Kinetic and product studies
for the oxidation of organic sulfides and sulfoxides
in the presence of transition metal complexes

by

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ABSTRACT

Rates and products of the oxidation of diphenyl sulfide, phenyl methyl sulfide, p-chlorophenyl methyl sulfide and diphenyl sulfoxide have been determined. Oxidants included t-BuO₂H alone, t-BuO₂H plus molybdenum or vanadium catalysts and the molybdenum peroxo complex MoO(O₂)₂·HMPT. Reactions were chiefly carried out in ethanol at temperatures ranging from 20° to 65°C.

Oxidation of diphenyl sulfide by t-BuO₂H in absolute ethanol at 65°C followed second-order kinetics with \( k_2 = 5.61 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1} \), and yielded only diphenyl sulfoxide. The Mo(CO)₆-catalyzed reaction gave both the sulfoxide and the sulfone with consecutive third-order kinetics.

Rate = \( k_3 [\text{Mo}] [t\text{-BuO}_2\text{H}] [\text{Ph}_2\text{S}] + k_3^* [\text{Mo}] [t\text{-BuO}_2\text{H}] [\text{Ph}_2\text{SO}] \), where \( \log k_3 = 12.62 - 18500/RT \), and \( \log k_3^* = 10.73 - 17400/RT \).

In the absence of diphenyl sulfide, diphenyl sulfoxide did not react with t-BuO₂H plus molybdenum catalysts, but was oxidized by t-BuO₂H-VO(acac)₂.

The uncatalyzed oxidation of phenyl methyl sulfide by t-BuO₂H in absolute ethanol at 65°C gave a second-order rate constant, \( k = 3.48 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1} \). With added Mo(CO)₆, the product was mainly phenyl methyl sulfoxide; Rate = \( k_3 [\text{Mo}] [t\text{-BuO}_2\text{H}] [\text{PhSCH}_3] \) where \( \log k_3 = 22.0 - 44500/RT \).
Both diphenyl sulfide and diphenyl sulfoxide react readily with the molybdenum peroxy complex, MoO(O_{2})_{2}\cdot HMPT in absolute ethanol at 35°C, yielding diphenyl sulfone.

The observed features are mainly in agreement with the literature on metal ion-catalyzed oxidations of organic compounds by hydroperoxides. These indicate the formation of an active catalyst and the complexation of t-BuO_{2}H with the catalyst. However, the relatively large difference between the activation energies for diphenyl sulfide and phenyl methyl sulfide, and the non-reactivity of diphenyl sulfoxide suggest the involvement of sulfide in the production of an active species.
To

İsmail and Handan Köseoğlu

and Ömer Erböyükbaşi
ACKNOWLEDGEMENTS

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Semih Sefa Köseoğlu
August 1980
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Heterolytic Reactions of Peroxides

Hydroperoxides are known where the attachment of O-H is to C, Si, Ge, Sn or S. However, compounds in which carbon is attached to O-H, ROOH and RC-O-OH are most commonly used and examined. Many papers have been written concerning the reactions of these compounds. There are at least ten reviews (1-10) and seven books dealing exclusively or partially with peroxides (11-17).

Free radical reactions are common in peroxide reactions. However, many reactions of peroxides proceed through polar mechanisms.

The earlier work for non-radical reactions of peroxides has been done by Swern (18). Excellent recent reviews have been covered by Swern (19). Also, there are some reviews by Edwards (1) and Bunton (20) who have reviewed the field with references through 1961. A particularly early study of the electrophilic behaviour of peroxides in reactions with electron pair donors has been done by Boeseken and Swern (21).

Reactions occur with a variety of peroxides with many types of substrates such as sulfides, sulfoxides, amines, hydroxylamines, olefins, phosphines and phosphites.

General characteristics and a proposed model have been given by J. O. Edwards (1) in the light of previous work.
On the basis of above model, the characteristics of the reaction should be as follows:

(a) Reaction should follow a second order rate law (first-order each in peroxides and in nucleophile).

(b) Reaction rate should be related to the basicity of the leaving group \( R'O^- \).

(c) Definite orientation of reactants in T.S. should result in a negative value of \( \Delta S^+ \).

(d) Because of unshared electrons on the oxygen atom, the rate should be sensitive to acid catalysts.

All of the substrates previously mentioned are rapidly oxidized by peroxycids. Smooth oxidations by hydroperoxides frequently requires a catalyst, however. Organic sulfides are an exception; oxidation to sulfoxides proceeds quite readily, so that the possibility of catalysis, other than by proton acids, has received little attention.

Oxidation of organic sulfides by perox acids, hydrogen peroxide and hydroperoxides

Reactions of organic sulfides with either hydrogen peroxide or hydroperoxides normally yield the sulfoxide whereas peracids readily produce sulfones. The rates of the oxidation of sulfide to sulfoxide
and sulfoxide to sulfone differ greatly. For example, peracetic acid in acetic acid oxidizes diphenyl sulfide to sulfoxide about a thousand times faster than the sulfoxide to sulfone (22). In contrast to the first stage of oxidation, there is little quantitative information about the second stage of oxidation. It is assumed that the same mechanism operates for it.

By Peroxy Acids

Overberger and Cummins (23) examined the oxidation of p,p'-dichloro-benzyl sulfide by peroxybenzoic acid and para substituted peroxybenzoic acids in toluene and isopropyl alcohol at -20 to -65°C.

They found the reaction to be first order in peroxyacid and first order in sulfide, with no apparent catalysis from the resulting benzoic acid. The reactions were characterized by low enthalpies of activation (5-11 kcal/mol) and large negative entropies of activation (-16 to -34 e.u.). Electron withdrawing substituents on the peroxyacid increased the rate, a Hammett plot giving $\rho = +0.91$. The authors suggested that the reaction occurs by a nucleophilic attack of a cyclic hydrogen bonded form of the peroxy acid by sulfide.

\[
\begin{align*}
R-\text{C}_6\text{H}_4\text{O}--\text{H} + \text{S}^- & \rightarrow R-\text{C}_6\text{H}_4\text{O}--\text{H} \rightarrow R-\text{C}_6\text{H}_4\text{O}^- + \text{S}^- \\
& [2]
\end{align*}
\]
The oxidation proceeds faster in toluene than in isopropyl alcohol with lower energies and entropies of activation. Rate studies by Modena and coworkers (24-26) with peroxybenzoic acid in a variety of solvents (CHCl₃, CH₂Cl₂, CCl₄, benzene, nitrobenzene, DMF, dioxane, t-BuOH, i-PrOH, EtOH, MeOH, CF₃CH₂OH) demonstrated a rate increase with a change of solvent character from basic to non-basic solvents. There appears to be a general correlation of the rates with the capacity of peroxo acids to exist in either a chelate form (A) or an open-chain, solvated configuration (B).

![Chemical structures](image)

The possibility of catalysis by strong acids seems to have been little explored. However, Modena and Todesco (24) do mention that presence of trifluoroacetic acid as a catalyst accelerates the reaction of diaryl sulfides with peroxybenzoic acid.

**By hydrogen peroxide and hydroperoxides**

The early mechanistic studies were performed by Bateman and coworkers (27-31) using both saturated and unsaturated sulfides with t-butyl and cyclohexenyl hydroperoxides. More recently, Curci and Edwards (32) have studied the reaction of H₂O₂ with thioxane.
In the hydroxylic solvents, the reaction is a second order overall, first order in both hydroperoxide (or H2O2) and sulfide. It is not retarded by free radical inhibitors, but is subject to acid catalysis. The stoichiometry is 1:1 as in equation 3.

\[ \text{R}_2\text{S} + \text{R'}\text{O}_2\text{H} \rightarrow \text{R}_2\text{SO} + \text{R'}\text{OH} \]  

[3]

Two mechanisms are offered to explain the above observations. The first (equation 4) consists of a one-step interaction of sulfide with hydroperoxide-solvent complex. The second (equations 5-7), involves an acid-base reaction between the peroxide and solvent with the resulting ion ROOH2 as the active oxidant.

\[ \text{RO} \quad \text{O} \equiv \text{SR}_2 \quad \text{H} \quad \text{H} \quad \rightarrow \quad \text{RO} \quad \text{O} \equiv \text{SR}_2 \]  

[4]

\[ \text{RO}_2\text{H} + \text{HX} \leftrightarrow \text{ROOH}_2 + \text{X}^- \]  

[5]

\[ \text{ROOH}_2 + \text{R}_2\text{S} \rightarrow \text{ROH} + \text{R}_2\text{SO} \]  

[6]

\[ \text{R}_2\text{SO} + \text{X}^- \rightarrow \text{R}_2\text{SO} + \text{HX} \]  

[7]

Both mechanisms require the catalytic effect of a solvent, which varies according to its acidity, or added acid which assumes the role of solvent HX. (See Tables 1 and 2.)
### TABLE 1<sup>a</sup>

Oxidation of cyclohexyl methyl sulfide by hydroperoxides

<table>
<thead>
<tr>
<th>Solvent</th>
<th>t-BuO&lt;sub&gt;2&lt;/sub&gt;H</th>
<th>cyclohexenyl-OOH</th>
<th>t-BuO&lt;sub&gt;2&lt;/sub&gt;H</th>
<th>cyclohexenyl-OOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuOH</td>
<td>1.43 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>16.9 -29</td>
<td>11.0 x 10&lt;sup&gt;-5&lt;/sup&gt; b</td>
<td>14.5 -32</td>
</tr>
<tr>
<td>n-BuOH</td>
<td>17.1 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>14.4 -31</td>
<td>165.0 x 10&lt;sup&gt;-5&lt;/sup&gt; b</td>
<td>12.0 -34</td>
</tr>
<tr>
<td>MeOH</td>
<td>22 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>13.5 -33</td>
<td>1270 x 10&lt;sup&gt;-5&lt;/sup&gt; b</td>
<td>10.4 -35</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>230 x 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>12.1 -34</td>
<td>560 x 10&lt;sup&gt;-5&lt;/sup&gt; c</td>
<td>10.9</td>
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<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td>670 x 10&lt;sup&gt;-5&lt;/sup&gt; c</td>
<td>8.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
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<sup>a</sup> Data from reference 29.

<sup>b</sup> Second order rate constants at 50°C in M<sup>-1</sup>s<sup>-1</sup>.

<sup>c</sup> Third order rate constants at 50°C in M<sup>-2</sup>s<sup>-1</sup>. 
TABLE 2

Hydrogen Peroxide Oxidation of Thioxane and related Cases

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Delta(k(H_2O)/k(solvent))$</th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta S^\ddagger$</th>
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<tr>
<td>CH$_3$CO$_2$H</td>
<td>0.106</td>
<td>--</td>
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<tr>
<td>H$_2$O</td>
<td>1.000</td>
<td>13.0</td>
<td>-27</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>1.68</td>
<td>12.9</td>
<td>-28</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>5.20</td>
<td>13.6</td>
<td>-28</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>41.8</td>
<td>14.5</td>
<td>-29</td>
</tr>
<tr>
<td>2-C$_3$H$_7$OH</td>
<td>226</td>
<td>15.3</td>
<td>-30</td>
</tr>
<tr>
<td>t-C$_4$H$_9$OH</td>
<td>473</td>
<td>17.4</td>
<td>-24</td>
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<tr>
<td>N-methyl acetamide</td>
<td>1170</td>
<td>18.7</td>
<td>-22</td>
</tr>
</tbody>
</table>

aData from reference 32.
Evidence to support the first mechanism comes from comparison of cyclohexenyl hydroperoxide and t-butyl hydroperoxide in their reactions with cyclohexylmethyl sulfide under identical conditions. Cyclohexenyl hydroperoxide reacts faster than the t-butyl hydroperoxide (Table 1). It is also more acidic, and thus presumably less basic towards protonation by solvent. Stronger acidity should facilitate the reaction if the first mechanism is correct, while weaker basicity should disfavour the equilibrium of reaction 5. The large negative $\Delta S^+$ values (Tables 1 and 2) have been cited as favouring the cyclic first mechanism. However, the second mechanism, involving unstable ions requiring solvation could very well also have negative entropies of activation.

Not surprisingly, the oxidizability of sulfide is enhanced by electron donating groups and lowered by electron withdrawing groups (33).

In the non-hydroxylic solvents (30), the reaction is more complicated. In the simplest case, the role of solvent (HX) is assumed by a second molecule of hydroperoxide, and kinetically the reaction becomes second order with respect to hydroperoxide and first order with respect to sulfide.
It is regarded as a bimolecular interaction of the sulfide with dimeric hydroperoxide. The dimer is the dominant component in the neat hydroperoxide solution as has been mentioned by Bateman and Hughes (30) in their infrared studies.

In the absence of alternative hydrogen bonding substances such as alcohols, the weakly basic product sulfoxide forms a bond with hydroperoxide which causes a retarding effect on the rate of reaction. Also, other organic bases cause a retarding effect.

Addition of an acid stronger than the hydroperoxide changes the order of hydroperoxide from two to one.

Fractional orders (0.4-0.7) in sulfide concentration have been observed in some solvents and the reaction is subject to catalysis by oxygen. This behaviour has never been satisfactorily explained. In general, it seems best to stay away from non-hydroxylic solvents.
**Metal catalyzed reactions of hydroperoxides**

The metal catalyzed reactions of hydroperoxides may be divided into two classes which can be designated as homolytic or heterolytic.

