Oxidation of Organic Sulfides by Electrophilically-Activated Hydrogen Peroxide: The Catalytic Ability of Methylrhenium Trioxide

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A family of organic sulfides was oxidized to the corresponding sulfoxides by hydrogen peroxide. Such reactions are, however, very slow and meaningless in practice without an effective catalyst. The oxidation was successfully catalyzed by CH_3ReO_3, a water-soluble organometallic oxide. A kinetic study was carried out in 1:1 (v/v) acetonitrile–water at pH 1 and at 25 °C. The kinetics can be resolved into two steps. First, H_2O_2 and CH_3ReO_3 react to form 1:1 and 2:1 rhenium peroxides, denoted as **A** and **B**, respectively. In the second step **A** and **B** react with the substrate forming the product. The rate constants for the various steps of these reactions were evaluated using steady-state techniques and are on the order of 10^3 L mol^{-1} s^{-1} for aryl methyl sulfides and 10^4 L mol^{-1} s^{-1} for dialkyl sulfides. Both **A** and **B** are reactive, **A** moreso than **B**. The kinetic results point to a mechanism that involves the nucleophilic attack of the sulfur atom on a peroxide oxygen of the rhenium peroxides. This formulation is consistent with the accelerating effects of electron-donating substituents.

Introduction

Reactions that take advantage of the oxidizing power of hydrogen peroxide have taken on new importance because of their environmental implications for the development of processes with fewer salt and other byproducts. Water is the only chemical byproduct of hydrogen peroxide oxidations, when the reactions proceed along the path in which an oxygen atom is transferred to the substrate. This desirable feature favors such processes from an environmental point of view. This concern has been expressed very effectively in recent writings.[1,2]

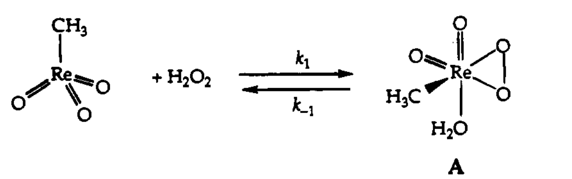
$$H_2O_2 + \text{substrate} \rightarrow H_2O + \text{substrate–O} \qquad (1)$$

Reactions with hydrogen peroxide as in eq 1 are usually very slow and often complicated by radical side reactions, particularly those that arise from free-radical pathways. Both features diminish the attractiveness of peroxide reactions, and a mixture of products is particularly undesirable. An electrophilic catalyst is necessary to activate the peroxide group to give the desired reaction as shown above. In so doing, two goals are achieved: the rates rise to a useful range and the free-radical pathways, not accelerated, become of negligible importance.

Oxo–metal complexes have been shown to be effective in this regard, and much work has been reported on molybdates and tungstates, in particular, and on the less-effective vanadates and chromates. These reagents are often used in aqueous solutions, which can be a limitation, and various pH equilibria can come into play. The acquisition of families of kinetic data that can be readily interpreted thus can be tedious and sometimes ambiguous. Also, in several instances, structural characterization of the catalysts has not proved possible.

The compound methylrhenium trioxide, CH_3ReO_3, sometimes referred to as MTO, does not pose these problems. It is, moreover, a stable compound, prepared rather easily from dirhenium heptoxide and tetramethyltin,[3] and it is a highly effective catalyst. It is stable far above its melting point (106 °C),[4] soluble and stable in water and in organic solvents and stable also to air and acid. Methylrhenium trioxide has been reported in the literature to be a good catalyst for olefin metathesis,[5] olefin oxidation,[6] and aldehyde olefination.[7] This compound also has the advantage of being able to be used as a homogeneous or supported heterogeneous catalyst.

Hydrogen peroxide and methylrhenium trioxide together form a good catalytic system. The catalytically active forms result from their interaction to form 1:1 and 2:1 peroxide compounds.[8] The 1:1 complex, denoted as **A**, is formed in a reversible reaction with an equilibrium constant $K_1 = 7.7$ L mol^{-1} in water[8] at 25.0 °C and ionic strength 0.1 M. The formation of **B**, the 2:1 complex, is also reversible, with $K_2 = 145$ L mol^{-1} in water. These equilibria are depicted in eqs 2 and 3.



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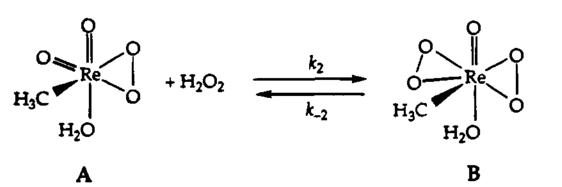

(3)

Compound **B** has been isolated as a pure solid[9] and the crystal structure of the diglyme adduct shows the presence of a water molecule attached to the rhenium center; it is to this coordinated

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(1) Sheldon, R. A. *Topics in Chemistry*; Herrmann, W. A., Ed.; Springer-Verlag: Berlin, 1993; Vol. 164, Chapter 2, pp 21–44.
(2) Strukul, G. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant;* Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.
(3) Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Romão, C. C. *Inorg. Chem.* **1992**, *31*, 4431.
(4) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. J. *Organomet. Chem.* **1989**, *272*, 351.
(5) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1636.
(6) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638.
(7) Herrmann, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641.
(8) Espenson, J. H.; Yamazaki, S.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4685.

water molecule that the diglyme is attached by hydrogen bonds. It is only a surmise as to whether **A** has a water molecule coordinated to the rhenium atom, although that seems plausible.

Our experiments indicate that both **A** and **B** are reactive toward the sufides examined in the course of the present study. Compound **A** is first formed in the equilibrium and seems to be at least three times more reactive than **B**.

Methylrhenium trioxide catalyzes the oxidation of a wide range of substrates,[10,11] and its versatility has already been demonstrated. The substrates include bromide ions and the thiolatocobalt complex[11] $(en)_2Co(SCH_2CH_2NH_2)^{2+}$. The coordinated sulfur atom of this species is oxidized in two steps, first yielding the sulfenato complex and then the sulfinato complex, eq 4.

$$CoSR^{2+} \xrightarrow{H_2O_2/MTO} CoS(O)R^{2+} \xrightarrow{H_2O_2/MTO} CoS(O)_2R^{2+} \quad (4)$$

This result, that the hydrogen peroxide–MTO catalytic system was effective for metal sulfide complexes, led us to test its applicability toward organic sulfides and thiols. This study will show the effectiveness of the catalytic system for the oxidation of a large group of sulfur-containing compounds. We have been motivated in part by the commercial importance of sulfoxides.

