron transfer reactions.

All of the peroxides in Table VII-1 undergo unimolecular decomposition, and in the presence of nucleophiles, the rate of peroxide disappearance is accelerated. We might expect that the magnitude of the acceleration would separate \( S_N^2 \) from ET reactions; however, as shown in Table VII-1, the relative rate of acceleration does not correlate with radical production. For example, both \( \text{Me}_2\text{S} \) and DMA accelerate the decomposition of BPO by a factor of approximately \( 4 \times 10^4 \), but the \( \text{Me}_2\text{S} \) reaction is ionic\(^1\) and the DMA reaction is an electron transfer reaction (p. 106). Furthermore, in some cases, the radical producing reaction is slower than the ionic reaction (compare TBP-\( \text{Me}_2\text{S} \) to BPO-\( \text{Me}_2\text{S} \)); in others, the radical producing reaction is faster (compare BPO-stilbene to BPO-tetramethylethylene). Clearly there are many factors other than the rate of reaction in determining when an ET reaction will occur.

The effect of solvent polarity on the reaction rate of nucleophile-peroxide reactions is very complex. Data for reactions in which the solvent effect has been evaluated are listed in Table VII-2. Surprisingly, both
### TABLE VII-2

The Effect of Solvent Polarity on the Reaction Rate of Some Peroxide-Nucleophile Reactions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>$\frac{\Delta \log k}{\Delta E_T} \times 10^2$</th>
<th>Percent $^b$ Radical</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP + Me$_2$S</td>
<td>0.7</td>
<td>2</td>
<td>li</td>
</tr>
<tr>
<td>o-Ph$_2$C=CH-BPO</td>
<td>1.5</td>
<td>11</td>
<td>lm</td>
</tr>
<tr>
<td>BPO + MeSSMe</td>
<td>4.3</td>
<td>0</td>
<td>lf</td>
</tr>
<tr>
<td>BPO + DMA</td>
<td>5.2</td>
<td>18</td>
<td>ld</td>
</tr>
<tr>
<td>TBP + Ph$_3$P</td>
<td>5.8</td>
<td>0</td>
<td>lj</td>
</tr>
<tr>
<td>o-Ph$_2$C=CH-TBP</td>
<td>7.3</td>
<td>80</td>
<td>lm</td>
</tr>
<tr>
<td>Br$_2$-BPO + ArCH=CHAr$^c$</td>
<td>8.2</td>
<td>10</td>
<td>lg</td>
</tr>
<tr>
<td>o-PhS-TBP</td>
<td>12</td>
<td>50</td>
<td>lk</td>
</tr>
</tbody>
</table>

a. Slope of a graph of log (rate constant for peroxide disappearance) vs. $E_T$ (see Figure V-1).

b. Percent of the total reaction that produces scavengeable free radicals.

c. For reaction of m,m'-Br$_2$-BPO with trans-p,p'-(MeO)$_2$-stilbene.
the least affected and most affected reactions are radical producing reactions. Obviously, the polar solvent effect is in no way correlative with radical production. The lack of correlation between polar solvent effect and radical production has been one of the most puzzling aspects of peroxide-nucleophile reactions. The solvent effect on the rate of decomposition of tert-butyl phenylthioperoxybenzoate (Table VII-1, reaction 8) is extremely large for a reaction that produces free radicals.³

As discussed in Section B, this large solvent effect can be explained by an electron transfer mechanism.

The above discussion indicates that the unique characteristic of an electron transfer reaction that is different from an S_N2 reaction is its ability to produce radicals at an accelerated rate; i.e., the peroxide produces radicals faster in the presence of nucleophile than in its absence. We have already shown that reactions 1, 2, and 6 in Table VII-1 are electron transfer reactions; if our hypothesis is correct, then reactions 4 and 8-11 must also be electron transfer reactions.

B. Other Nucleophile-Peroxide ET Reactions

1. **Internal nucleophile-peroxide reactions.** Martin and co-workers have extensively investigated the reactions of the o-thiyl substituted peresters 1.⁴ ¹k,¹f as well as the o-vinyl substituted peresters and peroxides 2.¹m,¹o
They found that sulfur and vinyl substituents greatly accelerate the rate of peroxide decomposition and that the accelerated decomposition produces free radicals. These properties were attributed to neighboring group participation in a homolytic bond cleavage of the O-O bond.

As mentioned earlier, the rate of decomposition of \( \text{lb} \) is very sensitive to solvent polarity.\(^{11}\) To account for this and for radical production and product data (a large yield of acetone indicates that tert-butoxy radicals are formed), Martin et al. suggested that the transition state for the sulfide-assisted decomposition of \( \text{l} \) is represented by three resonance contributors which are shown in Eq. 1.\(^{11k,11l}\)

\[
\begin{align*}
1a, \ R &= -\text{CH}_3 \\
1b, \ R &= -\text{C}_6\text{H}_5 \\
2a, \ R &= -\text{Bu-t} \\
2b, \ R &= -\text{C-Ph} \\
\end{align*}
\]
Structure 4 was included to explain the solvent sensitivity and structure 3 and 4 were necessary to explain the products and radical production. Martin has also measured substituent effects on this reaction using 1 in which R was X-C₆H₄ and found that $p = -1.3$. Martin then suggested that this $p$-value is indicative of a contribution to the transition state by 4.

The neighboring group participation by sulfide in the decomposition of 1 is equivalent to a nucleophile-peroxide reaction that produces radicals, and, therefore, may be classified as an ET reaction. The experimental results are consistent with an ET, and in fact, Martin's interpretation of the results is also consistent with an ET reaction which can be represented by Eq. 2. The initial

$$\begin{align*}
1 & \rightarrow \begin{array}{c}
\text{R}^+ \\
\text{S} \\
\text{O} \\
\text{O} - \text{Bu-t}
\end{array} & \rightarrow & \begin{array}{c}
\text{R} \\
\text{S}^* \\
\text{O} \\
\cdot\text{O-Bu-t}
\end{array} \\
& \leftrightarrow & \begin{array}{c}
\text{R} \\
\text{S}^* \\
\text{C} \\
\alpha\beta\text{O-Bu-t}
\end{array} \\
& \leftrightarrow & \begin{array}{c}
\text{R} \\
\text{S}^* \\
\text{C} \\
\alpha\beta\text{O-Bu-t}
\end{array}
\end{align*}$$

(2)

product of electron transfer, 6, would be very unstable and immediately decompose to 3 and 5 (see p. 168-169), which could be resonance structures of a single intermediate or separate intermediates. A comparison of Eq. 1 and Eq. 2 shows that the only difference between the ET mechanism
that we postulate (Eq. 2) and the mechanism that Martin postulates (Eq. 1) is that Martin includes the ionic resonance structure, 4; however, in his discussion of the reaction, Martin only uses 4 to account for the solvent effect and ρ-value. According to this discussion in the previous section, solvent effects and ρ-values cannot distinguish an ET reaction (3 and 5) from an S_N2 reaction (4). We suggest that the ET reaction can explain the solvent effects and ρ-value, and therefore, structure 4 is not needed. When 4 is omitted from Martin's reaction, his interpretation agrees completely with an ET mechanism. In all fairness to Martin and co-workers, who used magnificent insight in their discussion of the decomposition of 1, we are not proposing a new mechanism for this reaction, but are merely suggesting that the reaction can be classified as an electron transfer reaction. The postulation of an ET mechanism for the decomposition of 1 makes it much easier to understand the relative rate of reaction of 1a to 1b as well as the large solvent effect on this radical reaction.