The metal ion can cause homolytic decomposition of a hydroperoxide either through reductive or oxidative cleavage. Some metals, such as Co or Mn, can do both.

\[
\begin{align*}
RO_2H + \text{Co}^{II} & \rightarrow \text{Co}^{III} + RO^\cdot + OH^- & [9] \\
RO_2H + \text{Co}^{III} & \rightarrow \text{Co}^{II} + RO_2^\cdot + H^+ & [10]
\end{align*}
\]

In other cases, catalytic activity depends on regeneration of the reductive ion. For example, mixtures of copper(II) and copper(I) catalytically reduce tert-amyl hydroperoxide in acetonitrile-acetic acid at 0°C (34). Copper(I) is regenerated via electron transfer oxidation of the ethyl radicals formed by the fragmentation of tert-amyloxy radicals.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C(CH}_3\text{)}_2\text{O}_2\text{H} + \text{Cu}^I & \rightarrow \text{Cu}^{II}(\text{OH}) + \text{CH}_3\text{CH}_2\text{C(CH}_3\text{)}_2\text{O}^\cdot & [11] \\
\text{CH}_3\text{CH}_2\text{C(CH}_3\text{)}_2\text{O}^\cdot & \rightarrow (\text{CH}_3\text{)}_2\text{CO} + \text{C}_2\text{H}_5^\cdot & [12] \\
\text{C}_2\text{H}_5^\cdot + \text{Cu}^{II} & \rightarrow \text{C}_2\text{H}_4 + \text{Cu}^I + H^+ & [13]
\end{align*}
\]

Heterolytic reactions of hydroperoxides catalyzed by metal ions are distinguished from homolytic reactions in that no evidence exists for paramagnetic intermediates, products from \( \beta \)-scission of alkoxy radicals are not found, and product mixtures are generally simple. Rather few
metals, chromium, vanadium, molybdenum and tungsten, are effective. These, in their highest oxidation state \((\text{Cr}^{VI}, \text{V}^{V}, \text{Mo}^{VI}, \text{W}^{VI})\), as (frequently ill-defined) complexes, are sufficiently strong Lewis acids to complex the hydroperoxide (equation 14), reducing the electron density on the peroxidic oxygen, and permitting nucleophilic attack by a substrate (equation 15). Equally important, they are not such strong acids as to tear the hydroperoxide apart before the substrate gets there, as for example \(\text{AlCl}_3\) or \(\text{BF}_3\), nor are they strong one-electron oxidizing reagents.

\[
\begin{align*}
M^n + \text{RO}_2\text{H} & \rightleftharpoons k_c \frac{k}{k_c} [M^n\text{RO}_2\text{H}] \quad [14] \\
[M^n\text{RO}_2\text{H}] + S & \rightarrow k_e S\text{O} + \text{ROH} + M^n \quad [15]
\end{align*}
\]

The homolytic reduction/oxidation (equations 16 and 17) does compete, but usually ineffectually.

\[
\begin{align*}
[M^n\text{RO}_2\text{H}] & \rightarrow k_d M^{(n-1)} + \text{RO}_2^- + \text{H}^+ \quad [16] \\
M^{(n-1)} + \text{RO}_2\text{H} & \rightarrow \text{fast} M^n + \text{RO}^- + \text{HO}^- \quad [17]
\end{align*}
\]

In many respects, a hydroperoxide plus a suitable metal catalyst mimics the reactivity of a per oxyacid, epoxidizing olefins, oxidizing amines to amine oxides and sulfoxides to sulfones. Heterolytic oxidations which a hydroperoxide performs without catalysis, such as the
conversion of sulfides to sulfoxides or of phosphines to phosphine oxides are enormously accelerated by catalytic amounts of $V^{V}$ or $Mo^{VI}$. (It should be mentioned that the metal ion need not be in its high oxidation state when added to the reaction medium. The hydroperoxide itself quickly performs that oxidation.)

**Metal ion-catalyzed epoxidation of olefins**

The synthetic utility of hydroperoxide-molybdenum (or vanadium) combinations, particularly with respect to oxidation of alkenes and alkynes has been recently reviewed by Sharpless and Verhoeven (35). The kinetic and mechanistic aspects have been discussed previously by Hiatt (36) and by Sheng and Zajacek (37).

The kinetics of epoxidation have been reported for 1- and 2-octene, and 2-methyl-1-pentene, in the presence of molybdenum hexacarbonyl (37, 38) and for cyclohexene with vanadium acetylacetonate (39). Also the substitution effects in aromatic systems was investigated by Howe and Hiatt (40) (Table 3).

Sheng and Zajacek (37, 38) have reported the effects of catalysts, solvent, temperature, olefin structure, hydroperoxide structure, oxygen, carbon monoxide and the stereochemistry for the reaction of 1- and 2-octene with p-nitrocumene, cumene and tertiary butyl hydroperoxides in the presence of molybdenum hexacarbonyl.

They have shown that molybdenum compounds, including oxides, sulfides, halides, salts, heteropolymolybdic acids, salts of heteropolymolybdic acids, esters of heteropolymolybdic acids, and molybdenum
coordination compounds are superior catalysts in these reactions. Reactions are slow below 90°C, but increase with increasing temperature.

Non-polar solvents such as benzene and methylcyclohexane are more effective solvents than polar solvents such as ethyl alcohol, and tertiary butyl alcohol. Low effectiveness of the polar solvent comes from competitive reaction between the solvent and the hydroperoxide for the molybdenum catalyst. Also the reaction rate increases with the more alkyl substituents on the double bond. The substitution of an electron withdrawing group in the para position of cumene hydroperoxide increases the rate of reaction. Presence of oxygen in the oxidation showed no effect on the rate, but it reduced the life of the catalyst. However, under the carbon monoxide atmosphere, the reaction rate is retarded due to the need to change at least one ligand by hydroperoxide. Another of their findings was the stereospecificity of the reaction. Pure cis- and trans-2-butene oxidation gave exclusively the corresponding cis- and trans- epoxides respectively.

The data obtained by Sheng and Zajacek indicate that epoxidation reaction proceeds according to the rate law:

\[
\text{Rate} = k[t-\text{BuO}_2\text{H}][\text{olefin}][\text{Mo(Co)}_6]
\]  

Howe and Hiatt (40) also found this rate expression to apply for the epoxidation of styrene and some substituted styrenes with t-butyl hydroperoxide and molybdenum naphthanate (Table 3).
TABLE 3
Oxidation of olefins by t-BuO₂H in the presence of a metal catalyst

<table>
<thead>
<tr>
<th>Styrenes</th>
<th>Solvent</th>
<th>$k_2 \mathrm{d} \times 10^6 \mathrm{M}^{-1} \mathrm{min}^{-1}$</th>
<th>$k_3 \mathrm{c} \mathrm{L}^{-2} \mathrm{M}^{-2} \mathrm{s}^{-1}$</th>
<th>Temp $\degree \mathrm{C}$</th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta S^\ddagger$</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Cl</td>
<td>benzene</td>
<td>21.8</td>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>Mo(naphth)</td>
</tr>
<tr>
<td>p-Cl</td>
<td>benzene</td>
<td>30.5</td>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>Mo(naphth)</td>
</tr>
<tr>
<td>m-Br</td>
<td>benzene</td>
<td>26.1</td>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>Mo(naphth)</td>
</tr>
<tr>
<td>m-NO₂</td>
<td>benzene</td>
<td>31.0</td>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>Mo(naphth)</td>
</tr>
<tr>
<td>p-Me</td>
<td>benzene</td>
<td>3.10</td>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>Mo(naphth)</td>
</tr>
<tr>
<td>p-H</td>
<td>benzene</td>
<td>26.7</td>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>Mo(naphth)</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>cyclohexane</td>
<td>3.02</td>
<td></td>
<td>41.3</td>
<td>12.7</td>
<td>-19.8</td>
<td>V0(acac)$_2$</td>
</tr>
<tr>
<td>l-octene</td>
<td></td>
<td>0.059</td>
<td>84.2</td>
<td>19.1</td>
<td>-14.2</td>
<td>Mo(CO)$_6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.021</td>
<td>71.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Data from reference 40.

b Data from reference 39.

c Data from references 37, 38.

d Rate = $k[M][RO_2H][substrate]$; $k_3 = k$; $k_2 = k[M]$. 
On the other hand, in the epoxidation of cyclohexene by tertiary butyl hydroperoxide in the presence of vanadium acetylacetonate, Gould et al. (39) found first order dependence on cyclohexene and on catalyst, but the dependence on hydroperoxide concentration was analogous to the Michaelis-Menten equation for enzyme catalysis. The rate of epoxidation was retarded by tertiary-butyl alcohol which is a reaction product.

In contrast to molybdenum catalyzed oxidation, vanadium catalyzed oxidation showed a rapid catalyst deactivation. It appears that for epoxidation of olefins, molybdenum compounds are more active catalysts than vanadium compounds.

**Metal catalyzed oxidation of amines**

Sheng and Zajacek (41) have studied catalysis by groups VB and VIB transition metals of the oxidation of tertiary amines to amine oxides by hydroperoxides.

\[
\begin{align*}
\text{R}_2^2 & \quad \text{R}^1_1 - \text{N} - \text{R}^3_3 + \text{ROOH} \quad \text{cat.} \quad \text{R}^1_1 - \text{N} - \text{R}^3_3 + \text{ROH} \\
\end{align*}
\]

They found that vanadium is the most active species. Molybdenum also catalyzes the reaction, but it is less active than vanadium. Tungsten, niobium, tantalum, chromium, cobalt and manganese are poor catalysts. The relative reactivity of hydroperoxides was found to be t-amyl ≥ cumyl > t-butyl. Retardation of the rate by the alcoholic
solvents was interpreted a competitive complexing with catalyst and hydrogen bonding with the hydroperoxide.

Howe and Hiatt (42) have used $\text{VO(acac)}_2$ and $\text{t-BuO}_2\text{H}$ to oxidize anilines to the corresponding nitrobenzenes.

The reaction is first order in aniline but suffers from auto-inhibition by $\text{t-BuOH}$ and catalyst degradation. A Hammett plot obtained from initial rates gave a $\rho$-value of -1.63.

**Metal ion catalyzed oxidation of phosphines, arsines, stibines**

Oxidations of triphenylphosphine (43, 44), triphenyl arsine and triphenylstibine (45) by a hydroperoxide to their corresponding oxides is rapid, but can be made even faster by addition of catalytic amounts of molybdenum or vanadium compounds.

\[
\begin{align*}
\text{Ph}_3\text{P} + \text{RO}_2\text{H} \xrightarrow{\text{V(naphth)}} & \text{Ph}_3\text{PO} + \text{ROH} \\
\text{Rate} & = [\text{Ph}_3\text{P}][\text{RO}_2\text{H}](k_2 + k_3[V])
\end{align*}
\]

For triphenyl phosphine, it was found (44) that molybdenum naphthenate and $\text{MoO}_2\text{(acac)}_2$ were equally effective catalysts, while vanadium naphthenate was 1/10 as effective as the molybdenum compounds. n-Butyl hydroperoxide proved to be 10 times as reactive as t-butyl hydroperoxide.
The third-order rate constants for Ph₃P, Ph₃As and Ph₃Sb are shown in Table 4. It should be noted that while the reactions are all quite fast, they do not proceed at the same rate.

**Metal ion catalyzed reactions of organic sulfides**

Modena and coworkers (46, 47) have recently reported studies of the reaction of di-n-butyl sulfide with t-butyl hydroperoxide in dry ethanol at 25°C, catalyzed by dioxomolybdenum(VI) acetylacetonate (46) and by bisacetylacetonatooxovanadium(IV) (47). For individual reactions, the kinetics conform to a rate law which is first order with respect to sulfide, catalyst and hydroperoxide for both catalysts. However, the apparent rate constants are dependent on the initial concentration of hydroperoxide, and the data conform to a Michealis-Menton type rate law.

\[
\text{Rate} = k[\text{cat}]_0[t-BuO_2H]/(k_1 + [t-BuO_2H])_0
\]  

[23]

where \( k = k_{[n-Bu_2S]} \).

No sensitivity towards free radical inhibitors or towards nitrogen vs. air atmosphere was observed. Also the reaction products did not retard the rate.