Oxidation reactions capable of converting sulfides to sulfoxides and then to sulfones could perhaps be useful in the detoxification of harmful and poisonous substances like nerve agents and mustard gas.[12] Insecticides which are sulfoxides are commercially manufactured by oxidizing sulfides; they might be made in reactions that employ hydrogen peroxide.[13] Another important use of catalytic peroxide chemistry is in the oxidation of penicillin to their *S*-oxides,[14] which can in turn be converted into commercially important cephalosporin derivatives.

Experimental Section

Materials. Methylrhenium trioxide, CH_3ReO_3, was prepared from dirhenium heptoxide and tetramethyltin in the presence of perfluoroglutaric anhydride as described in the literature.[3] The product was purified by sublimation, recrystallization in dichloromethane/hexane, and a final sublimation. Its purity was checked as follows. IR: 999 cm^{-1} (w), 965 cm^{-1} (vs), in CS_2.[15] ^{1}H-NMR: 2.6 ppm in $CDCl_3$.[16] UV–vis in H_2O: 239 nm (ϵ 1900 L mol^{-1} cm^{-1}), 270 nm (ϵ 1300 L mol^{-1} cm^{-1}).[17] Stock solutions of CH_3ReO_3 in water–acetonitrile (1:1 v/v), typically of concentration 10^{-3} M, were kept at 5 °C for 2 days. The solution was protected from light and its concentration was determined spectrophotometrically.

Thiophenol and all the sulfides were from commercial sources, as were the hydrogen peroxide and perchloric acid. The solvent used in the reactions was a 50:50 v/v mixture of acetonitrile and water. High purity water was used, obtained by passing laboratory distilled water through a Millipore-Q water purification system. The acetonitrile used was HPLC grade. Solutions of hydrogen peroxide was standardized by iodometric titration on the same day as used.

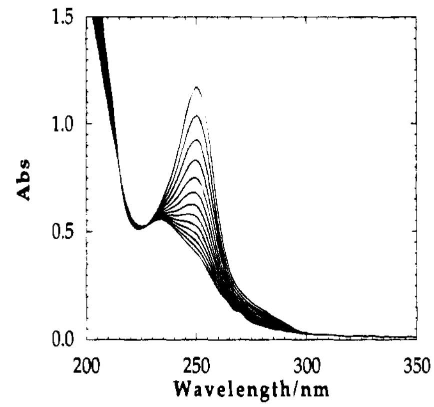


Figure 1. Spectral changes at 2.0 min intervals for the oxidation of methyl phenyl sulfide (8.5×10^{-5} M) with H_2O_2 (1.3×10^{-3} M) in the presence of 33 μM CH_3ReO_3 at pH 1.0 and 25.0 °C in 1:1 CH_3CN-H_2O.

Kinetic Studies. The reaction mixtures were nearly always prepared with the addition of hydrogen peroxide last. This was necessary in most cases to ensure that the catalytic intermediates **A** and **B** were formed in concentrations appropriate to the overall scheme. In a few instances, H_2O_2 was added before the sulfide. This allowed the prior equilibration of **A** and **B** with respect to CH_3ReO_3 and H_2O_2, but this procedure greatly enhanced the concentration of **B** and hence exaggerated its importance in the early stages of the reaction, over what would otherwise apply.

Kinetic data were obtained by the use of a Shimadzu UV-210 PC spectrophotometer. The reaction was followed between 240–260 nm, depending on the compound being investigated. The absorbances reflected the loss of the sulfide and the formation of the sulfoxide product. At these wavelengths the absorbances of CH_3ReO_3 and compound **A** are very minimal at the concentrations employed. When high concentrations of the sulfide were used, the kinetic data was collected at higher wavelengths where the sulfides absorb less strongly to keep the absorbances in a reliable range.

The initial rate method was employed in this study and therefore the full kinetic trace of the reaction was not always acquired. The reactions were studied at 25 ± 0.2 °C and at ionic strength and a perchloric acid concentration of 0.1 M.

Alkyl sulfides do not absorb in the UV and therefore an adjustment to this procedure was made to study these reactions. The reaction of the alkyl sulfide was allowed to compete with that of another sulfide, that absorbed in the UV and whose oxidation by H_2O_2, as catalyzed by CH_3ReO_3 had been previously studied. The absorbance in the UV was monitored, and from it the rate constant for the nonabsorbing compound could be calculated. The method of initial rates was also used in these competition reactions.

Results

Preliminary Experiments. CH_3ReO_3 was found to catalyze the oxidation of organic sulfides to sulfoxides. If the sulfide is reacted with H_2O_2 only, the UV spectrum remained nearly unchanged for several hours at least, indicating a slow uncatalyzed reaction. Once CH_3ReO_3 was present in the reaction mixture, however, the spectrum changed gradually to a final spectrum which could usually be identified as that of the corresponding sulfoxide. In cases where the authentic sulfoxide was not available for comparison, other methods, like GC-MS, was used to identify the product. Clean isosbestic points were observed in the repetitive scans as shown in Figure 1, which presents an experiment on the oxidation of methyl phenyl sulfide.

The sulfoxide was further oxidized to the sulfone under the conditions of study. This reaction was slower yet, even when catalyzed by CH_3ReO_3, and did not affect the formation of the sulfoxide in any way; it was not pursued further. The sulfone

(9) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1158.
(10) Espenson, J. H.; Pestovsky, O.; Huston, P.; Staudt, S. *J. Am. Chem. Soc.* **1994**, *116*, 2689.
(11) Espenson, J. H.; Huston, P.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.
(12) Yang, Y. C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729.
(13) (a) Snyerholm, M. E. US Patent 2,486,445, 1949. (b) Farbenfabriken Bayer Akt-Ges, US Patent 2,963,505, 1958. (c) Farbenfabriken Bayer; US Patent 2,952,700, 1959.
(14) Mangia, A. *J. Chem. Soc., Chem. Commun.* **1978**, 361.
(15) Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.
(16) Herrmann, W. A.; Kiprof, P.; Rydpal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527.
(17) Kunkely, H.; Türk, T.; Teixeira, C.; de Meric de Bellefon, C.; Herrmann, W. A.; Vogler, A. *Organometallics* **1991**, *10*, 2090.

was not observed by HPLC or GC methods in samples taken right after the sulfoxide formation appeared to be complete.