The methylthiyl-substituted perester (1a) decomposes 1.7 times more slowly than the phenylthiyl-substituted perester (1b). This reactivity ratio is what would be expected from an ET reaction of this type. Due to the internal nature of the reaction, the steric effect of the sulfide substituent is not as important in this reaction.
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as it is in the external sulfide displacement [from Table II-7, \((\text{rate of TBP + Me}_2\text{S})/(\text{rate of TBP + C}_6\text{H}_5\text{SCH}_3)\) is 14\)], and the reactivity ratio should depend on the electron donating ability of the sulfide; i.e., the sulfide ionization potential. Since the ionization potential of methyl phenyl sulfide is 8.07 and the ionization potential of diphenyl sulfide is 7.88, an electron transfer mechanism would predict that \(\text{la}\) should react slower than \(\text{lb}\), which is observed. The difference in reactivity may not be as large as what might have been expected, but this only indicates that steric requirements cannot be completely neglected.

An electron transfer mechanism can rationalize the abnormally large effect of solvent polarity on the rate of decomposition of 1. As shown in the discussion of electron transfer reactions in Chapter VI, the rate of these reactions can be very solvent dependent. The sensitivity to solvent polarity should depend on the degree of electron transfer in the transition state of the reaction; early transition states, as in the TBP-Me\(_2\)S reaction, have little charge development and are not influenced by changes in the solvent polarity. However, for reactions which have a later transition state, charge separation can develop and the reaction rate is then dependent on solvent polarity; for example, the decomposition of charge transfer complexes can be extremely sensitive to solvent polarity (p. 166-167).
Thus the large solvent effect on the rate of decomposition of \( \text{lb} \) can be explained by a late transition state in which a large amount of charge separation has developed. The late transition state may be due to the proximity of the sulfur atom to the oxygen-oxygen bond. The discussion in Chapter VI suggested that the lack of solvent effect on the rate of the TBP-Me\(_2\)S reaction is because the transition state of this reaction closely resembles a CT complex. Because of the nearness of the sulfur atom to the O-O bond in \( \text{I} \), it is easier for a CT complex to form in \( \text{I} \) than in the external reaction. The greater ease in the formation of a CT complex means that \( \text{I} \) should have a lower activation energy than the TBP-Me\(_2\)S reaction, and, according to the Hammond postulate,\(^6\) a later transition state. Therefore, the rate of decomposition of \( \text{I} \) is much more solvent sensitive than is the rate of the TBP-Me\(_2\)S reaction.

In these electron transfer reactions, solvent polarity can influence both the rate of the reaction and the rate of radical production. These two effects are completely different and should not be confused. The first is fairly well understood in that generally a high degree of charge development in the transition state of the interaction of neutral molecules will result in sensitivity of the reaction to changes in solvent polarity.\(^7\) However, the effect of solvent polarity on radical production is very complex because radical production is dependent on many
variables other than solvent polarity. For example, solvent viscosity, the H-bonding ability of solvent, and internal pressure of the solvent must be considered. The importance of these additional solvent parameters is illustrated in the following paragraphs.

Solvent viscosity is very important in determining the amount of radicals that escape the solvent cage. As viscosity increases, the extent of cage reactions also increases. However, viscosity is not the only determining factor in the amount of cage reaction. Niki and Kamiya have recently shown that the yield of cage recombination products formed in the decomposition of di-tert-butylperoxy oxalate is dependent on specific interactions of the tert-butoxy radicals with the surrounding molecules. For example, in alcoholic solvents, where hydrogen bonding is possible, the yield of cage products is much smaller than would have been predicted by the viscosity of the solvent. In fact, in methanol and ethanol, practically no cage products are formed. It appears that alcoholic solvents interact with the tert-butoxy radicals and help to free them from the solvent cage. A similar effect was observed by Sato et al. in their experiments on the rate of styrene polymerization of styrene initiated by the reaction of dimethyl aniline N-oxide with acetic anhydride (pp. 92-93). The rate of this reaction is independent of the concentration of ethanol, but the rate of styrene
polymerization is first order in ethanol. The authors suggest that ethanol helps to free the radicals from the solvent cage. This is a good example of the possible danger in attributing an increase in radical production to solvent polarity; at first glance, the experimental results might indicate that the increase is due to solvent polarity, but the lack of solvent effect on the reaction rate and the work of Niki and Kamiya indicate that this probably is not correct.

The internal pressure of the solvent is also important in determining the rate of reactions; for neutral reactions, such as radical reactions, it may be more important than solvent polarity.\(^{11}\) For instance, the decomposition of \(\frac{1}{2}\) is a unimolecular reaction and the reaction rate should increase as the internal pressure of the solvent decreases, and the \(\text{Me}_2\text{S-TBP}\) reaction is bimolecular and should show the opposite effect of changing the internal pressure.

The complexity of the effect of solvents on the efficiency of radical production in electron transfer reactions is demonstrated by the results of Tuleen, Bentrude, and Martin who measured the efficiency of radical production of \(\frac{1}{2}b\) as a function of solvent polarity.\(^{11}\) The results in Table VII-3 indicate that while the rate of the reaction depends on solvent polarity, the efficiency of the reaction in producing radicals is independent of solvent polarity. These results clearly show that solvent
TABLE VII-3

The Effect of Solvent Polarity on the Decomposition of o-Phenylthioperoxybenzoate

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( E_T )</th>
<th>( k \times 10^4 ) sec(^{-1})</th>
<th>By infrared ( b )</th>
<th>By scavenger ( c )</th>
<th>Percent ( d ) Radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>30.9</td>
<td>0.00985</td>
<td>0.0033</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>42.2</td>
<td>0.189</td>
<td>0.060</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>90% Dioxane</td>
<td>--</td>
<td>0.474</td>
<td>0.46</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>tert-Butyl Alcohol</td>
<td>43.9</td>
<td>0.526</td>
<td>0.16</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>45</td>
<td>1.01</td>
<td>0.66</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>80% Dioxane</td>
<td>--</td>
<td>1.38</td>
<td>0.95</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>48.6</td>
<td>1.33</td>
<td>0.54</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>51.9</td>
<td>2.31</td>
<td>1.2</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>55.5</td>
<td>8.21</td>
<td>2.7</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>
TABLE VII-3 -- continued

a. Ref 11, temperature 25°.

b. Rates followed by observing disappearance of the perester carbonyl absorption, infrared spectroscopy.

c. Rate is the average of runs following the zero-order disappearance of the absorption of the scavenger, galvinoxyl, in the presence of a large excess of perester.

d. Percent of the total reaction that produces scavangeable radicals.
polarity alone does not determine the amount of radicals that an electron transfer reaction can produce.

In conclusion, we have postulated that the decomposition of 1 and the TBP-sulfide reaction follow the same mechanism. However, solvent effects, efficiencies of radical production, and reaction rates are quite different for these two reactions. The difference in solvent effect has been explained by the degree of charge separation in the transition state, and the larger amount of radical production by 1 can be related to geometrical differences between 5 and the corresponding intermediate of the TBP-sulfide reaction (7). For example, the close proximity of the sulfur atom to the \( \alpha \)-oxygen atom in 5 should favor the combination of the \( \alpha \)-oxygen with the sulfur atom rather than the combination of the tert-butoxy oxygen with the sulfur atom; which is a result that is supported by the products. The favored combination for 5 produces 3 which is a radical product. In 7 either the benzoate ion or the tert-butoxy radical can combine with the sulfur atom.
Since neither one is favored by the geometry of \(_\varphi\), the more energetically favorable path will occur. Judging from the small efficiency of radical production, the radical destroying path, combination of tert-butoxy radicals with the sulfur moiety, is favored over the charge destroying path, combination of benzoate ion with sulfur. This is just one example of the many ways that geometrical considerations could cause differences between the reaction of \(\text{I}_\varphi\) and the reaction of TBP with sulfides; it is meant to be only one illustration of the possible differences. The proximity of the sulfur atom to the O-O bond in \(\text{I}_\varphi\) can also account for the differences in the reaction rates between \(\text{I}_{\text{lb}}\) and the TBP-sulfide reaction at 80° in 10 M methyl phenyl sulfide, where every perester molecule is adjacent to a sulfur molecule,\(^{12}\) TBP decomposes only 270 times more slowly than \(\text{I}_{\text{la}}\). Therefore, the difference in reaction rates is not really very large; especially considering the entropy differences between an internal and external reaction.