G. Modena et al. (48) have clarified the catalyst activation step, at least for VO(acac)₂. Both spectroscopic and potentiometric evidence indicates that in alcoholic solvents (ROH) and in the presence of t-butyl hydroperoxide, the oxoacetyl acetonate is rapidly oxidized and converted to a vanadate ester VO(OR)₃.
TABLE 4

The reaction of Group V nucleophile with t-BuO₂H and V naphthenate in ethanol.¹

<table>
<thead>
<tr>
<th>R₃M</th>
<th>k₃ \times 10^{-4} M^{-2} s^{-1}</th>
<th>E_a (kcal mol⁻¹)</th>
<th>log A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃P</td>
<td>1.0 (25)</td>
<td>11.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Ph₃As</td>
<td>0.42 (35)</td>
<td>15.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Ph₃Sb</td>
<td>2.7 (25)</td>
<td>9.7</td>
<td>6.7</td>
</tr>
</tbody>
</table>

¹ Data from references 44 and 45.

b Rate = [Ph₃M][RO₂H](k₂ + k₃[V])

It should be noted that while the reactions are all quite fast, they do not proceed at the same rate.
A mechanism for hydroperoxide-metal ion oxidation of nucleophiles

The previously cited workers are generally agreed on the basic features of the mechanism:

1. An initial complexation of hydroperoxide with the metal ion species, on which electron and steric features of the R group have predictable effects.

\[ \text{RO}_2\text{H} + \text{M} \xrightarrow{k_1} \text{H} \]

\[ \text{R-O-O}^-\text{M} \xrightarrow{k-1} \]

\[ [24] \]

2. A competitive complexation by the solvent, or products, here denoted as ROH

\[ \text{ROH} + \text{M} \xrightarrow{k_2} \text{H} \]

\[ \text{R-O}^-\text{M} \xrightarrow{k-2} \]

\[ [25] \]

3. Rate determining attack by the nucleophile

\[ \text{H} \]

\[ \text{R-O-O}^-\text{M} + \text{N} \xrightarrow{k_3} \text{R-O}^-\text{M} + \text{N}+\text{O} \]

\[ [26] \]

The resulting rate expression has been most clearly outlined by Koshi (34).

\[ -d[\text{RO}_2\text{H}]/dt = \frac{k_3[N:][\text{RO}_2\text{H}][\text{M}]}{K + (K_1/K_2)[\text{ROH}] + [\text{RO}_2\text{H}]} \]

\[ [27] \]

where \( K_2 = k_{-2}/k_2 \), \( K_1 = k_{-1}/k_1 \), and a steady state for concentration of
R–O–O––M is assumed, so that $k_1 k_1 = k_1 + k_3 [N:]$. If $k_1 \gg k_3$ and

$[\text{ROH}] = [\text{RO}_2\text{H}]_0 - [\text{RO}_2\text{H}]$, it follows that

$$\frac{-d[\text{RO}_2\text{H}]/dt}{k_3 [\text{N:}][\text{M}]} = \frac{k_3 [\text{N:}][\text{M}]}{K_1 /[\text{RO}_2\text{H}] + (K_1/K_2)[\text{RO}_2\text{H}]_0/[\text{RO}_2\text{H}] + (1 - K_1/K_2)} \tag{28}$$

Further simplification can be made if $K_1 = K_2$

$$\frac{-d[\text{RO}_2\text{H}]/dt}{\Delta t} = \frac{k_3 [\text{N:}][\text{M}][\text{RO}_2\text{H}]}{K_1 + (K_1/K_2)[\text{RO}_2\text{H}]_0} \tag{29}$$

This is the behaviour most often observed for catalysis by vanadium compounds. For molybdenum catalysis, where dependence on $[\text{RO}_2\text{H}]_0$ is usually not found, it is necessary only to point out that $K_1$ may easily be considerably larger than $(K_1/K_2)[\text{RO}_2\text{H}]_0$.

Objectives of this work

The similar reactivity of hydroperoxide-molybdenum or -vanadium combinations and organic peroxyacids has already been mentioned. Not surprisingly, an alternative mechanism has been advanced, that of an intermediate peroxyvanadic or peroxyvanadic acid—formed by reaction of hydroperoxides and metal complex—as the reactive species. The argument is not easily discounted, although peroxyvanadic and peroxyvanadic acids are known compounds and differ somewhat from hydroperoxide-metal ion in their reactivity towards substrates. Perhaps the most telling argument against is kinetic. If a metallic peroxyacid is the reactive
intermediate, it then follows that for the most reactive substrates, formation of the intermediate should be rate determining; structural changes in the substrate should not affect the rate of reaction. No such behaviour has been found. (Of course, for the phosphines, stibines and arsines, the necessary experiments have not been done. However, this group of highly reactive substrates forms a subclass for which it might be argued that given a reactive intermediate, surely $\text{Ph}_3\text{P}$, $\text{Ph}_3\text{Sb}$ and $\text{Ph}_3\text{As}$ should all react at the same rate. They do not.)

The reactive intermediate theory has recently been reactivated following on the isolation of a peroxomolybdenum complex, $\text{MoO(O}_2\text{)}_2\text{•HMPT}^*$ from reaction of $\text{H}_2\text{O}_2$ with $\text{MoO}_3$ (49, 50). The complex, unlike peroxy-molybdic acid, quite closely parallels the reactivity of $\text{RO}_2\text{H-Mo}$ with olefins (51, 52). Clearly, it has required further investigation.

The choice of organic sulfides and sulfoxides was based on the fact that of all the obvious substrates, these have been the least investigated. The previous work of Modena et al. (46, 47) was unsatisfactory in that structural effects were not treated, nor were sulfoxides as substrates given much consideration.

Thus the objectives: To establish a benchmark of reactivity/selectivity of $\text{RO}_2\text{H-Mo}$ with respect to aryl sulfides and sulfoxides and to compare this with reactivity/selectivity of $\text{MoO(O}_2\text{)}_2\text{•HMPT}$.

* Hexamethylphosphortriamide
EXPERIMENTAL

Materials used in this work and their purification steps

The sources of materials and their stated purity are shown in Table 5. The purities of diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, phenyl methyl sulfide, phenyl methyl sulfoxide, phenyl methyl sulfone, p-chlorophenyl methyl sulfide, p-bromophenyl methyl sulfide, t-butyl alcohol, ethanol and 1,2-dichloroethane were checked by gas chromatography. In some cases UV and mass spectrometry were also used for this purpose.

The purity of t-BuO₂H was found by iodine titration. Compounds of molybdenum were used as obtained from commercial sources. Molybdenum hexacarbonyl was examined by mass spectroscopy, which showed the presence of tungsten hexacarbonyl and chromium hexacarbonyl as impurities. Sublimation under reduced pressure did not remove these impurities.

Instruments used in this work

For UV, GC and ¹H NMR analyses, 6 m Ebert grating and Cary-14 Ultra-visible spectrometers, F & M Laboratories 700 Gas chromatograph and Bruker WP-60 multinuclear fourier transform tuned for ¹H at 60 MHz with a sweep width of 750 Hz from TMS and A-60 NMR spectrometers were used respectively. Calculations were done using either the Wang 2200B or the Burroughs 6700 computers.
TABLE 5

Reagents purchased and used in the present work

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Source</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenyl sulfide</td>
<td>Aldrich Chemicals</td>
<td>99</td>
</tr>
<tr>
<td>Diphenyl sulfoxide</td>
<td>Aldrich Chemicals</td>
<td>97</td>
</tr>
<tr>
<td>Diphenyl sulfone</td>
<td>Aldrich Chemicals</td>
<td>97</td>
</tr>
<tr>
<td>Thioanisole</td>
<td>Aldrich Chemicals</td>
<td>99</td>
</tr>
<tr>
<td>p-Bromothioanisole</td>
<td>Aldrich Chemicals</td>
<td>97</td>
</tr>
<tr>
<td>p-Chlorothioanisole</td>
<td>Colombia Organic Chem.</td>
<td>99</td>
</tr>
<tr>
<td>Molybdenum hexacarbonyl</td>
<td>Alfa division</td>
<td>--</td>
</tr>
<tr>
<td>Molybdenum naphthanate</td>
<td>ICN-K&amp;K Laboratories</td>
<td>3% Mo</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(by weight)</td>
</tr>
<tr>
<td>Molybdenum acetyl acetonate</td>
<td>ICN-K&amp;K Laboratories</td>
<td>--</td>
</tr>
<tr>
<td>Molybdenum trioxide</td>
<td>J. T. Baker Chemicals</td>
<td>100</td>
</tr>
<tr>
<td>t-Butyl hydroperoxide</td>
<td>Lucidol division</td>
<td>92.5</td>
</tr>
<tr>
<td></td>
<td>of Pennwalt Comp.</td>
<td></td>
</tr>
<tr>
<td>30% Hydrogen peroxide</td>
<td>BDH Chemicals</td>
<td>30</td>
</tr>
<tr>
<td>Hexamethyl phosphoramid</td>
<td>Aldrich Chemicals</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>Aldrich Chemicals</td>
<td>100</td>
</tr>
<tr>
<td>t-Butyl alcohol</td>
<td>BDH Chemicals</td>
<td>100</td>
</tr>
<tr>
<td>Sodium iodide</td>
<td>BDH Chemicals</td>
<td>100</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Commercial</td>
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<tr>
<td></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

*a as stated on the label

*b as checked
Syntheses

Preparation of MoO$_2$(O$_2$)$_2$-HMPT

This diperoxo molybdenum complex was synthesized according to the procedure of Ozaki et al. (51). 50 g (0.348 mole) of molybdenum trioxide was suspended in 250 mL of 30% H$_2$O$_2$ with stirring at 40°C for 2 hours. Then the temperature of the bath was reduced to 10°C and 60 mL (62.3 g, 0.348 mole) HMPT was added dropwise to the solution which was stirred for two more hours. A yellow precipitate was filtered off, washed three times with ethyl ether and recrystallized from methanol solution at 40°C. It was stored under vacuum in a dark, cool place.

Preparation of phenyl methyl sulfoxide

Initially, C. R. Johnson's method (53) was used to synthesize thioanisole oxide. The main problems in this method are the control of temperature, the composition of solvent which plays a quite important role in the solubility of NaIO$_4$ and PhSCH$_3$, and the tendency of the product to oxidize further.

Phenyl methyl sulfide (0.05 mole) was added to 0.0525 mole of sodium metaperiodate at 0°C in 110 mL of 50/50 (by volume) water and methanol mixture and the solution stirred overnight. The precipitated sodium iodate was removed by filtration, and filtrate was extracted with chloroform. The extract was dried over anhydrous magnesium sulfate. Finally, the solvent was removed under reduced pressure to get the products.

The $^1$H NMR spectrum of product showed two main peaks; PhSOCH$_3$ and PhSO$_2$CH$_3$ at $\delta = 2.7$ ppm and $\delta = 3.1$ ppm, respectively.
Most preparations of phenyl methyl sulfoxide were done as follows: 25 mL of a 1.0 M solution of PhSCH$_3$ in EtOH, containing a small amount of molybdenum hexacarbonyl (9.83 x 10$^{-3}$ mole) as a catalyst, was added into 100 mL round bottom flask with 1.0 M of t-BuO$_2$H in 25 mL EtOH. The solution was maintained at 35°C for approximately 1½ hours, while monitoring the disappearance of t-BuO$_2$H by iodometric titration. Removal of solvent from the mixture was done by vacuum distillation. Yields of the sulfoxide and the sulfone were 94% and 3% respectively.

**Titrations**

Two iodometric titration methods for t-BuO$_2$H were tried. Both of these methods are based on the reaction of the hydroperoxide with the iodide ion to produce iodine which can be titrated with sodium thiosulfate. The most commonly and conveniently used one is the "reflux" method (A). The other method (B) which has been used by Wibout and Van Leeuwen (54) is somewhat more discriminating than the reflux method in that it does not titrate hydroperoxide-carbonyl adducts.

Method A uses sodium iodide which is soluble in isopropanol-acetic acid mixture, provides good solubility conditions for organic compounds, and has the advantage of speed and lack of need for an inert atmosphere. In this method, oxygen in the solution is expelled by solvent vapour.

Method B uses potassium iodide in acetic acid at room temperature under a carbon dioxide atmosphere.

The Wibout method did not give consistent results in the presence of sulfur compounds so the "reflux" method was used for most of this work.
Rate studies

In ethanol:

Weighed amounts of catalyst (Mo(CO)$_6$, MoO$_3$ or VO(acac)$_2$) and the organic sulfide were added to a volumetric flask which was then filled with ethanol. A solution of t-BuO$_2$H was similarly prepared. Both flasks were equilibrated at reaction temperature for one hour before mixing aliquots to start the reaction.

Pre-mixing of the catalyst and organic sulfide seemed to be important. Pre-mixing of the catalyst with hydroperoxide, or no pre-mixing at all but rather preparation of three separate solutions, consistently gave slower and less reproducible reactions.

Mostly the reactions were followed for approximately 1$\frac{1}{2}$ hours at 35° or 65° C. Some reactions were done under Argon.

Samples (2 mL) were taken at 10 minute intervals. For reactions followed only by iodometric titration, a 500 μL aliquot was titrated immediately. For reactions followed by UV as well, the samples were quenched and stored in dry ice until the reaction was complete.

Preparation of samples for UV analysis

After bringing the sample to room temperature, 10 μL, or in some cases 20 μL, was added into 50 mL volumetric flask with Eppendorf Multivolume tip ejecting micropipet; then it was filled to the mark with ethanol.
Determination of extinction coefficients of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone

A series of Ph₂S, Ph₂SO and Ph₂SO₂ stock solutions were prepared at different concentrations. Extinction coefficients for each compound were measured at 230, 235, 240, 245, 250, 255, 260, 265, 270 and 275 nm.

Measurement of optical densities in the UV region was determined at room temperature in a quartz sample cell with a 10 mm path length within the cell compartment of a Cary-14 spectrometer.

After obtaining extinction coefficients, mixtures of Ph₂S, Ph₂SO and Ph₂SO₂ at known concentrations were prepared. Optical densities were measured at the 10 wavelengths for which extinction coefficients were calculated using a method for overdetermined simultaneous equations and compared to the known concentrations. The results are shown in Appendix 8.

These spectrometric parameters were measured also for the molybdenum peroxy complex and dichloroethane.

Treatment of concentrations vs time data

The data were fitted to a "model", i.e., the set of ordinary differential equations of the type \( \frac{3[C_i]}{3t} = F(C_i, t) \), thought to best describe the reaction, using a Burroughs 6700 computer. The program employed a Gauss-Newton type of non-linear least squares routine, and a Runge-Kutta numerical integrator.
In CDCl₃

^1H Nuclear Magnetic Resonance spectral studies

^1H spectra were obtained for substituted phenylmethyl sulfides and their oxidation products, in CDCl₃ at 60 MHz in 5 mm tubes using a Bruker WP-60 FT NMR spectrometer at room temperature.