Catalyzed Reaction: Excess Peroxide. In the presence of excess hydrogen peroxide the catalyzed sulfide reactions showed a kinetic trace which was initially zero order but then turned to first order toward the end. This pattern is typical for the Michaelis–Menten kinetics and was also to be expected here from our earlier work done on the thiolatocobalt complex.[8,11] We previously characterized (in pure water, however) the two equilibrium reactions to form **A** and **B**, eqs 2 and 3. To keep the kinetics from undue complexity, the hydrogen peroxide concentration was kept low. This minimized the amount of **B** formed from eq 3. When **B** has no time to be formed, then **A** will be the principal reactive species. (In separate experiments, of a different design, the reactivity of **B** was determined.) The rate-controlling step will therefore be the reaction between the substrate and **A** as shown in eq 5, the rate constant for which is labeled k_3 to be consistent with notation we have used earlier.

$$R_2S + CH_3Re(O)_2(O_2) \xrightarrow{k_3} CH_3ReO_3 + R_2SO \qquad (5)$$

The total concentration of rhenium is denoted $[Re]_T$, which is the sum $[CH_3ReO_3]$ + [**A**], [**B**] being negligible in these circumstances. The assumption was made that [**A**] obeys the steady-state approximation, in which case one readily arrives at eq 6.

$$\frac{d[R_2SO]}{dt} = \frac{k_3[Re]_T[H_2O_2][R_2S]}{\dfrac{k_{-1} + k_3[R_2S]}{k_1} + [H_2O_2]} \qquad (6)$$

Catalyzed Reaction: Variation of $[Re]_T$. The value for k_1 had been found to be 77 L mol^{-1} s^{-1} in water at 0.1 M ionic strength.[11] The solvent used in this study was 50:50 acetonitrile–water, which necessitated a re-determination of k_1 under these conditions. From eq 6, it can be seen that the condition needed to obtain k_1 most simply is to adjust the substrate concentration such that $[R_2S] \gg k_{-1}/k_3$. In this limit the rate simplifies to the form in eq 7, which is first-order with respect to hydrogen peroxide, the limiting reagent.

$$\frac{d[R_2SO]}{dt} = k_1[Re]_T[H_2O_2] \qquad (7)$$

The first-order plots were linear over a wide range of methylrhenium trioxide concentrations, each leading to a rate constant designated k_ψ. A plot of the values of k_ψ against $[Re]_T$ gave a straight line with slope k_1 and an intercept within experimental error of zero, as shown in Figure 2. The fact that the intercept is zero indicates that the uncatalyzed reaction is indeed negligible compared to the catalyzed reaction. The rate constant k_1 was found to be 30.0 ± 1.0 L mol^{-1} s^{-1} for the reactions done in 50:50 acetonitrile–water.

Catalyzed Reaction: Determination of k_{-1}. The concentration of hydrogen peroxide was kept low to ensure that the concentration of **B** would be very small and that eq 6 would be applicable. The variation of the sulfide concentration produced kinetic traces which did not fit first-order kinetics. The initial rate method was therefore used to analyze the kinetics. An increase in $[R_2S]$ should cause the initial rate to rise, and finally reach a plateau. This is shown for the oxidation of methyl phenyl sulfide in Figure 3. The rate constant k_{-1} was obtained by fitting the data to eq 6, fixing k_1 as 30 L mol^{-1} s^{-1} and k_3 as 2.7 × 10^3 L mol^{-1} s^{-1}, as reported below. The rate constant k_{-1} so determined was found to be 3.2 ± 0.1 s^{-1}.

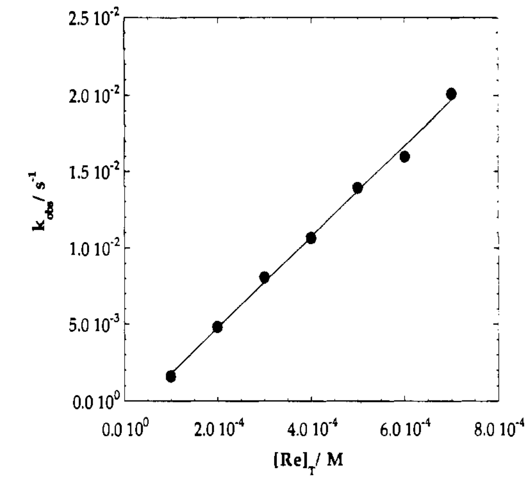


Figure 2. Observed first-order rate constants for the oxidation of methyl phenyl sulfide (0.03 M) by H_2O_2 (5 × 10^{-3} M) are shown to vary linearly with total catalyst concentration. The slope of this line corresponds to k_1 = 30 ± 1 L mol^{-1} s^{-1} in 1:1 acetonitrile–water at 25.0 °C and pH 1.

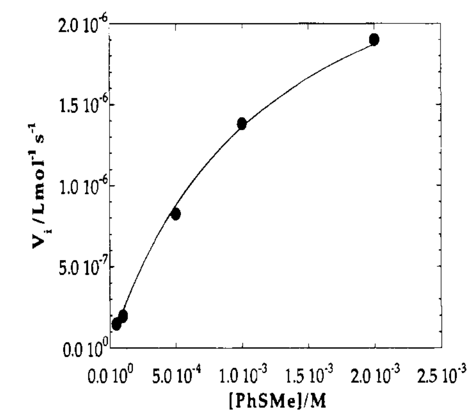


Figure 3. Variation of initial rate of reaction with $[PhSCH_3]$. The curve is a fit of these data to the rate law (eq 6) that is applicable when [**B**] is negligible, in which k_{-1} was floated and two parameters were fixed, k_1 = 30 L mol^{-1} s^{-1} and k_3 = 2.7 L mol^{-1} s^{-1}. Conditions used: 25 °C, pH 1 in 1:1 acetonitrile–water, with $[Re]_T$ = 1.0 × 10^{-3} M, $[H_2O_2]$ = 1.0 × 10^{-3} M.