2. **Internal Olefin-Peroxide Reactions.** Koenig and Martin found that the decomposition of \(\text{o-vinyl substituted peresters and peroxides (2)}\) is very similar to the decomposition of \(\text{l}_{\text{lm}}\) as is shown in Tables VII-1 and VII-2. They suggested that 2 and \(\text{l}_\varphi\) decompose by similar mechanisms; Eq. 3 shows the transition state that they postulated for the decomposition of 2.
Again we believe that this reaction is an electron transfer reaction because it is a nucleophile-peroxide reaction that produces radicals. The formation of the reactive intermediates can be represented by Eq. 4. This electron transfer mechanism is essentially the same as the mechanism postulated by Martin and Koenig except that $\mathbf{9}$ is omitted from Eq. 4. Structure $\mathbf{9}$ is similar to $\mathbf{5}$ and can be omitted for the same reasons that $\mathbf{5}$ can be omitted from the decomposition mechanism of $\mathbf{1}$; i.e., the solvent effect and substituent effects can be explained by an electron transfer mechanism. Otherwise, we agree completely with Koenig and Martin's discussion of the reaction and only wish to point out that this reaction can be considered to
be an internal electron transfer reaction.

The decomposition of trans-γ-benzylidenebutyryl peroxide (11), studied by Lamb and co-workers,\(^{13}\) is another intramolecular electron transfer reaction between olefin and peroxide. This peroxide decomposes about four times faster than its saturated analogue δ-phenylvaleryl peroxide (12). The decomposition rate of 11 is considerably more solvent dependent than is the rate of decomposition of 12; however, the efficiency of radical production by both peroxides is the same.\(^{13}\) Since the rate of radical production is the product of the efficiency of radical production and the rate of peroxide decomposition, 11 produces radicals at an accelerated rate, and therefore, according to our hypothesis, can be classified as an electron transfer reaction. Lamb et al. attributed the increased rate of decomposition of 11 to an "intramolecular reaction between the olefinic double bond and the peroxide linkage, via a rather polar transition state, forming radicals." They postulated that structures 13 and 14 contribute to the transition state. This is how we would
describe an electron transfer reaction.

\[
\begin{align*}
H & \quad \text{CH}_2\text{-CH}_2 & \quad H & \quad \text{CH}_2\text{-CH}_3 \\
+\text{C=C} & \quad \overset{\text{C=O}}{\text{OCR}} & \quad \overset{\text{C=C}}{\text{OC}\text{-R}}
\end{align*}
\]

3. A Bimolecular Olefin-Peroxide ET Reaction.

Usually olefins react with peroxides by a non-radical mechanism to form epoxide and peroxide reduction products; i.e., acids, alcohols, or anhydrides from peroxy acids, hydroperoxides, or acyl peroxides. These reactions, which are examples of nucleophilic displacement of olefin on peroxide, can be formulated as shown in Eq. 5.

\[
\begin{align*}
R & \quad OH(R'') \\
\overset{\text{O-O}}{\text{C=C}} & \quad \overset{\text{O-H(R')}}{\text{C=C}} & \quad \overset{\text{ROH(R')}}{+}
\end{align*}
\]

According to Eq. 5, the reaction of olefins with peroxides should not produce radicals. However, the addition of \(p, p'-\text{dimethoxy-trans-stilbene}\) to a solution of \(m,m'-\text{dibromobenzoyl peroxide}\) accelerates the rate of radical production by the peroxide. This is shown by the fact that when the stilbene is added to a solution of the peroxide, the rate of disappearance of the free radical scavenger galvinoxyl increases by a factor of four. Since
the addition of the same amount of stilbene increases the total rate of disappearance of the peroxide by a factor of forty, the rate of radical production by the bimolecular reaction is only 10% of the total reaction rate. However, in the closely related reaction of \textit{m,m}'-dibromobenzoyl peroxide with tetramethylethylene, the rate of decomposition of peroxide increases when the olefin is added, but the rate of radical production does not increase. This difference in radical production can be explained by the postulation that the radical producing reaction occurs by an electron transfer mechanism.

The occurrence of an electron transfer mechanism in the peroxide-stilbene reaction and not in the peroxide-tetramethylethylene reaction can be ascribed to the difference in the olefin ionization potentials. The ionization potential of tetramethylethylene is 8.53 \cite{17a} and the ionization potential of \textit{p,p}'-dimethoxy-trans-stilbene should be somewhat less than 7.95 \cite{17b} which is the ionization potential of \textit{trans}-stilbene. Therefore, we believe that the peroxide-tetramethylethylene reaction is a typical olefin-peroxide nucleophilic displacement, but because of the lower ionization potential of \textit{p,p}'-dimethoxy-trans-stilbene, an electron transfer reaction can occur between this olefin and \textit{m,m}'-dibromobenzoyl peroxide. It is this electron transfer reaction that causes the increase in radical production.
In this chapter we have separated peroxide-nucleophile interactions into two classes based on their ability to generate scavangeable free radicals, and we have postulated that the production of free radicals indicates an electron transfer mechanism. The widespread occurrence of these ET reactions suggests that they form an important class of peroxide-nucleophile reactions that have been largely neglected. In order to provide an easier method for distinguishing ET from $S_N2$ reactions and to provide additional evidence that the TBP-Me$_2$S reaction is an electron transfer, we have developed a kinetic isotope method that can distinguish electron transfer reactions from nucleophilic displacements.

C. A Kinetic Isotope Method for Distinguishing an ET Reaction from an $S_N2$ Reaction

1. Inadequacies of the Radical Production Method. The production of radicals by a nucleophile-peroxide reaction may not afford conclusive evidence for the occurrence of an electron transfer reaction because the radical production which is attributed to an ET reaction may be produced by side reactions. Careful analysis of the experimental results may be required to prove that an electron transfer reaction is the source of radicals. The reaction of BPO with DMA (discussed in Chapter IV) provides a good example of the difficulties involved in
determining if the radical production is the result of an ET reaction or if it is the result of a secondary reaction. For many years authors have postulated that this reaction is an $S_N^2$ reaction and that the source of radicals is homolysis of an acyloxyammonium ion (Eq. 6) which would be the expected product of an $S_N^2$ reaction. An extensive literature survey was required before we could show that Eq. 6 could not account for the radical production, and only after a significant contribution from Eq. 6 was excluded could we postulate that this reaction follows an ET mechanism.

Our own research on the TBP-Me$_2$S reaction provides another example of the problems encountered in using radical production as a diagnostic tool for electron transfer reactions. Because of the very low yield of scavengeable free radicals produced by this reaction, it was possible that side reactions could have been responsible for the radical production. In order to decide between an ET and an $S_N^2$ mechanism, we had to predict an $S_N^2$ mechanism for this reaction and show that it could not account for the radical production. After excluding an $S_N^2$ mechanism, we were able to consider an ET mechanism.
The above examples show that the radical production technique must be carefully applied in situations where the source of radicals is questionable. If correctly used, it is a reliable method, but it may be complicated and tedious. Also, this method may provide indeterminate results in that the failure of the investigator to detect radicals does not necessarily mean that the reaction in question is not an ET reaction. It is possible that an ET reaction may not produce scavangeable free radicals or that the lifetime of the radicals may be so short that they cannot be detected. Because of the problems inherent in the radical production method, we have developed a kinetic isotope method that should be more reliable and easier to use than the radical production method.