Preparation of samples

All NMR samples were prepared in two 5 mm NMR tubes, mixed quickly, and then replaced in the magnet of the spectrometer. One tube contained catalyst plus sulfide; the other contained t-butyl hydroperoxide. This mixing and replacement procedure took approximately two minutes.

The program used

A Bruker Automatic Tl/II program in kinetics mode was used. Different numbers of scans and timing were employed for each experiment depending on the concentration of reactants, catalyst and temperature.

Interpretation of ^1H NMR spectra

Information obtained from ^1H NMR spectra of phenyl methyl sulfide, sulfoxide and sulfone showed that the peaks found at δ = 8.1-7.3 correspond to phenyl group hydrogens.

The methyl peaks of phenyl methyl sulfide, sulfoxide and sulfone are singlets at δ = 2.34, 2.71, 3.05 ppm respectively. The peaks are well-defined from each other, so increase or decrease in the intensity of peaks could be observed without any interference.
Gas chromatographic analyses

An F & M 700 Laboratory Gas Chromatograph which has thermo-conductivity detector, equipped with a Honeywell recorder having a disc integrator, was used to record the chromatograms. Generally ethanol was used as a solvent for the substances and 10 μl of sample solution was injected to determine the retention times of diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, phenylmethyl sulfide, phenylmethyl sulfoxide and phenylmethyl sulfone.

Conditions in the determination of retention times of \( \text{Ph}_2\text{S} \), \( \text{Ph}_2\text{SO} \) and \( \text{Ph}_2\text{SO}_2 \) (Chromatograms Appendix 4)

<table>
<thead>
<tr>
<th>Column</th>
<th>6 feet, teflon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packing</td>
<td>20% silicon rubber gum on Chromosorb W, 80-100 mesh</td>
</tr>
<tr>
<td>Column temperature</td>
<td>220°C</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>210°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>290°C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium 100 mL/min</td>
</tr>
<tr>
<td>Retention times (min)</td>
<td></td>
</tr>
<tr>
<td>( \text{Ph}_2\text{S} )</td>
<td>2.33</td>
</tr>
<tr>
<td>( \text{Ph}_2\text{SO} )</td>
<td>5.27</td>
</tr>
<tr>
<td>( \text{Ph}_2\text{SO}_2 )</td>
<td>5.79</td>
</tr>
</tbody>
</table>
Conditions in the determination of retention times of PhSCH₃, PhS0CH₃, and PhS0₂CH₃ (Chromatograms Appendix 4)

The same column was used for this case, but the conditions were different.

Column temperature 250°C
Injector temperature 210°C
Detector temperature 355°C
Carrier gas Helium 100 mL/min

Retention times (min)

- PhSCH₃ 0.807
- PhS0CH₃ 1.397
- PhS0₂CH₃ 1.535

Conditions for runs #27 and #30

Column temperature 210°C
Injector temperature 205°C
Detector temperature 280°C
Carrier gas Helium 100 mL/min
Filament current 150 mA

Under these conditions, the separation is reasonable for EtOH, sulfide and sulfoxide. But there is an overlapping between the sulfoxide and the sulfone peaks. This problem was eliminated by using the temperature programming during the separation of components.

Unfortunately, another problem arose from the base line of chromatogram. This deviation of base line with change in oven temperature can be explained by the structure of thermocouple detector.
Gas chromatography was used to determine the concentration of each compound. Initially, calibration curves for diphenyl sulfide, diphenyl sulfoxide and diphenylsulfone were prepared by taking the known concentrations of each compound and recording their chromatograms. Graphs of concentration versus area of the peaks were linear.

This method of analysis was not useful sampling kinetic runs, however, for this case, because of the oxidation of sulfide to sulfoxide and sulfoxide to sulfone by unreacted t-BuO₂H proceeded in the injection port. See Appendix 4 for results of 2 runs, #27 and #30 which were analyzed by titrations, UV and gas chromatography. UV and titrations gave the same results, but GC analysis consistently indicated a larger extent of reaction.

To eliminate this problem, Ph₃P was added to the samples to reduce t-BuO₂H to t-BuOH prior to GC injection. This method brought its own difficulty, that of eluting Ph₃PO and excess Ph₃P in a reasonable length of time and avoiding condensation of Ph₃PO in the detector block. This method was therefore not used. (A sample chromatogram is to be found in the appendices.)
RESULTS AND DISCUSSION

Oxidations of sulfides and sulfoxides by t-butyl hydroperoxide

Products of oxidation Experiments were carried out by Modena et al. (46, 47) and Hargrave (27, 28) to establish the stoichiometry of both uncatalyzed and metal-catalyzed reactions of sulfides with t-butyl hydroperoxide. (In the following equations, C represents catalyst.)

\[ \text{t-Bu}_2\text{H} + \text{R}_2\text{S} \xrightarrow{[C]} \text{t-BuOH} + \text{R}_2\text{SO} \]  \[ 30 \]

They have isolated the sulfoxide as a major product of the oxidation in 90% yield. This was confirmed with GLC. The other product is t-butyl alcohol which comes from the reduction of t-butyl hydroperoxide. No sulfone was observed either in protic or in aprotic solvents at the temperatures of 25°C, 45.9°C and 50°C.

\[ \text{R}_2\text{SO} + \text{t-BuO}_2\text{H} \xrightarrow{[C]} \text{R}_2\text{SO}_2 + \text{t-BuOH} \]  \[ 31 \]

In this study, ultraviolet spectroscopy and titrations showed that the sulfoxide, the sulfone and t-butyl alcohol are the only products of oxidation. The stoichiometry of oxidation has been confirmed by comparisons of the decrease in t-butyl hydroperoxide concentration (via titrations) versus the decrease in sulfide concentration and the
increases in sulfoxide and sulfone concentrations (via UV). Some typical data are given in Table 6.

In the absence of sulfide, solutions of t-BuO₂H + molybdenum catalyst showed no detectable loss of t-BuO₂H for periods of up to 2 hours at 35°C or 65°C.

Iodometric titrations of t-butyl hydroperoxide and GC analysis of the products have shown, in agreement with the observations made by Modena et al., that there are no extraneous products in these reactions. Some byproducts are seen in the reaction of the allylic sulfides with hydroperoxides (31). That is not the case in this work.

**Selection of the catalyst and solvent**

Preliminary work showed that absolute ethanol was capable of dissolving sufficient molybdenum hexacarbonyl, sulfides, sulfoxides, sulfones and t-butyl hydroperoxide.

Ethanol is a reasonable solvent for UV and GC. But on the other hand, it is a poor solvent for ¹H NMR studies, because its high concentration in the mixture prevents digital and manual integrations of methyl hydrogens of phenyl methyl sulfide, sulfoxide and sulfone. Therefore deuterated solvents were used, such as CD₃CN, C₆D₆ and CDCl₃. The most convenient and inexpensive solvent was CDCl₃ which provides very good solubility for the catalyst. In most of the NMR work for p-chloro, p-bromo substituted, and for phenyl methyl sulfide, CDCl₃ was used as a solvent.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentrations</th>
<th>Changes in Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t-BuO₂Hᵇ</td>
<td>Ph₂Sᶜ</td>
</tr>
<tr>
<td>0</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>0.653</td>
<td>0.2322</td>
</tr>
<tr>
<td>20</td>
<td>0.59</td>
<td>0.1758</td>
</tr>
<tr>
<td>30</td>
<td>0.545</td>
<td>0.1413</td>
</tr>
<tr>
<td>40</td>
<td>0.512</td>
<td>0.1081</td>
</tr>
<tr>
<td>50</td>
<td>0.495</td>
<td>0.0947</td>
</tr>
<tr>
<td>60</td>
<td>0.477</td>
<td>0.0795</td>
</tr>
<tr>
<td>70</td>
<td>0.462</td>
<td>0.0678</td>
</tr>
<tr>
<td>80</td>
<td>0.452</td>
<td>0.0593</td>
</tr>
<tr>
<td>90</td>
<td>0.440</td>
<td>0.0417</td>
</tr>
<tr>
<td>100</td>
<td>0.429</td>
<td>0.0425</td>
</tr>
</tbody>
</table>

⁻ 0.002 M Mo(CO)₆ in ethanol at 65°C.
ᵇ,c Mol L⁻¹. ᵇ By titration. ᶜ By UV.
An important aspect in the selection of catalyst for UV work was that it should not have an absorption in the region where sulfides, sulfoxides and sulfones have absorptions.

Absolute ethanol was the solvent chiefly used for reactions monitored by UV and titration, although hexane and 1,2-dichloroethane were explored.

The solubilities of several catalysts in three solvents and UV limits for the solvent are given in Table 7.

**Purity of Mo(CO)\textsubscript{6}**

The purity of the molybdenum hexacarbonyl was checked by mass spectroscopy. It was shown to contain W(CO)\textsubscript{6} and Cr(CO)\textsubscript{6} as impurities. Reduced pressure sublimation did not remove these, probably because of their similar properties.

Atomic absorption analysis has shown that sublimed and unsublimed Mo(CO)\textsubscript{6} samples contain Cr(CO)\textsubscript{6} in 244 ppm and 148 ppm respectively. From relative mass spectrometric peak heights for W and Cr, the tungsten hexacarbonyl content was found to be 213 and 84.9 ppm for the sublimed and unsublimed molybdenum hexacarbonyl samples respectively.

Tungsten and chromium are known to be poor catalysts for the epoxidation of olefins (37). Their catalytic effects on the oxidation of sulfides and sulfoxides are not known, but would be expected to be similarly poor.

Therefore it seems safe to assume that these small amounts of W and Cr would not affect the rate of the reaction.
TABLE 7
Solubilities of several catalysts in, and UV limits of three solvents

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>n-hexane</th>
<th>absolute ethanol</th>
<th>1,2-dichloroethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>molybdenum naphthenate</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>MoO₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo(CO)₆</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>MoO₂(acac)₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

UV limits

| lower limit | 170 | 210 | 235 | nm  |


\(^{a}\) Based on visual observation of 0.01 g of the substance in 20 mL of solvent. "+" = no residual solid, "-" = residual solid.
Oxidation of diphenyl sulfide by t-butyl hydroperoxide

The uncatalyzed rate of t-butyl hydroperoxide consumption by diphenyl sulfide in absolute ethanol at 65°C was followed by iodometric titration (Table 8). The data (Figure 1) fit a second order rate law (Equation 32) with $k_2 = 5.61 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$.

$$\text{Rate} = k_2 [\text{RO}_2\text{H}][\text{Ph}_2\text{S}]$$  \hspace{1cm} \text{[32]}$$

For the catalyzed reaction, MoO$_3$ was first used. Addition of amounts calculated to give an Mo$^{VI}$ concentration of $1 \times 10^{-2}$ M accelerated the reaction greatly, and produced both sulfoxide and sulfone (Figure 2). The obtained data fit the rate law which is shown in Equation 33

$$\text{Rate} = k_2 [\text{RO}_2\text{H}][\text{Ph}_2\text{S}] + k^{\text{I}}_2 [\text{RO}_2\text{H}][\text{Ph}_2\text{SO}]$$  \hspace{1cm} \text{[33]}$$

where at 65°C, $k_2/k^{\text{I}}_2$ is about 30. But $k_2$ and $k^{\text{I}}_2$ turned out to be independent of the amount of MoO$_3$ added (Table 9) and upon closer inspection it was clear that not all of the MoO$_3$ had dissolved. Comparison with subsequent reactions using Mo(CO)$_6$ suggest that a saturated solution of MoO$_3$ in ethanol is about $5 \times 10^{-4}$ M.

The Mo(CO)$_6$ catalyzed reaction of diphenyl sulfide with t-butyl hydroperoxide at 65°C gave similar results to those using MoO$_3$ except that rate constants were proportional to added catalyst (Equation 34).
TABLE 8

The uncatalyzed oxidation of diphenyl sulfide by t-BuO$_2$H at 65°C in ethanol

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[t-BuO$_2$H]$^a$</th>
<th>[Ph$_2$S]$^a$</th>
<th>Plot$^b,c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.8944</td>
<td>0.798</td>
<td>0.0</td>
</tr>
<tr>
<td>145</td>
<td>0.8555</td>
<td>--</td>
<td>0.0571</td>
</tr>
<tr>
<td>295</td>
<td>0.8193</td>
<td>--</td>
<td>0.1155</td>
</tr>
<tr>
<td>445</td>
<td>0.7817</td>
<td>--</td>
<td>0.1822</td>
</tr>
<tr>
<td>1405</td>
<td>0.6539</td>
<td>--</td>
<td>0.4714</td>
</tr>
<tr>
<td>1645</td>
<td>0.6194</td>
<td>--</td>
<td>0.5718</td>
</tr>
</tbody>
</table>

$^b$ $\ln([R_2S]_0*[RO_2H]/([RO_2H]_0*([RO_2H] - ([RO_2H]_0 - [R_2S]_0))/([RO_2H]_0 - [R_2S]))$  

$^c$ $k_2 = 3.36 \times 10^{-4}$ M$^{-1}$min$^{-1}$; $r = 0.9985$

$^a$ mol L$^{-1}$
Fig. 1 Second-order rate plot for t-BuO₂H oxidation of diphenyl sulfide in ethanol at 65°C
TABLE 9
Reactions of diphenyl sulfide with t-BuO₂H catalyzed by MoO₃.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[t-BuO₂H]₀</th>
<th>[Ph₂S]₀</th>
<th>[MoO₃]</th>
<th>k₂</th>
<th>k₂'</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.799</td>
<td>0.408</td>
<td>0.005</td>
<td>6.69</td>
<td>2.04</td>
</tr>
<tr>
<td>6</td>
<td>0.799</td>
<td>0.399</td>
<td>0.010</td>
<td>7.45</td>
<td>3.31</td>
</tr>
<tr>
<td>7</td>
<td>0.800</td>
<td>0.402</td>
<td>0.010</td>
<td>9.03</td>
<td>4.70</td>
</tr>
<tr>
<td>10</td>
<td>0.799</td>
<td>0.399</td>
<td>0.020</td>
<td>8.55</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>0.800</td>
<td>0.200</td>
<td>0.010</td>
<td>6.26</td>
<td>1.37</td>
</tr>
<tr>
<td>11</td>
<td>0.800</td>
<td>0.200</td>
<td>0.010</td>
<td>7.45</td>
<td>2.94</td>
</tr>
</tbody>
</table>

a At 65°C in ethanol
b M L⁻¹.
c M L⁻¹ as calculated if all added MoO₃ had dissolved.
d M⁻¹min⁻¹ from \(-\frac{3\text{[t-BuO₂H]}}{t} = k₂\text{[t-BuO₂H][Ph₂S]} + k₂'\text{[t-BuO₂H][Ph₂SO]}\)
Fig. 2 Concentrations versus time of BuO₂H for the oxidation of diphenyl sulfide by t-BuO₂H in ethanol in the presence of MoO₃ at 65°C.
The reaction was so fast, however, that a lower temperature seemed more appropriate. However at 35°C in ethanol, a problem developed. The reaction more often than not showed a strong oscillation in apparent (i.e., titratable) hydroperoxide concentration (Figure 3). This behaviour, while very interesting was not reproducible either in period or amplitude of the oscillations. It could be eliminated, however, by blanketing the reaction with argon (Figures 3, 4). All subsequent reactions of diphenyl sulfide were carried out under an argon atmosphere. The data are given in Table 10.