Catalyzed Reaction: Determination of k_3. The conditions necessary to determine k_3 are those at low hydrogen peroxide concentration, with $[R_2S]$ adjusted such that k_{-1} and $k_3[R_2S]$ were comparable. In this series both $[Re]_T$ and $[H_2O_2]$ were varied. Again the initial rate method was used to obtain kinetic data. The initial rates in each series were fit to eq 6 and by fixing the values for k_1 and k_{-1} at the independently-known values, given above. This allowed k_3 to be calculated. These calculations were done with the program called KaleidaGraph on the Macintosh computer. Plots of the initial rates against $[Re]_T$ gave straight lines. The plots of the initial rates against $[H_2O_2]$ also gave straight lines at the low peroxide concentrations which were being used. Figures 4 and 5 show the results, again with the methyl phenyl sulfide reaction used as an example. Both sets of data gave k_3 values which agreed with each other.

Having all these sets of data from the various studies done, it was necessary to put them all together to obtain a single value for k_3. The PC program called GraFit allowed the global fit of all of the initial rate data simultaneously to the three *x* parameters, $[R_2S]$, $[H_2O_2]$, and $[Re]_T$. The values of k_3 that are presented in Table 1 are the results of this fitting procedure.

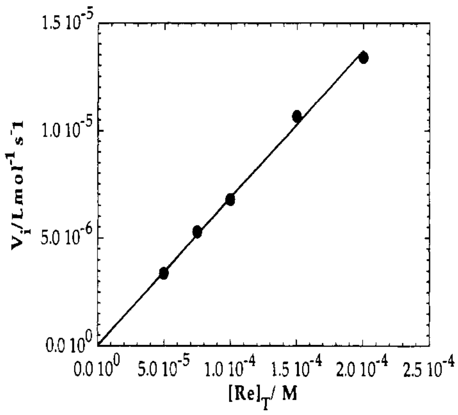


Figure 4. Variation of the initial rates of reaction of methyl phenyl sulfide with $[Re]_T$. The line is a fit of the data to the rate law (eq 6) and gave k_3 to be $(2.9 \pm 0.2) \times 10^3$ L mol^{-1} s^{-1}, with $k_1 = 30$ L mol^{-1} s^{-1} and $k_{-1} = 3.2$ s^{-1}. Conditions used: 25 °C, pH = 1 in 1:1 acetonitrile–water, with [MeSPh] = 3.0×10^{-3} M and $[H_2O_2] = 3.0 \times 10^{-3}$ M.

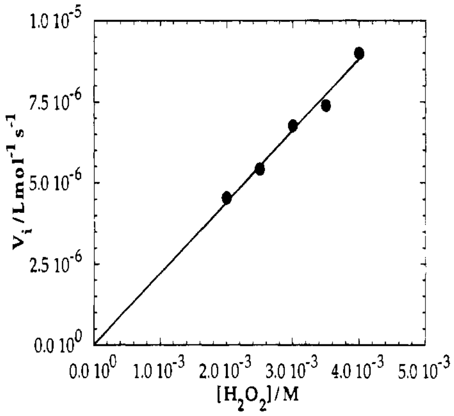
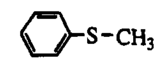
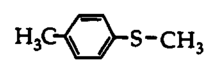
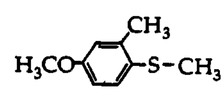
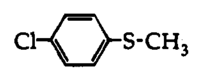
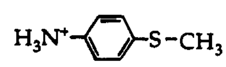
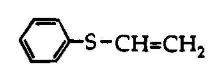
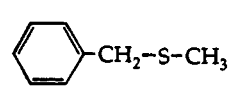
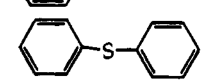
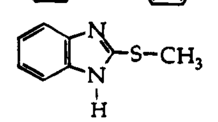


Figure 5. Variation of initial rates of reaction of methyl phenyl sulfide with $[H_2O_2]$. The line is a fit of the data to the rate law (eq 6) and gave k_3 to be $(2.6 \pm 0.1) \times 10^3$ L mol^{-1} s^{-1}, with $k_1 = 30$ L mol^{-1} s^{-1} and $k_{-1} = 3.2$ s^{-1}. Conditions used were 25 °C, pH = 1 in 1:1 acetonitrile–water, with [MeSPh] = 3.0×10^{-3} M and $[Re]_T = 1.0 \times 10^{-4}$ M.

Competition Reactions. A competition method was devised to deal with those sulfides whose oxidations were not accompanied by an appreciable change in the UV spectrum. This process was designated as a competition because the method uses two sulfides to compete for the oxidant with this experimental design. The first substrate, denoted as $(R_2S)_a$ can be any compound for which the desired reaction has already been studied. The k_{3a} value for it is known from the independent study just described. The substrate $(R_2S)_a$ must be one that gave rise to substantial changes in the UV spectra, and it provided the means by which both reactions could simultaneously be followed. The second substrate, $(R_2S)_b$, has the disadvantage of not absorbing in the UV, and therefore the kinetics of its oxidation cannot be followed directly by UV methods. The pair of substrates is together allowed to react with the oxidant. The kinetic curve for the absorbance changes in the one will indicate the level of competition between the two substrates.

To obtain the most precise data, it was desirable for one substrate to be somewhat more competitive than the other. This means that $k_{3b}[(R_2S)_b] > k_{3a}[(R_2S)_a]$, where k_{3a} and k_{3b} are the respective rate constants for the oxidation of the two. Small changes in $[(R_2S)_b]$ would therefore give large and reliable differences in the initial rates of the chemical reactions over the range of $[(R_2S)_b]$ studied. A typical set of kinetic curves is shown in Figure 6 for the competition between $(R_2S)_a$ = methyl tolyl sulfide and $(R_2S)_b$ = pentamethylene sulfide. The kinetic

Table 1. Rate Constants for the Oxidation of Aryl Thioethers with Hydrogen Peroxide with Two Rhenium Catalysts

Substrate	Reaction with A k_3/L mol^{-1}s^{-1}	Reaction with B k_4/L mol^{-1}s^{-1}
	$(2.65 \pm 0.08) \times 10^3$	$(9.65 \pm 0.02) \times 10^2$
	$(4.3 \pm 0.3) \times 10^3$	
	$(8.5 \pm 1.6) \times 10^3$	
	$(1.63 \pm 0.07) \times 10^3$	
	$(5.70 \pm 0.20) \times 10^2$	$(7.0 \pm 1.0) \times 10^1$
	$(1.49 \pm 0.04) \times 10^2$	
	$(5.4 \pm 0.3) \times 10^3$	
	$(1.18 \pm 0.06) \times 10^2$	$(3.2 \pm 0.05) \times 10^1$
	$(4 \pm 1) \times 10^{-1}$	$(4 \pm 1) \times 10^{-1}$