2. **Secondary Isotope Effects.** Deuterium isotope effects result from changes in the differences in zero point energy levels between a hydrogen bond and a deuterium bond in going from reactants to transition state. Primary isotope effects which occur when the isotopically substituted bond is broken are large: the rate of reaction of the deuterium compound may be 6 or 7 times slower than the rate of reaction of the protium compound. Secondary isotope effects are observed when the position of isotopic substitution is not directly involved in bond making or bond breaking, and for this reason they are smaller than primary isotope effects. Like primary isotope effects,
secondary isotope effects are also due to force constant changes at the position of isotopic substitution between reactant and transition state. Stronger force constants in the transition state result in inverse isotope effects ($k_H < k_D$), and weaker force constants produce normal isotope effects ($k_H > k_D$). The origin of these force constant changes are hyperconjugation, steric interactions, or inductive effects. Therefore, secondary isotope effects can detect subtle changes in reaction mechanisms.\textsuperscript{19}

The influence of deuterium substitution on reaction rates has long been used to elucidate reaction mechanisms. The $\alpha$-deuterium isotope effect has been widely used in solvolysis reactions to determine the degree of nucleophilic attachment in the transition state of a solvolytic substitution reaction.\textsuperscript{20} An $S_{N2}$ reaction should have an $\alpha$-deuterium isotope effect of between 0.95 and 1.06 per deuterium, and an $S_{N1}$ reaction should have a higher effect of between 1.1 and 1.2 (the $S_{N1}$ effect is somewhat dependent on the leaving group).\textsuperscript{20} This range of isotope effects has also been predicted by computer studies based on theoretical calculations.\textsuperscript{21}

Due to the similarity in isotope effects of $S_{N1}$ and $S_{N2}$ reactions, in order to be useful, it is necessary that the data be very accurate; if the data are good enough, very subtle differences in reaction mechanism can be detected by this method. For example, in a recent
application Raanen and co-workers sought to determine if the benzyl azide formed during the solvolysis of benzyl chloride in the presence of azide ion is formed by azide displacement on an ion pair. They measured the $\alpha$-deuterium isotope effect on azide formation and obtained a value of $1.033\pm0.007$ which indicates that the benzyl azide is formed by an $S_N^2$ reaction. Under similar conditions, the formation of 2-octyl azide during the solvolysis of 2-octyl brosylate has an $\alpha$-deuterium isotope effect of $1.106\pm0.007$. This slightly larger isotope effect indicates competing $S_N^1$ and $S_N^2$ reactions in the solvolysis of 2-octyl brosylate. This experiment shows that isotope effects can be a very powerful tool in investigating reaction mechanisms.

Deuterium substitution in the $\beta$-position can also serve as a mechanistic probe. These isotope effects can be caused by force constant changes due either to steric effects or hyperconjugation. For $S_N^1$ reactions the $\beta$-isotope effect is normal and the reduction of the force constant of the $\beta$-C-H bond in the transition state is probably due to hyperconjugative interaction of this bond with the developing vacant orbital at the reaction center. The effect of $\beta$-deuterium substitution in an $S_N^2$ reaction is not as large as for an $S_N^1$ reaction because in $S_N^2$ reactions steric effects (bonds become tighter in the transition state due to steric crowding).
and electronic changes (bonds become weaker as the old bond is broken) counterbalance one another. Thus $\beta$-deuterium isotope effects for substitution in the substrate tend to be only slightly greater than unity.$^{19c,23}$ However, if the point of isotopic substitution is in the nucleophile, steric effects become much more important than electronic effects and inverse isotope effects are observed.$^{26}$ For example in the $S_N2$ displacement of dimethylaniline on methyl tosylate, an inverse isotope effect of 0.88 is observed when the methyl groups are deuterium substituted.$^{26}$

3. Isotope Effects for $\beta$-Substituted Nucleophiles (Donors). Our method for distinguishing an electron transfer reaction from a nucleophilic displacement reaction utilizes a $\beta$-deuterium substituted nucleophile (donor). If the reaction is a nucleophilic displacement, the kinetic isotope effect should be inverse ($k_H<k_D$) because of increased steric crowding in the transition state.$^{26}$ However, if the reaction follows as ET mechanism, the donor develops a positive charge in the transition state, and we would expect the isotope effect to be similar to the isotope effect for an $S_{N1}$ reaction; *i.e.*, normal ($k_H>k_D$). Furthermore, since the reaction of the donor in an electron transfer reaction is very similar to the ionization of the donor, we would expect that the isotope effect of the ionization potential of the donor should parallel the
isotope effect of the electron transfer reaction. Since the zero point energies of deuterated compounds are lower than those of the analogous protium derivatives, normal isotope effects would be predicted for ionization for any molecule in which ionization comes from either a bonding or non-bonding orbital. (Ionization from an anti-bonding orbital could produce tighter bonding in the ion and inverse isotope effects). Thus, ET from all nucleophiles should have normal deuterium isotope effects. Measurements of the detailed spectra of Me₂S and (CD₃)₂S show the deuterated compound to have a higher ionization potential by about 230 cal/mole.²⁷ If this difference were fully realized in the transition state, an isotope effect for an ET reaction of 1.39 would be predicted at 80°.

In summary, a nucleophile in which the β-hydrogen atoms have been replaced by deuterium should react faster than the non-deuterated compound if it reacts by an Sₙ²⁻ reaction, but it should react slower than the non-deuterated compound if it reacts by an electron transfer mechanism. Therefore, to distinguish an ET mechanism from an Sₙ²⁻ mechanism, we need only to determine if the β-deuterated nucleophile reacts faster or slower than its protium analogue. The advantages of this method over the radical production method are twofold. First, because of the diametric nature of the Sₙ²⁻ and ET isotope effects, high data precision is not necessary because we only need to
know whether the isotopically substituted compound reacts faster or slower than the unsubstituted compound not whether the isotope effect is, for example, 1.03 or 1.10. Second, there is less ambiguity in this method than in the radical production method. As the discussion on the next page demonstrates, it is less difficult to prove that a normal isotope effect is the result of an ET reaction than it is to prove that radical production is the result of an ET reaction. Also, this kinetic isotope method should be able to identify ET reactions that do not produce scavengeable free radicals.

The data collected in Table VII-4 support our kinetic isotope effect method. Earlier work has shown that sulfide displacements on both tert-butyl hydroperoxide and BPO are nucleophilic displacements. In accord with the predictions of our method, we observe inverse isotope effects for both of these reactions. We were able to find only two examples in the literature of ET reactions for which the required isotope effects had been measured, and both of these reactions have normal isotope effects.1e,28 The isotope effects for the reactions of (CD$_3$)$_2$S with both TBP and 3,5-dinitro-substituted TBP have small but significant normal isotope effects. The data are not very precise, but they are reliable enough to show that the isotope effects are normal and not inverse. The comparatively small isotope effects for these reactions can be the result of
TABLE VII-4

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

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Nucleophile</th>
<th>Mechanism</th>
<th>( k_H/k_D )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{OTs} )</td>
<td>( \text{PhN(CD}_3\text{)}_2 )</td>
<td>( \text{S}_N^2 )</td>
<td>( 0.883 \pm 0.008 )</td>
<td>27a</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OTs} )</td>
<td>( \text{PhP(CD}_3\text{)}_2 )</td>
<td>( \text{S}_N^2 )</td>
<td>( 0.952 \pm 0.002 )</td>
<td>27a</td>
</tr>
<tr>
<td>( \text{CH}_3\text{COCCH}_3 )</td>
<td>( \text{CD}_3\text{SCD}_3 )</td>
<td>( \text{S}_N^2 )</td>
<td>( 2.9^c )</td>
<td>29</td>
</tr>
<tr>
<td>tert-BuOOH</td>
<td>( \text{CD}_3\text{SCD}_3 )</td>
<td>( \text{S}_N^2 )</td>
<td>( 0.93 \pm 0.03 )</td>
<td>1i</td>
</tr>
<tr>
<td>BPO</td>
<td>( \text{CD}_3\text{SCD}_3 )</td>
<td>( \text{S}_N^2 )</td>
<td>( 0.88 \pm 0.05 )</td>
<td>1i</td>
</tr>
<tr>
<td>BPO</td>
<td>( \text{Ph}_2\text{NOD} )</td>
<td>ET</td>
<td>( 1.53^d )</td>
<td>1e</td>
</tr>
<tr>
<td>( \text{ClO}_2 )</td>
<td>( (\text{CD}_3)_3\text{N} )</td>
<td>ET</td>
<td>( 1.3 )</td>
<td>28</td>
</tr>
<tr>
<td>TBP</td>
<td>( \text{CD}_3\text{SCD}_3 )</td>
<td>ET</td>
<td>( 1.08 \pm 0.06 )</td>
<td>1i</td>
</tr>
<tr>
<td>3,5-(\text{NO}_2)_2\text{TBP}</td>
<td>( \text{CD}_3\text{SCD}_3 )</td>
<td>ET</td>
<td>( 1.06 \pm 0.03 )</td>
<td>1i</td>
</tr>
</tbody>
</table>

a. Nucleophile.