A plot of \( \log k_3 \) versus \( 1/T \) gave an activation energy and A-factor for the first stage of the reaction (sulfide \( \rightarrow \) sulfoxide) (Figure 5) of 18.5 kcal and \( 10^{12.6} \) respectively.

Oxidation of diphenyl sulfide by t-butyl hydroperoxide in the presence of either MoO\(_3\) or Mo(CO)\(_6\) gave both diphenyl sulfoxide and diphenyl sulfone. Diphenyl sulfone, however, is not very soluble in ethanol, and started to precipitate when conversion had reached about 10%, thus presenting analytical problems for rate studies beyond this point. Rather than change the analytical method, it was decided to study the second stage of the reaction in isolation, starting with diphenyl sulfoxide, rather than the sulfide.

A typical result is shown in Figure 6. Solutions of Ph\(_2\)SO, t-BuO\(_2\)H and a molybdenum catalyst in ethanol are quite stable, showing no
Concentration of t-BuO₂H versus time for the oxidation of diphenyl sulfide at 35°C in ethanol under air in the presence of Mo(CO)₆

- Run 19
- Run 20
Fig. 4 Concentrations versus time for the oxidation of diphenyl sulfide by t-BuOOH at 35°C in ethanol under argon atmosphere in the presence of Mo(CO)$_6$ (1.97 x $10^{-3}$ M)
Fig. 4a  Concentrations versus time for the oxidation of diphenyl sulfide by t-BuO₂H at 65°C in ethanol under argon atmosphere in the presence of Mo(CO)₆ (8.9 x 10⁻⁴ mol)
### TABLE 10

**Mo(CO)₆-Catalyzed reactions of diphenyl sulfide with t-BuO₂H in ethanol.**

<table>
<thead>
<tr>
<th>Run #</th>
<th>T °C</th>
<th>$k_2^b$ $M^{-1}min^{-1} \times 10^3$</th>
<th>$k_3^b$ $M^{-1}min^{-1} \times 10^3$</th>
<th>Variance $^c$ $x 10^3$</th>
<th>[Mo]$^d$ $x 10^3$</th>
<th>$k_3^e,f$ $M^{-2}min^{-1}$</th>
<th>$k_3^e,f$ $M^{-2}min^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>20</td>
<td>3.27</td>
<td>--</td>
<td>0.55</td>
<td>1.00</td>
<td>3.27</td>
<td>--</td>
</tr>
<tr>
<td>24</td>
<td>35</td>
<td>14.4</td>
<td>1.32</td>
<td>0.16</td>
<td>0.97</td>
<td>14.8</td>
<td>1.36</td>
</tr>
<tr>
<td>30</td>
<td>35</td>
<td>16.5</td>
<td>1.49</td>
<td>4.5</td>
<td>0.96</td>
<td>17.2</td>
<td>1.55</td>
</tr>
<tr>
<td>25</td>
<td>35</td>
<td>40.3</td>
<td>2.94</td>
<td>1.3</td>
<td>1.97</td>
<td>20.4</td>
<td>1.49</td>
</tr>
<tr>
<td>31</td>
<td>35</td>
<td>39.5</td>
<td>2.40</td>
<td>6.4</td>
<td>2.01</td>
<td>19.7</td>
<td>1.19</td>
</tr>
<tr>
<td>148</td>
<td>65</td>
<td>208.2</td>
<td>15.2</td>
<td>1.2</td>
<td>0.895</td>
<td>237.6</td>
<td>17.4</td>
</tr>
</tbody>
</table>

---

$^a$ [Ph₂S]₀ = 0.400 M; [t-BuO₂H]₀ = 0.800 M; run under argon unless otherwise noted.

$^b$ From Rate = $k_2[R_2O_2H][R_2S] + k_3[R_2O_2H][R_2SO]$  

$^c$ Sum of squares, experimental - calculated values, for concentrations of t-BuO₂H, Ph₂S, Ph₂SO and Ph₂SO₂.

$^d$ Mol L⁻¹, calculated on added Mo(CO)₆.

$^e$ $k_3 = k_2/[Mo]$; $k_3 = k_2/[Mo]$.

$^f$ Arrhenius plots for $k_3$, $k_3^f$ give  

for $k_3$, $E_a = 18.5$ kcal mol⁻¹; log $A = 12.62$ (M⁻²s⁻¹), $r = 0.995$

for $k_3^f$, $E_a = 17.4$ kcal mol⁻¹; log $A = 10.73$ (M⁻²s⁻¹), $r = 0.996$.

$^g$ Run in air atmosphere.
Fig. 5 Arrhenius plot for t-BuO₂H oxidation of diphenyl sulfide in ethanol and in the presence of Mo(CO)₆.
Fig. 6 Concentration of t-BuO₂H versus time for the reaction with diphenyl sulfoxide in the presence of Mo(CO)₆ at 35°C in ethanol
reaction for up to 3 hours! Conditions employed were 65°C, and either saturated MoO₃ or 0.02-0.001 M Mo(CO)₆. After 24 hours, there is a detectable loss of t-BuO₂H, but this may be due to free radical decomposition.

On the assumption that small amounts of the sulfide are required to somehow activate the catalyst, small amounts were added, to no effect. In a typical instance, with 0.4 M each of t-BuO₂H and Ph₂SO and 0.001 M Mo(CO)₆, Ph₂S sufficient to make its initial concentration 0.001 M. After 100 minutes of no reaction, the amount of Ph₂S was increased tenfold. Still no reaction. Addition of Ph₂SO at the start of a Ph₂S reaction did not inhibit.

The conclusion seems to be that yes, Ph₂S is required, but in relatively large amounts, not small. The obvious alternative, that Ph₂SO is not the intermediate in conversion of Ph₂S to Ph₂SO₂ can be rejected by examination of the course of the Ph₂S + t-BuO₂H + Mo reaction (e.g., Figures 2 and 4). The relationship of Ph₂SO₂ production to Ph₂SO concentration is quite apparent. After all of the Ph₂S has been oxidized, the Ph₂SO concentration starts to drop and Ph₂SO₂ continues to increase. Computer modelling with \( \frac{3}{3} \) of Ph₂SO₂/3t = k[Mo][RO₂H][Ph₂SO] fits the data very well.

Since vanadium catalysts are reported (54) to work with sulfoxides, one experiment with VO(acac)₂ was tried. The conditions were 0.8 M t-BuO₂H, 0.2 M Ph₂SO, 0.004 M VO(acac)₂ in ethanol at 35°C in air. Since vanadium catalysts absorb strongly in the UV, the reaction was followed by titration alone, and a 1:1 stoichiometry assumed. The reaction is
slow* (Figure 7), but gives a third order rate constant of 2.35 M⁻²min⁻¹, about the same as for Ph₂S-activated Mo. Gc analysis of a parallel reaction after 335 minutes showed [Ph₂SO₂] = 0.170 M. The rate constant gives [Ph₂SO₂] at 335 minutes = 0.175 M.

Oxidation of phenyl methyl sulfide and substituted phenyl methyl sulfides

Reactions in CDCl₃

Still with the hope of using ¹H NMR analyses, attention was turned to phenyl methyl sulfides, where the methyl protons of sulfide, sulfoxide and sulfone are well separated singlets (Figure 8). Ideally, reactions could be run in an NMR tube, with periodic recording of peak intensities done automatically by the dedicated computer.

This, however, required a change of solvent, since the intensity of the ethanol protons overwhelmed the counting memory of the instrument. Reactions were therefore run in CDCl₃.

* As has been reported by Modena (46, 48) and Gould (39), addition of t-BuO₂H to the blue-green solution of VO(acac)₂ rapidly produces an intense red colour. Consequently an attempt was made to analyze mixtures of Ph₂S, Ph₂SO and Ph₂SO₂ by ¹H NMR. The aryl protons overlap considerably, but appear to fall into 3 separable regions (Appendix 6) which can be assigned to sulfone, sulfone + sulfoxide and sulfoxide + sulfide. In theory this is easily solvable. In practice, it didn't work possibly because for peaks with a lot of fine structure, the Bruker integrator is not always reliable.
Fig. 7 Second-order rate plot for the reaction of t-BuO₂H with diphenyl sulfoxide at 35°C in ethanol in the presence of VO(acac)₂
60 MC NMR
SPECTRUM NO RUN 15.01

OPERATOR 2 KASSELLIUCATE

SAMPLE 1H-CDCl3 + 5% BF3-ethylamine in 85% at 25°C
Sample was taken after 137.5min 22.5 hours.

SOLVENT
TEMPERATURE
FILTER BANDWIDTH
RF FIELD
SWEEP TIME
SWEEP WIDTH
SWEEP OFFSET
SPECTRUM AMP
INTEGRAL AMP.

REMARKS:

\begin{align*}
\delta & \text{ ppm} \\
6,5 & -\text{OH} \quad 0.88 \% \\
6,5 & -\text{CH}_3 \quad 3.06 \% \\
3,72 & \text{ } \text{-j-} 3.97 \% \\
\end{align*}

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315 ARBOR AVE E
LAKEVILLE N.J. 08046
Phone (609) 297-0029

A6L 440m 10
In a typical experiment, 1 M PhSCH\textsubscript{3} was oxidized by 2 M t-BuO\textsubscript{2}H in the presence of 0.01 M Mo(CO)\textsubscript{6} at 30°C in an NMR tube, using \textsuperscript{1}H peak intensities to monitor concentrations of the sulfur-containing species. A parallel run was carried out in CHCl\textsubscript{3} in a constant temperature bath, to obtain t-BuO\textsubscript{2}H concentrations. The method appeared to work extremely well, individual runs giving excellent pseudo second order plots (Figure 9) and a number of runs were carried out, using p-chlorophenyl and p-bromophenyl methyl sulfides as well as the unsubstituted starting material.

Three features distinctly different from the reactions of diphenyl sulfide in ethanol emerged (1). The second stage, oxidation of phenyl methyl sulfoxides to phenyl methyl sulfones was so slow as to be a negligible consideration (2). Reactions at 20°C were less than 1/10 as fast as those at 30°C, suggesting either a very large activation energy, or undetected solubility problems of Mo(CO)\textsubscript{6} in CDC\textsubscript{3} (3). The reactions were not reproducible, 2 runs under seemingly identical conditions giving rate constants differing by a factor of 2 or more.

Recalling difficulties encountered by earlier workers (29, 31) studying the uncatalyzed sulfide-hydroperoxide reaction in aprotic solvents, it was decided to abandon this line.
Fig. 9. Second order rate plots for the reaction of t-BuO₂H with phenyl methyl sulfide at 30°C in CDCl₃ and CHCl₃ in the presence of Mo(CO)₆. △ = NMR #1, ○ = NMR #2, □ = titrations.
Reactions in absolute ethanol

Unlike the diphenyl sulfide case, the UV spectra of PhSCH₃, PhSOCH₃ and PhSO₂CH₃ are so similar as to rule out this method of analysis. Therefore reactions were followed by iodometric titrations alone.

For the uncatalyzed reaction, a 1:1 stoichiometry, uncomplicated by oxidation to the sulfone could be assumed. At 65°C the second-order rate constant, \( k_2 \), \((\partial \text{[RO₂H]} / \partial t = k_2 \text{[RO₂H]} \text{[PhSCH₃]})\), was found to be \( 3.48 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} \), (Figure 10, Table 11). This is about 10 times larger than the corresponding rate constant for Ph₂S; probably this is an electronic effect, methyl being an electron donor, while, in this instance, phenyl may withdraw electron density.

For reactions catalyzed by Mo(CO)₆, it was assumed only that all of the t-BuO₂H consumed was used either to convert sulfide to sulfoxide or sulfoxide to sulfone. Three models were tested for matching computed t-BuO₂H concentrations with experimental values (A, B and C, below). Model C consistently gave good fits to the data, while A and B did not.