[a] For compounds **A** and **B**, see eqs **2** and **3**. [b] At 25.0 °C and pH 1 in 1:1 (v/v) acetonitrile–water.

traces from left to right corresponded to [MeSTol] = 1.00×10^{-3} M and $[C_5H_{10}S] = 0–4 \times 10^{-3}$ M. As the pentamethylene sulfide concentration increases, the initial rate of absorbance change arising from the reference reaction decreases; this indicates that the increasing demand for the oxidant by the pentamethylene sulfide, because of the increased rate of this reaction over that of the methyl tolyl sulfide reaction. The following reactions are the equations that govern this reaction.

$$CH_3ReO_3 + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{A} \tag{2}$$

$$\mathbf{A} + (R_2S)_a \xrightarrow{k_{3a}} CH_3ReO_3 + (R_2SO)_a \tag{8}$$

$$\mathbf{A} + (R_2S)_b \xrightarrow{k_{3b}} CH_3ReO_3 + (R_2SO)_b \tag{9}$$

The steady-state approximation for $[\mathbf{A}]_{ss}$ is

$$[\mathbf{A}]_{SS} = \frac{k_1[Re]_T[H_2O_2]}{k_{-1} + k_{3b}[(R_2S)]_b + k_{3a}[(R_2S)]_a + [H_2O_2]} \tag{10}$$

where again $[Re]_T = [CH_3ReO_3] + [\mathbf{A}]$. The initial rate of the reference reaction when the transparent substrate $(R_2S)_b$ is absent is given as $(V_a)_i$, and the initial rate when it is present is given as $(V_{ab})_i$. The relationship between these initial rates and the rate constants that govern reactions 8 and 9 is

$$\frac{(V_a)_i - (V_{ab})_i}{(V_{ab})_i} = \frac{k_{3b}[(R_2S)_b]}{k_{-1} + k_{3a}[(R_2S)_a] + k_1[H_2O_2]} \tag{11}$$

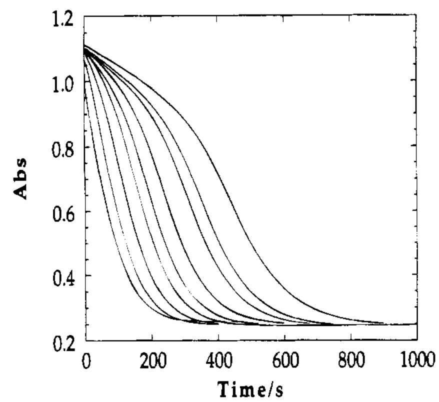


Figure 6. Absorbance–time data at λ = 254 nm for the catalyzed oxidation of methyl tolyl sulfide (1.0×10^{-3} M) in competition with pentamethylene sulfide $(0-4.0) \times 10^{-3}$ M. Conditions used were 25 °C, pH 1 in 1:1 acetonitrile–water, with $[Re]_T$ = 60.0 μM and $[H_2O_2]$ = 0.0100 M. The unusual pattern results from the cuncurrent reactions of two sulfides, only one of which absorbs appreciably at this wavelength.

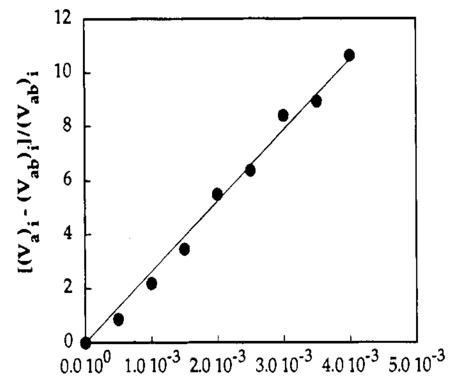


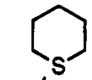
Figure 7. The initial rate ratio as defined in eq 11 is plotted against $[C_5H_{10}S]$ for the competition reactions between methyl tolyl sulfide and pentamethylene sulfide. The slope of the line gave $k_{3b} = (1.99 \pm 0.04) \times 10^4$ L mol^{-1} s^{-1} for the latter.

An increase in the concentration of the second substrate $(R_2S)_b$ leads to an increase in the term on the left of eq 11. The rate constant for reaction 8 can therefore be obtained by fitting the kinetic data to the above equation recalling that in both initial rate measurements only $-d[(R_2S)_a]/dt$ is being recorded. The plot of initial rate term on the left of eq 11 against the concentration of $(R_2S)_b$ is shown for pentamethylene sulfide in Figure 7. From the slope of this plot k_{3b} for pentamethylene sulfide was found to be 1.99×10^4 L mol^{-1} s^{-1}. Similar measurements were also out for diethyl sulfide and for diisopropyl sulfide. The rate constants for the oxidation of these substrates can be found in Table 2.

Labeling Studies with ^{18}O. When CH_3ReO_3 was dissolved in 10% ^{18}O-labeled water, whether under neutral or acidic (pH 1) conditions, it was shown with the aid of GC-MS that the three equivalent oxo groups exchange with the oxygen of water. The exchange was complete in 30 min; no attempt was made to measure the actual rate of exchange by working more rapidly. Peaks corresponding to the exchange of one and two oxo groups were clearly identified in the chromatogram. The low percentage of ^{18}O in the water used, ca. 10%, prevented the observation of peaks corresponding to the exchange of three oxygen atoms, due to their low statistical occurrence.

It was necessary to determine whether the oxygen atoms in the peroxide groups in compounds **A** and **B** are derived totally from hydrogen peroxide, or whether one originated from the hydrogen peroxide and the other from CH_3ReO_3. Likewise, it was desired to trace the origin of the oxygen atom of the resulting sulfoxide. These questions were answered by the following experiment. The rhenium-catalyzed oxidation of methyl phenyl sulfide by hydrogen peroxide was carried out in 10% ^{18}O-labeled water at pH 1; that is to say, the oxygens of the parent rhenium compound were labeled. The methyl phenyl sulfide was present in excess over the hydrogen peroxide, $H_2(^{16}O)_2$. The results from the GC-MS analysis showed that the methyl phenyl sulfoxide contained ^{16}O only.

Table 2. Rate Constants for the Oxidation of Selected Dialkyl Sulfides by H_2O_2 with CH_3ReO_3 as Catalyst[a]

Substrate	$k_3/10^4$ L mol^{-1} s^{-1}
$(CH_3CH_2)_2S$	2.0 ± 0.6
	1.99 ± 0.04
$((H_3C)(H_3C)CH)_2S$	1.6 ± 0.4

[a] At 25.0 °C and pH 1 in 1:1 (v/v) acetonitrile–water.