b. Per molecule.

c. Includes a contribution from a primary isotope effect.

d. May include a contribution from a primary isotope effect.
an early transition state; an early transition state is supported by small polar solvent effect and a relatively small $\rho$-value. However, it is the direction of the isotope effect and not the magnitude that is important. The kinetic isotope effects indicate that both of these perester-sulfide reactions are electron transfer reactions. These results and the radical production results prove that the TBP-sulfide reaction is an electron transfer reaction and not a nucleophilic displacement.

A possible objection to our interpretation of the isotope effect for the TBP-Me$_2$S reaction is that the reaction could be an $S_N^2$ displacement, and the normal isotope effect could arise from a small contribution of a primary isotope effect. The reaction of DMSO with acetic anhydride (Eq. 7) illustrates this possibility. In Eq. 7 the

\[
\text{CD}_3\text{SCD}_3 + \text{CH}_3\text{COCH}_3 \xrightarrow{k_1} \text{CD}_3\text{SCD}_3 + \text{CH}_3\text{CO}_2^- \xrightarrow{k_D} \text{CD}_3\text{S}=\text{CD}_2 + \text{CH}_3\text{COD}
\]

unstable intermediate $15$ is formed reversibly and the product forming step, $k_D$, should have a primary isotope effect. The observed rate constant for this reaction is given by Eq. 8. If $k_D$ is much less than $k_{-1}$, then Eq. 8 can be replaced by Eq. 9 and $k_{\text{obs}}$ depends on all three
rate constants. Thus when $k_D \ll k_{-1}$, $k_{obs}$ depends in part on $k_D$, and the isotope effect on $k_{obs}$ will include a contribution from the primary isotope effect on $k_D$. On the other hand, if $k_D$ is much greater than $k_{-1}$, then Eq. 8 can be replaced by Eq. 10. Therefore, when $k_D \gg k_{-1}$, only the isotope effect on $k_1$ will contribute to the isotope effect on $k_{obs}$. For reactions like the one shown in Eq. 7

$$k_{obs} = \frac{k_1 k_D}{k_{-1} + k_D} \quad (8)$$

$$\text{if } k_D \ll k_{-1}, \quad k_{obs} = \frac{k_1 k_D}{k_{-1}} \quad (9)$$

the observed isotope effect will then depend on the relative rates of $k_{-1}$ and $k_D$. For example, the isotope effect for the reaction of DMSO-d$_6$ with acetic anhydride (Eq. 7) is 2.9, which indicates that for this reaction $k_D$ is much smaller than $k_{-1}$ and the observed isotope effect contains a large contribution from a primary isotope effect. Since the primary isotope effect makes such a large contribution to the observed isotope effect of this reaction, we must consider the possibility of a similar contribution to the isotope effect of the TBP-Me$_2$ reaction.
which could be caused by a reversible $S_N^2$ displacement.

The hypothetical nucleophilic displacement of $(CD_3)_3S$ on TBP can be represented by Eq. 11. If $k_{-1}$ is faster than $k_D$, then the isotope effect on $k_{obs}$ would contain a contribution from the primary isotope effect on $k_D$ (Eq. 9). However, if $k_D$ is faster than $k_{-1}$, then the observed isotope would depend only on $k_1$ (Eq. 10) and we should observe an inverse isotope effect. In order to show that the normal isotope effect that we observe for the TBP-Me$_2$S reaction is due to an electron transfer reaction and not to a small contribution from a primary isotope effect, we must estimate the relative rate of $k_D$ to $k_{-1}$ in Eq. 11.

The needed estimation can be arrived at by comparing Eq. 11 to the nucleophilic displacement of $(CD_3)_2S$ on BPO (Eq. 12). The isotope effect for Eq. 12 is 0.88, which is
typical for an $S_N2$ reaction,\textsuperscript{24} and therefore, $k_D$ must be much larger than $k_{-1}$. Thus for Eq. 12, $k_{\text{obs}}$ must be equal to $k_D$ (Eq. 10). The formation of DMSO and Bz$_2$O in Eq. 12 should not significantly influence the ratio $k_D/k_{-1}$, and, therefore, we can compare $k_D/k_{-1}$ for reaction 12 to $k_D/k_{-1}$ for reaction 11. For these reactions $k_{-1}$ should be less affected by the nature of the leaving group than $k_D$ should be. Since $k_D$ for Eq. 12 is for the abstraction of a deuteron by benzoate anion and $k_D$ for Eq. 11 is for the abstraction of a deuteron by a tert-butoxide anion, $k_D$ for Eq. 11 should be much faster than $k_D$ for Eq. 12. Therefore, $k_D/k_{-1}$ for Eq. 11 must be larger than $k_D/k_{-1}$ for Eq. 12, and $k_{\text{obs}}$ for Eq. 11 must then be equal to $k_{1}$. Thus the normal isotope effect observed for the TBP-Me$_2$S reaction is not due to a contribution from a primary isotope effect on an $S_N2$ reaction.

A similar contribution by a primary isotope effect has also been postulated by Chalfont and Perkins to explain the apparently high isotope effect observed for the reaction of diphenylhydroxylamine with BPO (Eq. VI-3,4).\textsuperscript{1e} When the hydroxyl hydrogen is replaced by deuterium the reaction rate decreases by a factor of 1.53 (Table VII-4). In order for a primary isotope to make a contribution to the observed isotope effect, the reactants must reversibly form a reactive intermediate which decomposes to products by abstraction of an isotopically substituted hydrogen.
Also, the rate of the reversion of the reactive intermediate to reactants must be faster than the decomposition of the intermediate to products. We believe that this condition cannot exist for a peroxide-nucleophile electron transfer reaction because the reversible step in this reaction is formation of the nucleophile cation-radical and the peroxide radical-anion. The formation of the reactive intermediate occurs when the peroxide radical anion undergoes non-reversible oxygen-oxygen bond breakage. Therefore, the subsequent proton abstraction will have no effect on the rate determining step and will not influence the isotope effect on \( k_{obs} \). The large isotope effect observed for the diphenylhydroxylamine-BPO reaction may not be unusual for a \( \beta \)-deuterium that is bonded to an oxygen atom instead of to a carbon atom. In the transition state of the electron transfer reaction the \( p \)-orbitals of oxygen probably interact with the electron deficient \( p \)-orbital of the nitrogen atom, and the resulting weakening of the \( O-D \) bond in the transition state would be much greater than it would be for a \( C-D \) bond.