A. Rate = \( k_3 \text{[Mo(CO)₆]}_0 \text{[ArSMe]} [\text{t-BuO₂H}] + k_3 \text{[Mo(CO)₆]} \text{[ArSOMe]} [\text{t-BuO₂H}] \)

B. Rate = \( k_3 \text{[Mo(CO)₆]}_0 [\text{t-BuO₂H}] \text{[ArSMe]} / [1 + K\text{[t-BuO₂H]}] \)

C. Rate = \( k_3 \text{[Mo(CO)₆]}_0 \text{[ArSMe]} [\text{t-BuO₂H}] \)
Fig. 10 Second order rate plot for t-BuO₂H oxidation of phenyl methyl sulfide in ethanol at 65°C
TABLE 11

The uncatalyzed oxidation of phenyl methyl sulfide at 65°C in ethanol.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[t-BuO₂H]&lt;sup&gt;a&lt;/sup&gt;</th>
<th>[PhSCH₃]&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Plot&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.7699</td>
<td>0.400</td>
<td>0.0</td>
</tr>
<tr>
<td>239</td>
<td>0.664</td>
<td>--</td>
<td>0.4314</td>
</tr>
<tr>
<td>317</td>
<td>0.634</td>
<td>--</td>
<td>0.5972</td>
</tr>
<tr>
<td>368</td>
<td>0.616</td>
<td>--</td>
<td>0.7102</td>
</tr>
<tr>
<td>623</td>
<td>0.546</td>
<td>--</td>
<td>1.2889</td>
</tr>
<tr>
<td>1040</td>
<td>0.484</td>
<td>--</td>
<td>2.1363</td>
</tr>
</tbody>
</table>

<sup>a</sup> Mol L<sup>-1</sup>

<sup>b</sup> \( \ln([R₂S]₀*[RO₂H]/([RO₂H]₀*([RO₂H] - ([RO₂H]₀ - [R₂S]₀)))/([RO₂H]₀ - [R₂S]₀) \)

<sup>c</sup> \( k = 2.09 \times 10^{-3} \text{ M}^{-1}\text{min}^{-1}; r = 0.9993 \)
Results for phenyl methyl sulfide are summarized in Table 12 and for p-chlorophenyl methyl sulfide in Table 13. Figure 11 shows a sample plot.

In only one instance was any significant amount of oxidation to the sulfone observed. This was a run at 65°C with the Mo(CO)$_6$ concentration 100 times that normally used for conveniently measurable rates, and an initial mole ratio of t-BuO$_2$H to PhSCH$_3$ of 2:1. After 10 minutes, slightly more than 1 equivalent of t-BuO$_2$H had been consumed, and the concentration of t-BuO$_2$H continued to decrease with time. Evidently, the sulfoxide to sulfone reaction could be measured, but under conditions where it is difficult to measure the sulfide to sulfoxide conversion.

It was shown that t-BuOH did not inhibit the reaction. Initial addition of t-BuOH in an amount equivalent to initial t-BuO$_2$H gave no change in the rate (Table 12).

Figure 12 shows an Arrhenius plot of the data from Table 12, giving for molybdenum catalyzed oxidation phenyl methyl sulfide to sulfoxide an $E_a$ of 44.5 kcal and $\log A = 22.0$. These values are very different from those found for Ph$_2$S, a matter reserved for later discussion.

Another surprising fact is that p-chlorophenyl methyl sulfide reacts somewhat faster than the unsubstituted compound (Table 12 versus Table 13). It is difficult to ascribe significant electron donor character to a para-chlorine. Indeed, in similar reactions, metal-catalyzed oxidations of styrenes (40) and anilines (42), substitution of the ring by chlorine reduces the rate, as expected. This seems to be yet another strange feature of sulfide oxidations.
Mo(CO)$_6$-Catalyzed reactions of phenyl methyl sulfide with t-BuO$_2$H in ethanol.$^a$

<table>
<thead>
<tr>
<th>Run #$^b$</th>
<th>[t-BuO$_2$H]$_0$</th>
<th>[PhSCH$_3$]$_0$</th>
<th>[Mo(CO)$_6$]$_0$ $\times 10^3$</th>
<th>T °C</th>
<th>k(M$^{-2}$min$^{-1}$)</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>0.767</td>
<td>0.400</td>
<td>1.00</td>
<td>25</td>
<td>0.836</td>
<td>0.000066</td>
</tr>
<tr>
<td>55, 57$^d$</td>
<td>0.413</td>
<td>0.400</td>
<td>2.04</td>
<td>35</td>
<td>17.5</td>
<td>0.0010</td>
</tr>
<tr>
<td>60, 54$^d$</td>
<td>0.827</td>
<td>0.400</td>
<td>1.03</td>
<td>35</td>
<td>17.0</td>
<td>0.0102</td>
</tr>
<tr>
<td>53, 58$^d$</td>
<td>0.826</td>
<td>0.400</td>
<td>1.94</td>
<td>35</td>
<td>17.2</td>
<td>0.004</td>
</tr>
<tr>
<td>165</td>
<td>0.768</td>
<td>0.423</td>
<td>0.984</td>
<td>45</td>
<td>69.6</td>
<td>0.00249</td>
</tr>
<tr>
<td>15</td>
<td>0.100</td>
<td>0.400</td>
<td>0.0101</td>
<td>65</td>
<td>7126.</td>
<td>0.00010</td>
</tr>
<tr>
<td>14</td>
<td>0.100</td>
<td>0.400</td>
<td>0.0202</td>
<td>65</td>
<td>6394.</td>
<td>0.00010</td>
</tr>
<tr>
<td>09</td>
<td>0.200</td>
<td>0.400</td>
<td>0.0100</td>
<td>65</td>
<td>7885.</td>
<td>0.00010</td>
</tr>
<tr>
<td>08</td>
<td>0.200</td>
<td>0.400</td>
<td>0.0201</td>
<td>65</td>
<td>6090.</td>
<td>0.00006</td>
</tr>
<tr>
<td>07</td>
<td>0.400</td>
<td>0.400</td>
<td>0.0105</td>
<td>65</td>
<td>9488.</td>
<td>0.0006</td>
</tr>
<tr>
<td>06</td>
<td>0.400</td>
<td>0.400</td>
<td>0.0211</td>
<td>65</td>
<td>7697.</td>
<td>0.0010</td>
</tr>
<tr>
<td>11</td>
<td>0.800</td>
<td>0.400</td>
<td>0.0101</td>
<td>65</td>
<td>10840.</td>
<td>0.0025</td>
</tr>
<tr>
<td>10</td>
<td>0.800</td>
<td>0.400</td>
<td>0.0201</td>
<td>65</td>
<td>7238.</td>
<td>0.0057</td>
</tr>
<tr>
<td>16$^e$</td>
<td>0.400</td>
<td>0.400</td>
<td>0.0203</td>
<td>65</td>
<td>7618.</td>
<td>0.0010</td>
</tr>
<tr>
<td>18, 19</td>
<td>0.400</td>
<td>0.200</td>
<td>0.0102</td>
<td>65</td>
<td>9828.</td>
<td>0.0007</td>
</tr>
<tr>
<td>17</td>
<td>0.400</td>
<td>0.200</td>
<td>0.0204</td>
<td>65</td>
<td>8325.</td>
<td>0.0014</td>
</tr>
<tr>
<td>23</td>
<td>0.400</td>
<td>0.800</td>
<td>0.0101</td>
<td>65</td>
<td>5427.</td>
<td>0.0077</td>
</tr>
<tr>
<td>22</td>
<td>0.400</td>
<td>0.800</td>
<td>0.0202</td>
<td>65</td>
<td>7122</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

$^a$ In air unless otherwise specified.  $^b$ If more than one run is shown, the results are averaged.

$^c$ Rate = k[Mo][RO$_2$H][PhSCH$_3$]; $E_a$ = 44.5 kcal mol$^{-1}$; log A = 22.0 M$^{-1}$s$^{-1}$
<table>
<thead>
<tr>
<th>Run #s(^b)</th>
<th>([t-\text{BuO}_2\text{H}]_0)</th>
<th>([p-\text{ClPhSCH}_3]_0)</th>
<th>([\text{Mo(CO)}_6]_0) x 10(^3)</th>
<th>T °C</th>
<th>(k(\text{M}^{-2}\text{min}^{-1}))^c</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>0.416</td>
<td>0.422</td>
<td>1.02</td>
<td>35</td>
<td>21.0</td>
<td>0.0008</td>
</tr>
<tr>
<td>77,78</td>
<td>0.416</td>
<td>0.422</td>
<td>2.02</td>
<td>35</td>
<td>22.3</td>
<td>0.0009</td>
</tr>
<tr>
<td>73,74,75</td>
<td>0.826</td>
<td>0.422</td>
<td>0.989</td>
<td>35</td>
<td>20.6</td>
<td>0.0051</td>
</tr>
<tr>
<td>79,80</td>
<td>0.826</td>
<td>0.422</td>
<td>2.01</td>
<td>35</td>
<td>19.6</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

\(^a\) Run in an argon atmosphere

\(^b\) If more than one run is shown, results are averaged.

\(^c\) Rate = \(k[\text{Mo}][\text{RO}_2\text{H}][p-\text{ClPhSCH}_3]\)
Fig. 11 Concentrations versus time for the oxidation of phenyl methyl sulfide by t-BuO₂H at 35°C in ethanol and in the presence of Mo(CO)₆.
Fig. 12 Arrhenius plot for t-BuO₂H oxidation of phenyl methyl sulfide
Oxidations Using MoO(O₂)₂·HMPT

The molybdenum peroxo complex was prepared by the method of Mimoun et al. (49). It yielded 2 moles of I₂/mol on iodometric titration.

A reaction with diphenyl sulfide (0.2 M Ph₂S, 0.2 M MoO(O₂)₂·HMPT in ethanol at 35°C), appeared to be complete after 4 hours. The white crystals which precipitated were shown by UV (Appendix 5) and mass spectrometry to be pure diphenyl sulfone.

Reaction with diphenyl sulfoxide (0.2 M Ph₂SO, 0.1 M MoO(O₂)₂·HMPT in ethanol at 35°C) required 7.5 hours, again yielding the sulfone.

Rate studies were not pursued because iodometric titration of the reaction solutions produced a precipitate, making the end point difficult to observe.

The Mechanism of Metal-catalyzed Oxidation of Organic Sulfinides and Sulfoxides by Hydroperoxides

Activation of the catalyst

Both theory and experience suggest that the metal should be in a high oxidation state (see Introduction). For V₃ or V₄ salts or complexes, a small amount of the hydroperoxide is consumed in a rapid spectroscopically observable oxidation to V₅. No other species seems to be required for this "activation".

The molybdenum in Mo(CO)₆ requires oxidation to Mo₆. Since Mo(CO)₆ is a tight, relatively unreactive species, ligand exchange and oxidation might be expected to be less than instantaneous. Short induction periods have been observed both in this work (Figures 4 and
11) and in previous research (41). However, Mo as MoO₃ requires no oxidation, and yet in this work (Figure 2) short induction periods were also found when molybdenum was added in that form.*

In no previous reports has there been any suggestion that the substrate plays a part in the "activation" of a molybdenum catalyst. But in this work, many observations point to the involvement of the organic sulfide, required apparently in much greater than catalytic concentrations. Among these are:

1) The non-oxidation of diphenyl sulfoxide unless the medium contains, or has previously contained gross concentrations of diphenyl sulfides.

2) The "best" way to make up a run for sulfide oxidation (EXPERIMENTAL), which was found not to be pre-equilibration of molybdenum species with t-BuO₂H, as might be expected, but rather pre-equilibration of the catalyst with the organic sulfide. The "worst" procedure was no pre-equilibration at all. Such runs showed strong auto-acceleration (Table 14, Figure 14).

3) Reactions carried out at low (0.1-0.2 M) initial sulfide concentrations gave longer, but unfortunately non-reproducible induction periods. Of two runs carried out at 35°C with initial concentrations of 0.2 M PhSCH₃, 0.8 M t-BuO₂H and 0.001 M Mo(CO)₆, one gave no reaction for nearly 40 minutes while the other started reacting after 10 minutes.

Finding out just what is going on and what the structural features of the actual catalyst are, requires further work.

* Solutions of MoO₃ or Mo(CO)₆ and t-BuO₂H in ethanol were quite stable, showing no loss of t-BuO₂H for many hours (Figure 13).
Fig. 13 Concentration of t-BuO₂H versus time in the presence of Mo(CO)₆ in ethanol at 35°C and 65°C
TABLE 14

Mo(CO)$_6$-Catalyzed oxidations of phenyl methyl sulfide at 45°C in ethanol showing the effect of different catalyst preparations.$^a$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Run #1$^b$</th>
<th>Run #2$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[t-BuO$_2$H]</td>
<td>[PhSCH$_3$]</td>
</tr>
<tr>
<td>0</td>
<td>0.713</td>
<td>0.417</td>
</tr>
<tr>
<td>10</td>
<td>0.676</td>
<td>--</td>
</tr>
<tr>
<td>20</td>
<td>0.653</td>
<td>--</td>
</tr>
<tr>
<td>30</td>
<td>0.619</td>
<td>--</td>
</tr>
<tr>
<td>40</td>
<td>0.590</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>0.555</td>
<td>--</td>
</tr>
<tr>
<td>60</td>
<td>0.532</td>
<td>--</td>
</tr>
<tr>
<td>70</td>
<td>0.505</td>
<td>--</td>
</tr>
<tr>
<td>80</td>
<td>0.476</td>
<td>--</td>
</tr>
<tr>
<td>90</td>
<td>0.449</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>0.424</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ Under argon with Mo(CO)$_6 = 1.0 \times 10^{-3}$ M

$^b$ Catalyst added as solution in ethanol at the start of the reaction.