Catalytic Contributions from Compound B. The oxidation of substrates with an excess of hydrogen peroxide yields absorbance–time curves that did not follow first-order kinetics. This was as expected since data that fit the Michaelis–Menten type equation would not simplify in that manner in the limit of high $[H_2O_2]$.

At very high concentrations of hydrogen peroxide, however, the absorbance–time traces did adhere more closely to first-order kinetics. At these higher peroxide concentrations eq 6 was no longer applicable. Under these conditions, the equilibrium in eq 3 produced a higher concentration of compound **B** that then needed to be considered in the kinetic analysis. Under these conditions the following reactions were important:

$$CH_3ReO_3 + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Re(O)_2(O_2) \tag{2}$$

$$CH_3Re(O)_2(O_2) + H_2O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3Re(O)(O_2)_2(H_2O) \tag{3}$$

$$CH_3Re(O)_2(O_2) + R_2S \xrightarrow{k_3} CH_3ReO_3 + R_2SO \tag{5}$$

$$CH_3Re(O)(O_2)_2(H_2O) + R_2S \xrightarrow{k_4} CH_3Re(O)_2(O_2)(H_2O) + R_2SO \tag{12}$$

The steady state approximation was then applied to both $CH_3Re(O)_2(O_2)$, **A**, and to $CH_3Re(O)(O_2)_2(H_2O)$, **B**. The total rhenium concentration is given as $[Re]_T = [CH_3ReO_3] + [\mathbf{A}] + [\mathbf{B}]$. The rate of the reaction as it is affected by both **A** and **B** is given by eq 13.

$$\frac{d[R_2SO]}{dt} = \frac{k_1k_3[Re]_T[H_2O_2][R_2S] + \dfrac{k_1k_2k_4[Re]_T[R_2S][H_2O_2]^2}{k_4[R_2S] + k_{-2}}}{k_{-1} + k_3[R_2S] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_4[R_2S] + k_{-2}}} \tag{13}$$

The best fits to eq 13 were obtained when the data at high hydrogen peroxide concentration were combined with previously-presented data obtained for the same reaction under conditions where the catalytic effect of **B** was minimal. All these data were fit to the eq 13 globally, again with three x variables, with the use of the GraFit program. The values of k_4 are given in Table 1 for those substrates for which the reactivity of **B** was determined.

Oxidation of Thiophenol and Hydrogen Sulfide. Some studies were done on the oxidation of these compounds. The uncatalyzed oxidation of thiophenol by H_2O_2 at pH 1 gave the disulfide as the sole product. Upon inclusion of CH_3ReO_3 as a catalyst, two products were formed. The disulfide was again formed, but now in small amounts, the major product being benzenesulfonic acid. The product mixture depended on the ratio of the reactants, consistent with competing reactions of intermediates. The oxidation of the thiol will be reported in detail later. Hydrogen sulfide was oxidized slowly to sulfur without a catalyst. The catalytic reaction with CH_3ReO_3 is fast and efficient in converting hydrogen sulfide to sulfur.

Discussion

The oxidation of the organic sulfides, when studied under conditions of excess hydrogen peroxide, gave absorbance–time plots that were initially zero order with respect to the concentration substrate but then tended to first order toward the end. The variation of the sulfide concentration showed that there was a saturation point, such that the rate attained a plateau in the limit of high sulfide concentration. This pattern conforms to that usually found for typical enzyme-catalyzed reactions, with kinetics portrayed by the Michaelis–Menten equation. Our previous study on the oxidation of the thiolatocobalt complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ fitted this mechanism well. It appeared reasonable that the organic sulfides might follow the same scheme, and we proceeded accordingly.

Methylrhenium trioxide reacts with hydrogen peroxide to form two adducts, **A** and **B**, eqs 2 and 3. In this reaction scheme it was possible for either adduct or both to be active catalysts. It was not possible from preliminary studies to decide which is reactive. It is however possible to adjust reaction conditions to make the contribution of one species negligible enough so that conclusions can be drawn about the other and vice versa.

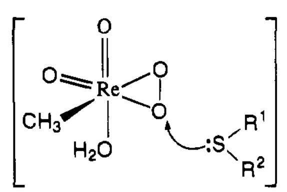
The value calculated for the first equilibrium constant from the kinetic results is the calculation of K_1 as k_1/k_{-1}. The value so determined is $K_1 = 10$ L mol^{-1} at 25.0 °C in 1:1 acetonitrile–water. This agrees with an independently determined value of 13 L mol^{-1} using equilibrium studies. This value of the equilibrium constant is not very different from that previously obtained in water, 7.7 L mol^{-1}.[10] However the component rate constants themselves, k_1 and k_{-1}, are roughly halved in moving from aqueous medium to 1:1 acetonitrile–water.

The k_1 value of 30 L mol^{-1} s^{-1} in the mixed sovlent was found to be the same irrespective of the substrate, as the kinetic model being used required. The k_{-1} value was obtained by fixing the k_1 value and floating k_{-1} and k_3 in a global analysis with the GraFit program. Again, the value of k_{-1} was independent of the nature of the substrate. These values, once known, were used in fitting the equation to determine k_3 for all the substrates studied. In order to determine k_3 reliably it was essential to keep the hydrogen peroxide concentration as low as possible, to control the fate of **A** once it is formed. Compound **A** reacted with hydrogen peroxide at a rate of k_2[**A**][H_2O_2] to form **B**, and **A** reacted with substrate at a rate k_3[**A**][R_2S] to form product. Provided $k_3[R_2S] \gg k_2[H_2O_2]$, the formation of **B** would be negligible compared to the formation of the product through the rate constant k_3. This was the desirable circumstance as long as the goal was to evaluate k_3. Equation 6 was derived on the basis of this limit, and it was used in this form for the determination of the k_3 values.

The rate constants for the oxidation of the substrates by **A** are given by the rate constant k_3, its values for these sulfides are shown in Table 1. The catalyzed rates are a factor of approximately 10^6 greater than those for the uncatalyzed reaction based on studies we have done for diphenyl sulfide.