We believe that the use of kinetic isotope effects will prove very useful in discovering additional electron transfer reactions. Because it is not necessary to have extremely precise data, this method can be used with many analytical techniques. This method should be especially
useful in detecting electron transfer reactions that do not produce scavengable free radicals.
D. References Chapter VII

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APPENDIX I

Collected Graphs
Figure AI-1. A Plot of $\log\left(\frac{d[TBP]}{dt}\right)_0$ vs. $\log$ TBP for the Reaction of TBP with Me$_2$S; 1.0 M Me$_2$S in CCl$_4$ at 80°.
Figure AI-2. A Plot of $\log k^i$ vs. $\log [Me_2S]$ for the Reaction of TBP with $Me_2S$; 0.01 M TBP in CCl$_4$ at 80°.
Figure AI-3. A Plot of $\log \left( \frac{d[TBP]}{dt} \right)_0$ vs. $\log [TBP]$ for the Reaction of TBP with $\text{Me}_2\text{S}$ in 0.2 M Styrene; 1.0 M $\text{Me}_2\text{S}$ in $\text{CCl}_4$ at 80°.
Figure AI-4. A Plot of $\log k^i_S$ vs. $\log [Me_2S]$ for the Reaction of TBP with $Me_2S$ in 0.2 M Styrene; 0.01 M TBP in $CCl_4$ at 80°.
Figure AI-5. A Plot of the Arrhenius Equation for the Homolysis of Phenyl-Substituted tert-Butyl Peroxybenzoates; 0.01 M Perester in CCl₄, p-CH₃O-TBP ●, TBP △, p-Cl-TBP ○, p-NO₂-TBP ■, 3,5-(NO₂)₂-TBP ▲.
Figure A1-6. A Plot of $\log \left( \frac{dC}{dt} \right)_H$ vs. $\log$ [Perester] for Perester Homolysis; 6x10$^{-4}$ M Galvinoxyl in CCl$_4$ at 80°, p-CH$_3$O-TBP , TBP △, p-Cl-TBP ○, p-NO$_2$-TBP ■.
Figure AI-7. A Plot of $\log \left( \frac{dG}{dt} \right)_S$ vs. $\log [p^{-\text{NO}_2-\text{TBP}}]$ for the Reaction of $p^{-\text{NO}_2-\text{TBP}}$ with $\text{Me}_2\text{S}$; $6 \times 10^{-4}$ M $\text{Galvinoxyl}$, 1.0 M $\text{Me}_2\text{S}$ in $\text{CCl}_4$ at $80^\circ$. 

SLOPE = 1.04
Figure AI-8. A Plot of \( \log \left( \frac{dG}{dt} \right)_S \times 10^8, \text{M sec}^{-1} \) vs. \( \log 10 \left[ \text{Me}_2 \text{S} \right] \) for the Reaction of \( p-\text{NO}_2\)-TBP with \( \text{Me}_2 \text{S} \); \( 6 \times 10^{-4} \text{ M} \) Galvinoxyl, \( 0.05 \text{ M} \ p-\text{NO}_2\)-TBP in \( \text{CCl}_4 \) at \( 80^\circ \).
Figure AI-9. A Plot of $\log \, R_p$ vs. $\log [TBP]$ for Styrene Polymerization Initiated by TBP Homolysis; Neat Styrene at 80°.
Figure AI-10. A Plot of $\log R^i_p$ vs. $\log [\text{TBP}]$ for Styrene Polymerization Initiated by the Reaction of TBP with $\text{Me}_2\text{S}$; 1.0 M $\text{Me}_2\text{S}$ in Styrene at 80°.
APPENDIX II

Styrene Polymerization

The best procedure for following styrene polymerization is dilatometry. In this method the change in volume of a styrene solution is measured during polymerization. After proper calibration of the apparatus, the rate of polymerization can be calculated from the rate of volume change. Thus the rate of change of monomer concentration \( \frac{dM}{dt} \) at any time can be found. Equation 1 gives the rate of monomer disappearance where \([M]\) is the monomer concentration, \(k_p\) is the rate of propagation, \(k_t\) is the rate of termination, and \(R_i\) is the rate of initiation. For perester homolysis \(R_i\) is given by Eq. II-18. Substitution of Eq. II-18 into Eq. 1 yields Eq. 2 which can be rearranged to Eq. 3. Equation 3 predicts that a plot of

\[
\frac{-dM}{dt} = [M] \left( \frac{k_p^2}{2k_t} \right)^{1/2} (R_i)^{1/2} \quad (1)
\]

\[
R_i = 2f_{H^eH^k}^H[I]_0 e^{-k_Ht} \quad \text{II-18}
\]

\[
R_p = -\frac{dM}{dt} = \left\{ \frac{k_p^2}{k_t} [I]_0 \right\}^{1/2} e^{-k_Ht/2} (f_{H^eH^k}^H)^{1/2}[M] \quad (2)
\]

\[
\frac{1}{[M]} \frac{dM}{dt} = \left\{ \frac{f_{H^eH^k}^H k_p}{k_t} [I]_0 \right\}^{1/2} e^{-k_Ht/2} \quad (3)
\]

233
\[
\ln \left( \frac{\text{d}M}{\text{d}t} \right) \text{ versus time yields a line of slope } k_H/2 \text{ with an intercept:}
\]
\[
f_H^2 \frac{\varepsilon_H k_H}{k_t} \left( \frac{[I]}{[M]} \right)^{1/2}.
\]

If \( k_p^2/k_t \) is known, then \( f_H^2 \varepsilon_H k_H \) and \( k_H \) can be measured in one experiment. Dilatometry is necessary in using Eq. 3 because \( \text{d}M/\text{d}t \) must be measured as a function of time; it is very time consuming to obtain the data required for graphing Eq. 3 by gravimetric analysis.

In some special cases Eq. 2 can be used to obtain results from gravimetric data. For example, we used this equation to determine the efficiency of perester homolysis in initiating styrene polymerization. The reaction time was sufficiently short so that the perester concentration remained constant and thus Eq. 2 was replaced by Eq. 4.

\[
R_p = \left( \frac{k_p^2}{k_t} \right) \left( \frac{[I]}{[M]} \right)^{1/2} (f_H^2 \varepsilon_H k_H)^{1/2} \]

The product \( f_H^2 \varepsilon_H \) reported in Table II-8 was obtained from Eq. 4 using gravimetrically determined polymerization rates and a literature value for \( k_p^2/k_t \) at 80°C.¹

For the measurement of \( R'/R \) we need only a ratio of polymerization rates and Eq. 3 can be simplified so that gravimetric analysis can be used. Eq. 5 gives the rate of

\[
R_i' = 2(f_H^2 \varepsilon_H k_H + f_S^2 \varepsilon_S k_S') [I]_0 e^{-(k_H+k_S')t}
\]
radical production by perester in the presence of sulfide. Substitution of Eq. 5 into Eq. 1 gives the rate of polymerization initiated by the perester sulfide solution (Eq. 6).

\[
R'_p = \left[ \frac{k_p}{k_t} \right]^{1/2} [M]^{1/2} [I]^{1/2} \left( k_H \varepsilon H + k_S \varepsilon S \right)^{1/2} - (k_H + k'_S) t/2 e^{-k_H t/2} 
\]

(6)

The ratio of the rate of polymerization initiated by perester in the presence of sulfide to the rate of polymerization initiated by perester alone (Eq. 5/Eq. 2) is expressed by Eq. 7. Solving Eq. 7 for \( R'/R \) yields Eq. 8 which affords a simple method for determining \( R'/R \).

\[
\frac{R'_p}{R_p} = \frac{[M]'(k_H \varepsilon H + k_S \varepsilon S)^{1/2}}{[M](k_H \varepsilon H)^{1/2}} e^{-k'_S t/2} 
\]

(7)

\[
\frac{R'}{R} = \frac{f_H \varepsilon H \varepsilon H + f_S \varepsilon S \varepsilon S}{f_H \varepsilon H \varepsilon H} = \left[ \frac{\frac{dM'}{dt}}{\frac{dM}{dt}} \right]^{2} k'_S t e^{-k'_S t/2} 
\]

(8)

When \( R'_p \) and \( R_p \) are calculated from polymer weights and used in Eq. 7, the reaction time must be short enough so that \( R_p \) is constant over the reaction time; i.e., \( e^{-k'_S t/2} \) between \( t_0 \) and \( t \) must not change. This occurs only over the first few percent of the reaction. For longer reaction times, the rate of polymerization decreases as perester
concentration decreases. Under these conditions the rate of polymerization measured gravimetrically is no longer $dM/dt$; instead it is the integral of $dM/dt$ integrated over the reaction time. Therefore, to use gravimetric analysis over long reaction times Eq. 2 and Eq. 6 must be integrated over the time interval and the ratios of the integrated equations must be used to determine $R'/R$.