$^c$ Catalyst and PhSCH$_3$ dissolved together in ethanol and kept at 45° for one hour before adding t-BuO$_2$H to start the reaction.
Fig. 14  Second-order rate plot for the Mo(CO)$_6$-catalyzed oxidation of phenyl methyl sulfide by t-Bu$_2$O where the sulfide and catalyst were not pre-equilibrated
Complexation of the metal ion

Two types of evidence have, in the past, suggested that it is the metal ion-hydroperoxide complex that leads to reaction rather than a metal ion-oxidizable substrate complex (INTRODUCTION).

(1) Substituents which increase electron density at the reactive site of the substrate facilitate reaction, showing that the function of the substrate is nucleophilic. The substrate may very well form complexes with the metal ion, but the effect would be to make them less nucleophilic. Moreover, the hydroperoxide bond required a decrease in electron density in order to make it receptive to nucleophilic attack; this presumably is the purpose of the metal ion.

(2) High concentrations of hydroperoxide, but not of substrate, frequently lead to saturation effects similar to enzyme-substrate reactions. That is, if more than a small fraction of the metal ions are complexed by a reactant to form a reactive intermediate, the concentration of the intermediate does not increase linearly with increased concentration of the reactant.

The fact that molybdenum-catalyzed reactions usually do not show saturation effects indicates that Mo\textsuperscript{VI} complexes the hydroperoxide weakly.

\[
t{-\text{Bu}}_2\text{O}_2\text{H} + \text{Mo}_{\text{L}_6} \underset{K}{\xrightleftharpoons{} } \text{t{-Bu}{-O-Mo}}_{\text{L}_5} + \text{L} \tag{35}
\]

where L represents any ligand.
As explained by Kochi (34) (INTRODUCTION), competition by the alcohol formed by reduction of the hydroperoxide for the metal ion may lead to a rate expression identical to that for saturation. With ethanol as the solvent, however, this could hardly be a factor, since the concentration of total alcohol remains effectively constant throughout the reaction.

**Reaction of the substrate with the complex**

The mechanism shown in Equation (36) has been proposed by Modena et al. (46).

\[
\begin{align*}
    & \text{R}_2\text{S} : \text{O} \quad \text{t-Bu} \quad \text{H} \quad \text{Mo} \quad \text{H}^+ \quad \text{Et} \\
\text{R}_2\text{S} & \xrightarrow{k} \text{R}_2\text{SO} \\
\text{R}_2\text{S} & \quad \text{t-Bu} \quad \text{H} \quad \text{Mo} \quad \text{H}^+ \quad \text{Et}
\end{align*}
\]

[36]

It is essentially the same as has been proposed for other substrates (36, 37), and would apply equally well to sulfoxides.

The rate expressions follow:

\[
\begin{align*}
    -\frac{\partial [\text{R}_2\text{S}]}{\partial t} & = k(\text{complex})[\text{R}_2\text{S}] \quad [37] \\
    -\frac{\partial [\text{R}_2\text{S}]}{\partial t} & = kK[\text{RO}_2\text{H}][\text{MoL}_6][\text{R}_2\text{S}] \quad [38] \\
    \frac{\partial [\text{R}_2\text{SO}_2]}{\partial t} & = k'[K[\text{RO}_2\text{H}][\text{MoL}_6][\text{R}_2\text{SO}]] \quad [39]
\end{align*}
\]

(where \( k' \) is the rate constant analogous to \( k \) for \( \text{R}_2\text{SO} \) as substrate)
\[ \frac{\partial [R_2SO]}{\partial t} = -\frac{\partial [R_2S]}{\partial t} - \frac{\partial [R_2SO_2]}{\partial t} \quad [40] \\
\frac{\partial [t-BuO_2H]}{\partial t} = -\frac{\partial [R_2S]}{\partial t} - \frac{\partial [R_2SO_2]}{\partial t} \quad [41] \\
(\text{since an insignificant amount of } t-BuO_2H \text{ is complexes at any given time}) \\
\text{In the case that } k >> k' \text{ and } [R_2S] > [R_2SO], \\
\frac{\partial [t-BuO_2H]}{\partial t} = kK[R_2H][MoL_6][R_2S] \quad [42] \\
\]

This work has shown equation 42 to apply to the oxidations of diphenyl sulfide and phenyl methyl sulfide in ethanol using Mo(CO)\(_6\). The first-order dependence on [RO\(_2\)H] was demonstrated over an eightfold range in initial t-BuO\(_2\)H concentrations. In fact, the first order dependence on [R\(_2\)S] and on [RO\(_2\)H] is established for catalysis by MoO\(_3\) in ethanol and for Mo(CO)\(_6\) in CDCl\(_3\)/CHCl\(_3\) as well.

This contrasts with the results of Modena et al. (46) for n-Bu\(_2\)S, t-BuO\(_2\)H and MoO\(_2\)(acac)\(_2\) in ethanol. The rate expression is

\[ -\frac{\partial [R_2O_2H]}{\partial t} = k[MoL_6][R_2S][t-BuO_2H]/(1 + K[t-BuO_2H]) \quad [43] \\
(\text{where } k \text{ and } K \text{ are not related to equations 35-42}) \\
\]

Equation 43 (developed in Appendix 7) implies saturation of the catalyst by t-BuO\(_2\)H; i.e., a relatively strongly bonded molybdenum-hydroperoxide complex. The only real difference between Modena's work and that reported here is the sulfide. (The particular molybdenum compound thrown into the pot has little or no effect on the reaction subsequent to formation of active catalyst (36, 37).)
The enormous effect even a small change in sulfide structure can have is shown by the apparent activation energies, 18.5 kcal for Ph₂S and 44.5 kcal for PhSCH₃. From equation 42, these are really thermal coefficients for kK, or the sums of Eₐ for reaction 36 and E for equilibrium 35. It cannot be seriously argued that replacing a phenyl by methyl would increase the activation energy for nucleophilic substitution (reaction 36) by nearly 30 kcal. Ordinarily it would seem equally unlikely that an equilibrium should be so affected.
CONCLUSION

The results of this work fall short of the objectives stated in the introduction, but are more interesting. An apparently straightforward reaction has proved to be not simple at all.

The most striking discovery, perhaps, is the oscillating reaction. Clearly oxygen is required, and thus it is easy to avoid. Unfortunately the other requirements for getting it started are not so easy to determine. The real cause may have been a trace impurity in one of the reactants.

The non-reactivity of diphenyl sulfoxide unless the catalyst has been liberally doped with the sulfide is also puzzling. If a high concentration of sulfide is necessary, why does the reaction keep going when the sulfide is apparently all gone? IF the active catalyst is active because of some tightly bound sulfide ligands, why was a large amount of sulfide necessary in the first place?

Finally, the differences in behaviour of diphenyl sulfide, phenyl methyl sulfide and di-n-butyl sulfide are so great as to be hard to believe. But the data appear to be reliable. One is forced to conclude that the sulfide has a profound influence on the structure of the active catalyst. What that structure is remains to be seen.
REFERENCES


25. G. MODENA et al., Gazzeta (a) 1957, 87, 1906; 1959, 89 (b) 884, (c) 843: 1960, 80 (d) 3, (e) 12, (f) 382, (g) 621, (h) 682 (i) Ricerca Sci. 1960, 30, 128.


34. KOCHI, chapter in Koehi book.


36. "Oxidation", Ed. by R. L. Augustine and D. J. Trecker, V. 2 (1971) ch. 3 by R. R. Hiatt, pp. 113-


APPENDICES
### TABLE 1: THREE SETS OF RESULTS WHICH ARE OBTAINED FROM TWO DIFFERENT METHODS.

<table>
<thead>
<tr>
<th>TIME MIN.</th>
<th>H NMR#1 T-BU02H</th>
<th>H NMR#2 T-BU02H</th>
<th>TITRATIONS#1 T-BU02H</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.010</td>
<td>2.094</td>
<td>2.050</td>
</tr>
<tr>
<td>4</td>
<td>1.993</td>
<td>1.979</td>
<td>1.785</td>
</tr>
<tr>
<td>8</td>
<td>1.958</td>
<td>1.879</td>
<td>1.748</td>
</tr>
<tr>
<td>12</td>
<td>1.952</td>
<td>1.776</td>
<td>1.702</td>
</tr>
<tr>
<td>16</td>
<td>1.927</td>
<td>1.679</td>
<td>1.621</td>
</tr>
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<td>1.593</td>
<td>1.559</td>
</tr>
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<td>1.508</td>
<td>1.501</td>
</tr>
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</tr>
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<td>1.402</td>
</tr>
<tr>
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<td>1.733</td>
<td>1.322</td>
<td>1.359</td>
</tr>
<tr>
<td>40</td>
<td>1.646</td>
<td>1.274</td>
<td>1.319</td>
</tr>
<tr>
<td>52</td>
<td>1.329</td>
<td>1.171</td>
<td>1.232</td>
</tr>
</tbody>
</table>

H NMR#1,2 AT 30°C AND IN CDCL
TITRATIONS#1 AT 30°C AND IN CHCL
\*ET=39.5 PT=0.3 IO=1.1
APPENDIX 2
Program for recording

5 PRINT "PR0G1 ON SULFIDE OXIDN DATA TAPE 'SEFA DATA 1'"
10 DIM L1(12),T(15),O(15,12),TI(15),R1(15),Q$1
20 DATA LOAD "FREC":DATA LOAD F:BACKSPACE 1F
30 INPUT "DATE OF RUN,RUN NUMBER, NOTEBOOK PAGE,TEMP,SOLVENT,INIT PEROXIDE CONC,INIT SULFIDE CONC, MOLYB CONC,DILUTION FACTOR FOR UV,NO OF UV PTS",D$,R0,N0,T5,S$,H0,S0,M0,D6,U6
35 INPUT "NO OF UV LAMBDA'S USED,NO OF TITRATION PTS",L,T6
40 PRINT "KEY IN LAMBDA VALUES STARTING WITH LOWEST":FOR I= 1 TO L:INPUT "LAMBDA",L1(I):NEXT I
60 PRINT "KEY IN TIMES AND TITRATION VALUES FOR PEROXIDE CONC":FOR I=1 TO T6:I NPUT "TIME, PER CONC",TI(I),R1(I):NEXT I
70 PRINT "THE INPUT WILL NOW BE LISTED FOR ERROR CHECK. TURN ON TYPEWRITER, PLEASE":STOP
75 SELECT PRINT 211
80 PRINT "DATE OF RUN(D$) ";D$;" RUN NO(R0) ";R0;" NOTEBOOK PAGE(N0) ";N0;PR
90 PRINT "TEMP(T5) ";T5;" SOLVENT(S$) ";S$;" DILUTION FACTOR(D6) ";D6;PRINT
100 PRINT "INIT CONC'S: PEROXIDE(H0) ";H0;" SULFIDE(S0) ";S0;" MOLYB(M0) ";M0;PRINT
110 PRINT "NO OF UV PTS(U6) ";U6;" NO OF LAMBDA'S PER PT(L) ";L;" NO OF TITR PTS(T6) ";T6:PRINT
120 PRINT "LAMBDA'S","TIMES AND O.D.'S";PRINT :PRINT " ";:FOR I = 1 TO U6:
PRINT USING 200,T(I);:NEXT I:PRINT
130 FOR I = 1 TO L:PRINT L1(I);" ";:FOR J = 1 TO U6:PRINT USING 210,O(J,I);:NEXT J:PRINT :NEXT I
140 PRINT :PRINT "TIMES AND TITRATION VALUES"
150 FOR I = 1 TO T6:PRINT USING 200,T1(I);:NEXT I:PRINT :FOR I=1 TO T6:PRINTUSING 210,R1(I);:NEXT I:PRINT
160 SELECT PRINT 005:PRINT HEX(03):PRINT :PRINT
170 PRINT "YOU CAN DO CORRECTIONS IN ACTIVE MODE AT NEXT STOP. SIMPLY KEY IN [ SYMBOL] = [CORRECT VALUE]. MOST SYMBOLS HAVE BEEN GIVEN IN THE PRINT OUT."
175 PRINT "FOR THE REST: LAMBDA'S ARE L1(I), UV TIMES ARE T(I),O.D. VALUES ARE O(I,J), TITR TIMES ARE T1(I), TITR VALUES ARE R1(I)":STOP :INPUT "RE-PRINT, YES OR NO",Q$:IF Q$="Y" THEN 75
180 PRINT "IS ALL CORRECT? THE NEXT 'CONTINUE' MAKES THE TAPE !":STOP :GOTO 300
200%####.
210%##.###
300 F=F+1:DATA LOAD "FREC":DATA RESAVE F:SKIP FF
310 DATA SAVE OPEN "DFILE":DATA SAVE D$,RO,NO,T5,S$,HO,SO,M0,D6,U6,L,T6,L1(),T () ,O() ,T1() ,R1() :DATA SAVE END :REWIND
999 END
Program for UV data