The rate law could be verified at different reactant concentrations. At low hydrogen peroxide concentration, where the term in the denominator containing [H_2O_2] was much smaller than the other two, and the $k_3[R_2S]$ term was much greater than k_{-1}, then $k_3[R_2S]$ was the dominant term in the denominator and canceled out with the corresponding term in the numerator. The rate was then directly proportional to $[Re]_T$ and [H_2O_2]. Since [H_2O_2] was limiting, a plot of the observed rate against $[Re]_T$ should give a straight line. The straight line plot was indeed observed, see Figure 2, lending credence to this mechanism.

The mechanism that we have proposed is one in which the sulfur atom of the substrates nucleophilically attacks the peroxo group of the 1:1 complex **A**, formed in a prior equilibrium step. From such a transition state the sulfoxide product would be formed directly and CH_3ReO_3 regenerated. The hydrogen peroxide is activated by the electron-poor, high-valent rhenium center. This increases the electrophilicity of the peroxide group making nucleophilic attack more facile. A diagram of the proposed transition state is



The correctness of this diagram for the transition state could be tested by increasing or decreasing the electron donating ability of one of the substituents on the sulfur atom. The rate constant k_3 for the catalyzed reaction should increase or decrease accordingly.

A series of substrates was studied in which the para substituents were placed on the phenyl ring. From the rate constants listed in Table 1, one can see that increasing the electron donating ability of the substrate from methyl phenyl sulfide to methyl p-tolyl sulfide increased the rate of the reaction. The o-methyl-p-methoxyphenyl methyl sulfide showed an even larger increase owing to the two donating groups attached to the phenyl ring. Electron-withdrawing substituents like chlorine and a protonated amine group on the phenyl ring resulted in a decrease in k_3 as would be expected by this mechanism. This results could be correlated by the Hammett linear free-energy relationship

$$\log(k/k_H) = \varrho\sigma \qquad (14)$$

where k is the second-order rate constant k_3 and σ is the substituent constant for para-substituted benzoic acids relative to benzoic acid. The constant ϱ represents the reaction constant.

A plot of log k_3 against σ for substituted methyl phenyl sulfides gives a straight line with a negative slope, $\varrho = -0.98$. The Hammett plot is shown in Figure 8. As expected from the mechanism, and shown by the kinetics, the rate is enhanced by electron-donating substituents and decreased by electron-withdrawing substituents. The fact that the reaction constant ϱ is negative means that the reaction center in the transition state has a partial positive charge relative to that in the ground state. The value of ϱ is close to -1 indicating a substantial charge

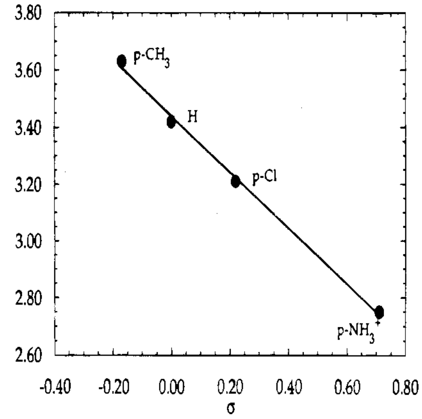


Figure 8. Hammett plot for the oxidation of substituted methyl phenyl sulfides by hydrogen peroxide with CH_3ReO_3 as catalyst. The rate constants are the values of k_3, relative to k_3 for the parent compound. The slope of the line gives $\varrho = -0.98$.

buildup at the reaction center. The electronic effect extended to members that could not be treated according to the Hammett equation. In the case of the phenyl vinyl sulfide and diphenyl sulfide, a substantial decrease in rate relative to that of PhSMe was observed. The vinyl group and the second phenyl group are both less electron donating than the methyl group that they have replaced in the reference compound.

In the reaction studied the activated form of the catalyst, **A**, readily oxidized the nucleophilic sulfide to sulfoxide. However the less nucleophilic sulfoxide was converted to the sulfone only very slowly. The reduction in rate provides further substantiation for the propsal that the reaction occurs by the attack of the nucleophilic substrate on the metal peroxide.

The chemistry of the metal peroxides has been well established.[18] Hydrogen peroxide can be activated by many metal ions, some of which are molybdenum(VI),[19] tungsten(VI),[20] and vanadium(V).[21] The $[MoO(O_2)_2pic]^-$ complex[22] is similar in structure to the rhenium catalysts and has similar catalytic activity.

The methyl *p*-tolyl sulfide was used as a probe in the competition reactions. The oxidation of this sulfide was studied, and a k_3 value of 4.3×10^3 L mol^{-1} s^{-1} was obtained. The kinetic traces for this oxidation showed the usual loss in absorbance to form the product. On inclusion of the alkyl sulfide in this reaction mixture the initial rate decreased. This was because **A** underwent competing, concurrent reactions. The use of low hydrogen peroxide concentrations ensured that species **B** was present in negligible amounts.

The kinetic traces compared well to theoretical curves obtained by numerical solutions of this family of differential equations, as carried out through a program called KinSim.[23] Another part of this program, called FitSim, was able to take the kinetic information from several of these reactions along with the relevant concentrations and rate constants, and use them to simulate and fit calculated values to the actual curves. The calculated rate constants obtained agreed very well with that obtained in the kinetics through the use of eq 11.

The oxidation of the methylmercaptobenzimidazole (see Table 1, last entry) is seen to be extremely slow in comparison to the other sulfides studied. Its rate constant is $<10^{-3}$ that of PhSMe. In this study high hydrogen peroxide concentrations were used to obtain reasonable rates. As a result the k_3 and k_4 rates were obtained together from the fitting of the full equation (eq 13) using GraFit. The increased aromaticity in the molecule along with the two nitrogen groups which would be protonated (becoming electron withdrawing) must be the underlying factors for the exceptional slowness of this oxidation.

When an aromatic group was replaced by an alkyl group, the reaction became about 10 times faster. For an estimate of the rates of the dialkyl sulfide reactions, the reaction of benzyl methyl sulfide reaction was studied. With the CH_2 group between the phenyl ring and the sulfur atom this compound is quite similar to alkyl sulfides. The rates for the pentamethylene sulfide and ethyl sulfide reactions are the same, which is not surprising since these compounds are quite similar. Pentamethylene suifide has one more CH_2 group which joins the others in a ring. The diisopropyl sulfide rate was not much less reactive. The probability of steric hindrance can be considered but either it is quite unimportant, as we believe, or a fortuitous cancellation of offsetting factors must be invoked.