Integration of Eq. 2 yields Eq. 10 which is the integrated expression for polymerization initiated by perester homolysis. Integration of Eq. 6 yields Eq. 12

\[
\int_{M_0}^{M_t} \frac{-d[M]}{[M]} = \left( \frac{k_p}{k_t} \right)^{1/2} \left( f_H e_{H/H} k_H \right)^{1/2} \int_0^t e^{-k_H t/2} dt \tag{9}
\]

\[
\ln \frac{[M]_o}{[M]_t} = 2\left( \frac{k_p}{k_t} \right)^{1/2} \left( f_H e_{H/H} k_H \right)^{1/2} \frac{\left( e_{H/H} + f_S e_{S/S} k_S \right)^{1/2}}{k_H + k_S} \int_0^t e^{-(k_H + k_S) t/2} dt \tag{10}
\]

\[
\int_{M_0}^{M_t} \frac{-d[M]}{[M]_t} = \left( \frac{k_p}{k_t} \right)^{1/2} \left( f_H e_{H/H} k_H + f_S e_{S/S} k_S \right)^{1/2} \int_0^t \left[ -\left( k_H + k_S \right) t/2 \right] e^{-(k_H + k_S) t/2} dt \tag{11}
\]

\[
\ln \frac{[M]_0}{[M]_t} = 2\left( \frac{k_p}{k_t} \right)^{1/2} \left( f_H e_{H/H} k_H + f_S e_{S/S} k_S \right)^{1/2} \frac{\left( e_{H/H} + f_S e_{S/S} k_S \right)^{1/2}}{k_H + k_S} \left( 1 - e^{-(k_H + k_S) t/2} \right) \tag{12}
\]
which is the integrated expression for polymerization initiated by perester-sulfide solution. The integrated form of Eq. 7 is obtained by dividing Eq. 12 by Eq. 10 to yield Eq. 13. Upon rearrangement this equation yields an expression for \( \frac{R'}{R} \) (Eq. 14) which can be used to determine \( \frac{R'}{R} \) by gravimetric analysis for any reaction time. \( \frac{R'}{R} \) measured in this way is independent of degree of perester reaction.

\[
\ln \frac{[M]_0'}{[M]_t'} = \left\{ \frac{f_H k_H f_S + f_S k_S}{f_H k_H + f_S k_S} \right\}^{1/2} \frac{k_H}{k_H + k_S} \frac{-(k_H + k_S) t/2}{(1-e^{-(k_H + k_S) t/2})}
\]

(13)

\[
\frac{R'}{R} = \left[ \ln \frac{[M]_0'}{[M]_t'} \frac{k_H + k_S}{k_H} \frac{(1-e^{-k_S t/2})}{-(k_H + k_S) t/2} \right]^2
\]

(14)

Both Eqs. 8 and 14 were used to calculate \( \frac{R'}{R} \) for the perester-sulfide reactions. Table AIX-1 shows the data.

For the slower reacting peresters the rate of initiation \( -k_p' t/2 \) remained constant over the reaction time (\( e^{-(k_H + k_S) t/2} \) indicates the decrease in \( R_p' \)), and the integrated or non-integrated equation produces the same results. However, because the nitro-substituted perester has such a low efficiency, longer reaction times were necessary. Furthermore since
### TABLE AII-1

Styrene Polymerization Initiated
by the Methyl Sulfide Perester Reaction

<table>
<thead>
<tr>
<th>Perester</th>
<th>Reaction Substituent Time hr.</th>
<th>e^{-k'_s't/2}</th>
<th>$\frac{R'}{R}$ From Eq. 8</th>
<th>$\frac{R'}{R}$ From Eq. 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>1</td>
<td>0.98</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>0.97</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
<td>0.94</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>1.5</td>
<td>0.64</td>
<td>13</td>
<td>20</td>
</tr>
</tbody>
</table>

a. 0.05 M perester at 80°.

b. Calculated from weight of polymer formed during reaction time.
this perester reacts very fast, the rate of initiation was not constant. This resulted in a difference in \( R'/R \) calculated by the two equations. As expected, the integrated equation gives a lower value than the non-integrated equation. Therefore, when the rate of polymer initiation is not constant, Eq. 14 must always be used for gravimetric analysis. The necessity of using Eq. 14 is demonstrated by the work of Pryor and Bickley.²

As mentioned earlier, the method used in these experiments is the same method that Pryor and Bickley used to show that the benzoyl peroxide-disulfide reaction does not yield radicals. Thus \( f^S_e S_k^i \) is not included in the previous equations and Eq. 7 is simplified to Eq. 15 and Eq. 13 is simplified to Eq. 16. According to Eq. 15, if the benzoyl

\[
\frac{R'_p}{R_p} = \frac{[M]}{[M]^s} e^{-k^t_s t/2} \quad (15)
\]

\[
\ln \frac{[M]_t'}{[M]_t^0} = \frac{k_H}{(k^t_s + k_H)} \left( 1 - \exp \left( \frac{-(k^t_s + k_H) t/2}{(1 - \exp(-k_H t/2))} \right) \right) \quad (16)
\]

peroxide-disulfide reaction does not produce radicals, then the observed ratio of polymerization rates \( (R'_p [M]/R[M]^s) \) should be equal to the calculated ratio of polymerization rates \( e^{-k^t_s t/2} \). The results for several
disulfides are listed in Table AII-2. Because of different reaction rates, the extent of the reaction was variable for each disulfide; all reactions were run for the same time. As more of the peroxide reacted, the agreement in the observed and calculated values lessened. As \( e^{-k_s't/2} \), a measure of the extent of reaction, decreased, the ratio of the observed value to the calculated value increased. According to the results of the fastest reaction, four times as much polymer is being formed than should be. This is not because the benzoyl peroxide-disulfide reaction is producing radicals but because an integrated expression was not used to calculate \( R_p^t/R_p \).

The calculated value of \( R_p^t/R_p \) from Eq. 15 gives the rate of polymerization at time \( t \). The observed value of \( R_p^t/R_p \) measured by gravimetric analysis gives the average rate of polymerization between \( t_0 \) and \( t \). As \( dM/dt \) becomes slower at high peroxide conversion, the agreement in \( dM/dt \) and the average rate of polymerization becomes poorer. These results show that at high peroxide conversion Eq. 15 leads to erroneous results.