5 PRINT "PROG3 ON SEFA 1. A READER AND CALCULATOR FOR SEFA DATA 1"

8 COM T(15), Z(15, 4), U6

10 DIM L1(12), O(15, 12), T1(15), R1(15), A(5, 1), B(5, 5), C(5), D(5, 5), E(10), V(10), W(10), R(10, 3), G(10), Q$1

15 INPUT "DATE OF THIS CALCULATION", Z$: INPUT "ONLY FINAL RESULTS", Q$

20 INPUT "RUN NO", R9

22 DATA LOAD "DFILE"; DATA LOAD D$, R0, N0, T5, S$, H0, S0, D6, U6, L, T6, L1(); T(); O();

25 INPUT "NO OF VARIABLES", N; MAT REDIM B(N, N), A(N, 1): U = 0

30 DATA 1, 2.1552, 2, 3.988, 2, 9.715, 1, 4.688, 1, 9.875, 1, 60.727, 1, 82374, 1, 3.1066, 2.4662, 1, 29.358, 2.0637, 1, 3.6481, 3.4185, 1, 3.7275, 4.326, 1, 29.634, 2.8161, 1, 21.672, 27304

35 FOR I = 1 TO L: FOR J = 1 TO N: READ R(I, J): NEXT J: NEXT I

40 U = U + 1: FOR I = 1 TO L: V(I) = O(U, I): NEXT I: P = 1: SELECT PRINT 211

45 FOR I = 1 TO L: G(I) = O(1, I) * D6 / S0: NEXT I

50 MAT A = ZER: MAT B = ZER: FOR K = 1 TO L: FOR I = 1 TO N: E(I) = R(K, I) * G(K): NEXT I

60 FOR J = 1 TO N: FOR I = 1 TO N: B(J, I) = B(J, I) + E(J) * E(I): NEXT I

70 A(J, 1) = A(J, 1) + E(J) * V(K): NEXT J: NEXT K

90 MAT D = INV(B): MAT C = D * A

100 S = 0

110 FOR I = 1 TO L: W(I) = 0


125 FOR I = 1 TO N: C(I) = C(I) * D6: NEXT I
130 IF Q$="Y" THEN 150: IF P$ = "Y" THEN 140: PRINT "WORKING DATA": PRINT "VARIANCE", "SULFIDE", "SULFOXIDE", "SULFONE": PRINT
140 PRINT S, C(1), C(2), C(3)
150 S1 = 0: FOR I = 1 TO N: C(I) = ABS(C(I)): S1 = S1 + C(I): NEXT I
160 IF S1 > 1.01 * S0 THEN 200: IF S1 > 0.99 * S0 THEN 200
180 FOR I = 1 TO L: PRINT L1(I), G(I), V(I), W(I): NEXT I: PRINT: PRINT
190 IF U = U6 THEN 350: GOTO 40
200 P = P + 1: IF P > 3 THEN 170: FOR I = 1 TO L: G(I) = G(I) * S1 / S0: NEXT I: GOTO 50
350 PRINT "DATE OF CALCULATION = "; Z$: PRINT
360 PRINT TAB(20), "SUMMARY": PRINT: PRINT USING 540, "PT", "MIN", "ROOH", "SULFIDE", "SULFOXIDE", "SULFONE"
370 FOR I = 1 TO U6: PRINT USING 550, I, T(I), Z(I, 1), Z(I, 2), Z(I, 3), Z(I, 4): NEXT I: PRINT: PRINT: IF Q$ = "Y" THEN 500
400 PRINT "DATE OF RUN(D$) "; D$: PRINT: PRINT USING 550, D$: "ROOH", "NOTEBOOK PAGE(NO) "; R$: PRINT
430 PRINT "TEMP(T5) "; T5: PRINT: PRINT "SOLVENT(S$) "; S$: PRINT: PRINT "DILUTION FACTOR(D6) "; D6: PRINT
440 PRINT "INIT CONC'S: PEROXIDE(HO) "; HO: PRINT: PRINT "SULFIDE(SO) "; SO: PRINT: PRINT "MOLYB(MO) "; MO: PRINT
450 PRINT "NO OF UV PTS(U6) "; U6: PRINT: PRINT "NO OF LAMBDA'S PER PT(L) "; L: PRINT: PRINT "NO OF TITR PTS(T6) "; T6: PRINT
460 PRINT "LAMBDA'S", "TIMES AND OD'S"; PRINT " "; FOR I = 1 TO U6:
PRINT USING 520, T(I); NEXT I; PRINT
470 FOR I = 1 TO L; PRINT L1(I); " "; FOR J = 1 TO U6; PRINT USING 530, O(J, I); NEXT J; PRINT : NEXT I
480 PRINT : PRINT "TIMES AND TITRATION VALUES"
490 FOR I = 1 TO T6; PRINT USING 520, T1(I); NEXT I; PRINT : FOR I = 1 TO T6; PRINT USING 530, R1(I); NEXT I; PRINT
495 Q$ = "Y"; GOTO 350
500 SELECT PRINT 005: INPUT "LOAD GAUSFIT", Q$: IF Q$ = "Y" THEN 510: LOAD "PROG4"
510 END
520%###.
530%##.
540%## ### #### ####### ######### #######
550%## ### ##.##### ##.##### ##.##### ##.#####
APPENDIX 3
\begin{align*}
\text{if } M \Rightarrow M', & \quad i, j, \ii \Rightarrow F v^5 i \Rightarrow t^3 \Rightarrow t^3, \\
M' & \Rightarrow M', \\
M' \Rightarrow F, \\
M' \Rightarrow F M' ,
\end{align*}
TABLE 10

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<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>A</td>
<td></td>
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<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Sample data for columns 1 to 5.
j, it
RUNNING 7196
DATA FROM FILE ?

?Y

POINT YOU ARE USING FOR TIME ZERO?
KEY IN 0, OR 1, OR 2, ETC, NOT ACTUAL TIMES
?1

1     21     0.05892053836
2     31     0.04132214659
3     41     0.02941075621
4     51     0.02114562022
5     61     0.0153114818
6     71     0.0114237059

THE VARIANCE IS
NUM  OLD PARAMETER  CORRECTION  NEW PARAMETER
1    5025.0307041    1096.2713317    6121.3020357
1    21            0.05444608340
2    31            0.03557126429
3    41            0.02367686924
4    51            0.01594877612
5    61            0.01082750000
6    71            0.00738916536

THE VARIANCE IS
NUM  OLD PARAMETER  CORRECTION  NEW PARAMETER
1    6121.3020357    108.72120501    6230.0232407
1    21            0.05402415848
2    31            0.03505121103
3    41            0.02317767740
4    51            0.01551250210
5    61            0.01046438699
6    71            0.00709598790

THE VARIANCE IS
NUM  OLD PARAMETER  CORRECTION  NEW PARAMETER
1    6230.0232407    -4.4513742936    6225.5718664

#ET=1.05.4 PT=2.0 ID=1.4
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14100 11 , 0.0859 ,
14200 21 , 0.0586 ,
14300 31 , 0.0364 ,
14400 41 , 0.0216 ,
14500 51 , 0.0133 ,
14600 61 , 0.0087 ,
14700 71 , 0.0063 ,
## CSEFA/SEFARUN23

```plaintext
#FILE (C6590SK)CSEFA/SEFARUN23 ON PACK
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23100 21   0.3724
23200 31   0.3232
23300 41   0.2043
23400 51   0.1296
23500 61   0.081
23600 71   0.0577
23700 81   0.0318
23800 91   0.0218
```
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<table>
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<tr>
<td>Value 7</td>
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Note: The table content is placeholder text for demonstration purposes.
CSEFA/SEFARUN78

FILE (CG590SK) CSEFA/SEFARUN78 ON PACK

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<td>71</td>
<td>0.1728</td>
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</tr>
</tbody>
</table>
Figure Al. Chromatogram of diphenyl sulfide
Figure A2. Chromatogram of diphenyl sulfoxide.
$\varphi_{50} = 0.600M$

5 µL
Figure A3. Chromatogram of diphenyl sulfone
Figure A4. Chromatogram of mixture of diphenyl sulfoxide and diphenyl sulfone.
\( \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_3 \)

\( \text{H}_2\text{SO}_4 = 0.120\text{M} \)

\( \text{H}_2\text{SO}_3 = 0.040\text{M} \)
Figure A5. Chromatogram of mixture of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone.
Figure A6. Sample chromatogram of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone in the presence of triphenyl phosphine.
Figure A7. Chromatogram of zero point sample of Run 30.
APPENDIX 5
Figure A8. UV spectrum of diphenyl sulfide
Aldrich Chem. Corp.

Ph₃S (99%) in EtOH

2 in / min

0.1 scale

6.07 x 10⁻⁵ M
Figure A9. UV spectrum of diphenyl sulfoxide.
Figure A10. UV spectrum of diphenyl sulfone.
Aldrich Chem. Corp.

$\text{Ph}_2\text{SO}_2$ (97%)

in EtOH

2 in/min

0.2 scale

$9.75 \times 10^{-5}$ M
Figure All. UV spectrum of the product of the reaction of molybdenum peroxo complex with diphenyl sulfoxide.
Figure A12. NMR spectra of the reaction mixture of phenyl methyl sulfide, t-BuO₂H and molybdenum hexacarbonyl.
60 MHz - 1H- Spectrum

Sample: $\text{H}_2\text{Me}_2\text{C}=\text{C}=\text{CH}_2$ H$_2$O

Conc., std. 10% 2.3 M

Int. Standard: TMS

Temp. atm. (°F)

$\text{H}_2\text{O}$ 1.05 M
$\text{t-BuOH}$ 2.09 M
$\text{Me}_{2}\text{C} \text{C} \text{H}$ 0.0125 M

Signal 1:
Pulse width (FWHM): 1.3 sec
Points (512) 8 W Y

Spectrum:
width (FWHM): 2.50 Hz
Time: 5.5 sec
Errors (4): 4 score
Time constant (TC):

Decoupling:
Frequency: 100 Hz
Power:

Date: 17/11/79
Operator: S. E. McC.
Figure A13. NMR spectra of mixtures of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone.
\[
\begin{align*}
\text{Mo} + H & \xrightarrow{k_1} \text{Mo-H} \\
\text{Mo-H} + S & \xrightarrow{k_2} SO + \text{Mo-A}
\end{align*}
\]

\[
\frac{[\text{Mo-H}]}{t} = k_1[\text{Mo}][H] - k_4[\text{Mo-H}] - k_2[\text{Mo-H}][S] = 0
\]

\[
k_1[\text{Mo}][H] - k_4[\text{Mo-H}] - k_2[\text{Mo-H}][S] = 0
\]

\[
[\text{Mo}]_o = [\text{Mo}] + [\text{Mo-H}]
\]

\[
[\text{Mo}] = [\text{Mo}]_o - [\text{Mo-H}]
\]

\[
k_1[\text{Mo}]_o[H] - k_4[\text{Mo-H}][H] - k_2[\text{Mo-H}][S] = 0
\]

\[
k_1[\text{Mo}]_o[H] - k_1[\text{Mo-H}][H] - k_4[\text{Mo-H}] - k_2[\text{Mo-H}][S] = 0
\]

\[
k_1[\text{Mo}]_o[H] = k_1[\text{Mo-H}][H] + k_4[\text{Mo-H}] + k_2[\text{Mo-H}][S]
\]

\[
k_1[\text{Mo}]_o[H] = [\text{Mo-H}][k_1[H] + k_4 + k_2[S]]
\]

\[
[\text{Mo-H}] = \frac{k[\text{Mo}]_o[H]}{k_1[H] + k_4 + k_2[S]}
\]

\[
\frac{\partial[S]}{\partial t} = \frac{\partial[SO]}{\partial t} = k_2[\text{Mo-H}][S]
\]

\[
v = \frac{k_1k_2[\text{Mo}][S][H]}{k_1[H] + k_4 + k_2[S]}
\]
\[
v = \frac{k_2[S][H]}{[K^+ + [H]]}
\]

Where \( K = \frac{k_1 + k_2[S]}{k} \)

Treatment of the data according to the method of Lineweaver and Burk,

\[
\frac{1}{v} = \frac{k'}{k [M_o] [S][H]} + \frac{1}{k_2 [M_o][S]}
\]

Plotting \( \frac{1}{v} \) versus \( \frac{1}{[H]} \) would give \( K \) and \( k_2 \).
ERROR CALCULATIONS

\[ I_3^- + 5 I^- + 6 H^+ = 3 I_2^- + 3 H_2O \]
\[ 3 I_2^- + 6 S_2O_3^- = 3 S_4O_6^- + 6 I^- \]

\[
\begin{align*}
W & = \frac{V_1 \times M_2}{M_1} \\
& = \frac{1000}{1000}
\end{align*}
\]

\[ RO_2H + 2 I^- + H^+ = I_2 + ROH + H_2O \]
\[ I_2 + 2 S_2O_3^- = S_4O_6^- + 2 I^- \]

\[
T-BuO_2H = \frac{V_1 \times M_1 \times 1000}{1000 \times 2 \times 0.5}
\]

\[
T-BuO_2H = \frac{V_1 \times 3 \times W \times 1000}{0.5 \times M_1 \times V_2}
\]

\[
(P) = \frac{V_1 \times W \times 3000}{M_1 \times V_2 \times V_3}
\]

\[ V_1 = \text{VOLUME OF } Na_2S_2O_3 \text{ USED FOR STANDARDIZATION} \]
\[ W = \text{WEIGHT OF } KIO_3 \text{ WHICH IS USED IN STANDARDIZATION} \]
\[ M_1 = \text{MOLECULAR WEIGHT OF } KIO_3 \]
\[ V_3 = \text{VOLUME USED FOR SAMPLING OF THE REACTION MIXTURE} \]
\[ V_2 = \text{VOLUME USED FOR SAMPLE (DETERMINATION OF } RO_2H \text{)} \]
\[ M_2 = \text{MOLECULAR WEIGHT OF } Na_2S_2O_3 \]
\[ P = \text{[T-BuOH]} \]