At high hydrogen peroxide concentrations the kinetics of the oxidation of the substrates with CH_3ReO_3 as catalyst became more complicated. This is because at these higher peroxide concentrations not only the 1:1 complex **A** was present, but also the 2:1 complex **B**. Equation 13 defines the rate under these conditions. It is more difficult to solve this equation, in that the k_2 and k_{-2} terms were not determined independently under these conditions. In water at pH 1, the known values are $k_2 = 5.2$ L mol^{-1} s^{-1} and $k_{-2} = 0.04$ s^{-1}. When these values were used and the data fitted as described by GraFit, the result was $k_3 = 2.5 \times 10^3$ L mol^{-1} s^{-1}, a value very close to that obtained with the simple equation. The k_4 rate constant obtained in the same calculation was $(9.6 \pm 1.7) \times 10^2$ L mol^{-1} s^{-1}.

If we should assume that the effect of solvent change from water to 1:1 acetonitrile:water on the rate constant for the second equilibrium (eq 3) is the same as the effect on the first (eq 2), then in 1:1 acetonitrile–water, $k_2 \sim 2$ L mol^{-1} s^{-1} and k_{-2} $\sim$0.013 s^{-1}. When these values were substituted into eq 13, then $k_3 = (2.6 \pm 0.1) \times 10^3$ L mol^{-1} s^{-1} and $k_4 = (1.1 \pm 0.3) \times 10^3$ L mol^{-1} s^{-1}. Although k_4 could not be determined with as high a degree of accuracy as k_3, the data clearly suffice to show that **B** is a reactive catalyst. From the data in Table 1, it is obvious that the reactivity of **B** is not much less than that of **A**. The rate constants from the study of various substrates indicated that the relative reactivities of **A** and **B** depend on the identity of the substrate. Changes in the solvent also affect the relative reactivities. It is probable that **A** is a better electrophile than **B** because the electron-poor rhenium center is now occupied by two peroxo groups in **B**. It is also likely that steric hindrance plays some part, albeit minor, depending on the structure of the substrate. The difference in the reactivity of species **A** and **B** is small. This is not surprising since the difference between these peroxo species is not too great.

Indeed, the oxidation of bromide ions[24] and of phosphines[25] show the kinetic similarity of the two peroxides in those cases. This stands in contrast to our findings for the cobalt thiolate complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ for which $\nu_A \gg \nu_B$. This may be a unique case, as it turns out, and the ionic charge on the substrate cannot be ruled out as a contributing factor. This

(18) Reference 2, Chapter 6.
(19) Bortolini, O.; Di Furia, F.; Modena, G.; Scardellato, C.; Scrimin, P. *J. Mol. Catal.* **1981**, *11*, 107.
(20) Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688.
(21) Mimoun, L.; Daire, S. E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.
(22) Campestrini, S.; Conte, V.; Di Furia, F.; Modena, G.; Bortolini, O. *J. Org. Chem.* **1988**, *53*, 5721.
(23) Barshop, B. A.; Wrenn, C. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134.
(24) Espenson, J. H.; Pestovsky, O.; Huston, P.; Staudt, S. *J. Am. Chem. Soc.* **1994**, *116*, 2869.
(25) Abu-Omar, M.; Espenson, J. H. Submitted for publication.

very complex has also been oxidized by molybdenum(VI), tungsten(VI), and (more slowly) vanadium(V). In these cases, however, the diperoxide reagents are more reactive than the monoperoxides.[26]

There is another report,[9] for alkenes, that the rates of epoxidation are characterized as $v_A \ll v_B$. Our recent but as yet incomplete kinetic study of the alkene epoxidation reaction has shown that the two rates are comparable under the conditions we have used, and we believe that the earlier results reflects the consequence of certain reaction conditions; the full details will be presented in due course.[27] In any event, it now known that the similar reactivities of **A** and **B** toward bromide ions applies to these organic sulfides, and may be more general.

The question arises about the origin of the oxygen atoms in the coordinated peroxo groups on species **A** and **B**. Do both oxygen atoms originate from the hydrogen peroxide? That is, is the O−O bond unbroken or does it contain one oxygen atom from the hydrogen peroxide and another from the CH_3ReO_3? To answer this question we used ^{18}O-labeled water first to verify the report[9] that there is a natural exchange between water and the oxo groups on the rhenium center of CH_3ReO_3 itself. The exchange of oxygen atoms between H_2O and CH_3ReO_3 was observed both in neutral and acidic conditions. The facility of the exchange had previously been reported for the rhenium peroxide **B**,[9] and had been reported for a molybdenum peroxide as well.[28]

Upon oxidation of methyl phenyl sulfide in ^{18}O-labeled water, and thereby with ^{18}O-labeled CH_3ReO_3, we observed that the product consisted only of ^{16}O-sulfoxide. This indicated that in the formation of **A** and **B** the peroxo group remained intact and proved capable of transferring to methyl phenyl sulfide an oxygen atom originating the original hydrogen peroxide.

We also consider an alternative mechanism that involves a prior association between the rhenium catalyst and the organic sulfide. The reaction scheme and the corresponding rate equation can be represented by the following equations:

$$CH_3ReO_3 + R_2S \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathbf{C} \tag{15}$$

$$\mathbf{C} + H_2O_2 \xrightarrow{k_6} CH_3ReO_3 + R_2SO \tag{16}$$

$$\frac{d[R_2SO]}{dt} = \frac{k_5[\mathrm{Re}]_T[H_2O_2][R_2S]}{\dfrac{k_{-5}}{k_6} + \dfrac{k_5[R_2S]}{k_6} + [H_2O_2]} \tag{17}$$

These mechanisms are not considered to be important, since spectral analysis gave no evidence for intermediate **C**. Also, the formation constant and rate of formation and dissociation of this intermediate would differ from one type of substrate to another. That is to say, the leading denominator term in eq 17, k_{-5}/k_6, would obviously be sulfide-dependent. Contrast this with the form in eq 6 where the analogous term, k_{-1}/k_1, is not. Since the value of this parameter was found to be the same for different sulfides under the same conditions, this scheme can be eliminated from consideration.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82. We are grateful to Oleg Pestovsky for some of the oxygen-18 labeling results.

(26) Ghiron, A. F.; Thompson, *Inorg. Chem.* **1990**, *29*, 4457.
(27) Al-Ajlouni, A.; Espenson, H. J. Unpublished results.
(28) Postel, M.; Brevard, C.; Arzoumanian, H.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 4922.