We have recalculated the data for benzoyl peroxide-disulfide reactions using the integrated expression for \( R_p^t/R_p \) (Eq. 16). These results in Table AII-2 do not vary with reaction rate. There is a constant error; however, the observed rate is always less than the calculated rate.
TABLE AII-2

The Benzoyl Peroxide Initiated Polymerization of Styrene in the Presence of Disulfides

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>[RSSR]</th>
<th>k_s x10^{-4}</th>
<th>( \frac{R'_p[M]}{R'<em>p[M]</em>{obs}} )</th>
<th>-k_S't/2</th>
<th>( \frac{obs}{calc} )</th>
<th>( \frac{cal}{Eq. 16} )</th>
<th>( \frac{obs}{calc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl</td>
<td>0.183</td>
<td>0.640</td>
<td>0.44</td>
<td>0.56</td>
<td>0.78</td>
<td>0.84</td>
<td>0.52</td>
</tr>
<tr>
<td>t-Butyl</td>
<td>0.191</td>
<td>0.707</td>
<td>0.45</td>
<td>0.53</td>
<td>0.85</td>
<td>0.74</td>
<td>0.61</td>
</tr>
<tr>
<td>t-Amyl</td>
<td>0.234</td>
<td>1.01</td>
<td>0.48</td>
<td>0.40</td>
<td>1.2</td>
<td>0.66</td>
<td>0.61</td>
</tr>
<tr>
<td>Methyl</td>
<td>0.198</td>
<td>1.13</td>
<td>0.20</td>
<td>0.36</td>
<td>0.56</td>
<td>0.64</td>
<td>0.31</td>
</tr>
<tr>
<td>t-Butyl</td>
<td>0.596</td>
<td>2.20</td>
<td>0.24</td>
<td>0.14</td>
<td>1.7</td>
<td>0.44</td>
<td>0.55</td>
</tr>
<tr>
<td>t-Butyl</td>
<td>0.963</td>
<td>3.60</td>
<td>0.16</td>
<td>0.04</td>
<td>4.0</td>
<td>0.29</td>
<td>0.55</td>
</tr>
</tbody>
</table>

a. 60°, data from ref. 1, reaction time is 5 hr.

\[
\ln \frac{[M]_0}{[M]_t}
\]

b. Equivalent to \( \ln \frac{[M]_0}{[M]_t} \).

c. Column 4/column 5.
e. Calculated from rate constant at 100°.
This proves that in all the reactions no radicals are being produced by the reaction of benzoyl peroxide with disulfide.
APPENDIX III

An Alternate Decomposition Path for the TBP Radical-Anion

Scheme AIII-1 presents an alternate mechanism for the electron transfer reaction between TBP and Me₂S. Both this scheme and Scheme VI-1 have the same rate determining electron transfer step, but differ in the decomposition products of the TBP radical anion. In Scheme VI-1 we assumed that the decomposition products are a tert-butoxy radical and a benzoate anion, which are consistent with the expected radical and anion stabilities and with the products of the internal electron transfer reaction of sulfide and TBP studied by Martin and Bentrude. However, we cannot exclude the possibility that the TBP radical-anions may decompose to form tert-butoxide anions and benzoyloxy radicals. The following discussion demonstrates that if this were the mode of TBP radical-ion decomposition, the experimental results would still be consistent with an electron transfer reaction.

Eq. 1. This equation is identical to Eq. 6 of Scheme VI-1 except for the formation of benzoyloxy radicals and tert-butoxide ions, and the same discussion that applies to Eq. 6 also applies to this equation.

Eq. 2. If the TBP-Me₂S reaction produced a large number of scavangeable free radicals, it would be possible to identify the radicals in the system and thus determine
SCHEME AIII-1

An Alternate Electron Transfer Mechanism for the Methyl Sulfide-TBP Reaction

\[ \text{CH}_3\text{SCH}_3 + \text{TBP} \xrightarrow{\text{1}} \text{CH}_3\text{S}^+ \xrightarrow{\text{2}} \text{CH}_3\text{SCH}_3 + \text{PhCO}_2^- + \text{t-BuO}^- \] (1)

\[ \text{3} \rightarrow \text{CH}_3\text{SCH}_3 + \text{PhCO}_2^- + \text{t-BuO}^- \] (2)

\[ \text{CH}_3\text{S}^- \xrightarrow{\text{4}} \text{CH}_3\text{S}=\text{CH}_2 + \text{PhCO}_2\text{H} \rightarrow \text{CH}_3\text{SCH}_2\text{OBu-t} \] (3a)

\[ \text{CH}_3\text{S}=\text{CH}_2 + \text{HOBu-t} \rightarrow \text{CH}_3\text{SCH}_2\text{OCPh} \] (3b)
245

(4)

(5)
the decomposition products of the TBP radical-anion. However, since scavengable free radicals amount to only 2-3% of the total reaction products and since nearly 75% of the radical products are derived from TBP homolysis (which produces both tert-butoxy and benzoyloxy radicals, we are not able to determine which radicals are produced by the TBP radical-anion. An attempt to identify the anion product of the TBP radical anion will be complicated by the well-documented propensity of alkoxy sulfonium salts to undergo alkoxy exchange (pp 145-146). Undoubtedly, both benzoate and tert-butoxide ions are present in this system. Therefore, it is not feasible to identify the path of the TBP radical anion decomposition by attempting to trap and identify the reactive intermediates.

Eq. 3. The ionic components of 3 can combine to form 4, and the radical components of 3 can combine to form 7. In either case, further combinations within 4 and 7 can lead to the tetracovalent sulfur compound 6. As discussed on pp. 147-148, 5, 6, and 7 are probably in equilibrium, and reaction products are formed from the equilibrium as a result of proton abstraction by tert-butoxide to form the ylide 8, which rearranges to BOMS (Eq. 3b). When the reaction is run in styrene to reduce induced decomposition, Eq. 3b can account for 90% of the reaction products (Table II-15). The transformation of 5 to 11 would not be expected because benzoate, a weaker base than tert-butoxide,
would rather displace tert-butoxide to form 7 rather than abstract a proton to form 11, and therefore, products are only formed from 5, 6 and 7 via ylide 8. Ylide 11 could be formed from 4 by hydrogen atom abstraction by the benzoyloxy radical. However, the absence of a detectable amount of benzoic acid when the reaction is run in styrene indicates that the formation of 11 from either 4 or 5 must be a minor pathway.

Eq. 4. Eq. 4 is very similar to Eq. 3a; the only difference is the sequence of ion combination and radical abstraction. Due to the non-detection of benzoic acid, this reaction must also be a minor reaction.

Eq. 5. Intermediate 10 can be formed from 3 if tert-butoxide abstracts a proton from the methyl sulfide cation-radical. A rapid cage recombination of the radical components of 10 would then produce BOMS. It is possible that Eq. 5 is the source of radicals; however, it is not a major pathway because the large yield of BOMS in styrene indicates that it is formed by the ionic path, Eq. 3b, and not by a radical path.

A comparison of Scheme VI-1 and Scheme AIII-1 shows that in both reactions the major reaction products are intermediates 5, 6, and 7. Because of the ease of alkoxy exchange between 5 and 7 and because of the unstability of 6, these intermediates are in equilibrium. Since the equilibrium decomposes mostly, if not totally through ylide
8, the reaction products are the same for the initial formation of 5 (Scheme VI-1) or for the initial formation of 7 (Scheme AIII-1). The two schemes differ in the radical producing reactions, but because these are minor reactions, it is not possible to ascertain the actual reaction path. Nevertheless, the important characteristic of this reaction is not the subsequent reactions of the reactive intermediates, but is instead the rate determining electron transfer reaction. The subsequent reactions are of some importance, but they do not have the significance of the electron transfer step.
REFERENCES TO APPENDICES


4. The rate of radical production by the TBP-Me₂S system (R₃) is only about 25% of the rate of the radical production by TBP homolysis (Table II-13).
VITA

William Harwell Hendrickson, Jr.

Place and Date of Birth:
Ruston, Louisiana; April 23, 1948

Education:
Public School System, Ruston, Louisiana, 1954-1966
Louisiana Tech University, 1966-1970 (B.S., 1970)
Louisiana State University, 1970-1974 (Ph.D., 1974)

Professional Societies:
The Society of Sigma Xi

Positions:
Petroleum Research Fund Undergraduate Research Participant Louisiana Tech University, Summers of 1968 and 1969
N.D.E.A. Fellow 1970-1973
L.S.U. Dissertation-Year Fellow 1974-1974
Candidate:       William H. Hendrickson, Jr.

Major Field:     Chemistry

Title of Thesis: Electron Transfer in Peroxide-Nucleophile Interactions, The
               Reaction of tert Butyl Peroxybenzoates with Sulfide.

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

November 15, 1974