J. Org. Chem. **1999,** *64,* 6374−6379

Kinetics and Mechanism of the Methyltrioxorhenium-Catalyzed Sulfoxidation of Thioketones and Sulfines

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Received April 13, 1999

Kinetic studies have been carried out on the oxidation of thiobenzophenones and thiocamphor by hydrogen peroxide and on the second step in the sequence, oxidation of the resulting sulfines ($Ar_2C{=}S{=}O$). The first reaction follows the pattern now common to methyltrioxorhenium/H_2O_2 reactions, in that the rate constant for the reaction between the peroxorhenium intermediate and the thioketone follows a Hammett correlation such that electron-releasing substrates react more rapidly. The reaction constant is $\rho = -1.12$. However, the plot of $\log(k_X/k_H)$ for the sulfines against 2σ, determined over the range $-1.6 < 2\sigma < +1.5$, is markedly U-shaped. This suggests a mechanism for the sulfines in which the direction of the electron flow in the transition state changes with the electron demand of the substituents on the sulfines. The product of oxidation of the sulfine is a transient sultine (from epoxidation of the C═S bond). It cannot be detected, however, because it so rapidly yields sulfur monoxide. The SO was oxidized to SO_2 under these conditions rather than undergoing disproportionation to SO_2 and S. Also, SO was trapped with a 1,3-diene as a thiophene-1-oxide.

Sulfines (thioketone S-oxides) are attractive heterocumulenes that participate in the thioepoxidation of alkenes,[1] nucleophilic addition,[2] and cycloaddition reactions.[3−6] They are usually prepared by oxidizing the thioketones with peracids,[7−13] ozone,[10,14] or singlet oxygen.[15] The sulfines can be further oxidized, leading ultimately to the ketone. The sequence of conversions, disregarding other intermediates at this point, is outlined in eq 1.

$$R_2C{=}S \xrightarrow{[O]} R_2C{=}S{=}O \xrightarrow{2[O]} R_2C{=}O + SO_2 \qquad (1)$$

We have found that hydrogen peroxide can carry out both stages of this transformation when methyltrioxorhenium (CH_3ReO_3, abbreviated as MTO) is used as the catalyst. We have undertaken a study of these reactions to describe their mechanisms. A point of particular mechanistic interest in this system is whether peroxide is activated for nucleophilic or electrophilic attack. We have studied the kinetics and mechanism of both steps in eq 1, with a particular reference to the substituent effects on the rate constants of ring-substituted thiobenzophenones.

Experimental Section

Materials. The starting thiobenzophenones were prepared according to the literature method,[15,16] except for commercially available thiocamphor, which was used as received. The thiobenzophenones are deep blue materials. The absorption maxima for the compounds $(XC_6H_4)_2C{=}S$, given as λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}), are X = *p*-NMe$_2$ 458 (2.7×10^4), *p*-OMe 355 (2.46×10^4) and 570 (407), *p*-Me 587 (262), H 590 (170), *p*-Cl 600 (215), *m*-NO$_2$ 598 (203). Thiocamphor has λ_{max} 250 nm (ϵ 8.7×10^3 L mol^{-1} cm^{-1}).

Instrumentation. The reaction progress for thioketones was monitored at these wavelengths spectrophotometrically with a Shimadzu UV-3101PC instrument. The second stage, oxidation of sulfines, did not give suitable absorbance changes. Those reactions were followed by ^{1}H NMR with a Bruker DRX-400 spectrometer. The ^{1}H NMR chemical shifts were measured relative to the residual resonance of the solvent, CD_2HCN, δ 1.92 ppm. The solvent in both cases was water−acetonitrile (or, in ^{1}H experiments, D_2O) 1:4 by volume, and it contained 0.10 M trifluoromethanesulfonic acid to stabilize the catalyst.[17] Throughout, the temperature was maintained at 25 °C.

Equilibrium Measurements. The equilibrium constants for the two stepwise MTO−H_2O_2 interactions defined in Scheme 1 were evaluated in this medium by ^{1}H NMR methods. The intensities of the CH_3 groups of the three species MTO, **A**, and **B** were integrated relative to a standard. The determined constants are $K_1 = 91$ L mol^{-1} and $K_2 = 347$ L mol^{-1} at 25 °C, with the activity of water being ignored. These values are much as one might interpolate from other media.[18] As in other circumstances, the values reflect the phenomenon of cooperativity, in that $K_2 > K_1$. We interpret that to mean that the rhenium−oxo multiple bonds are strengthened relative to

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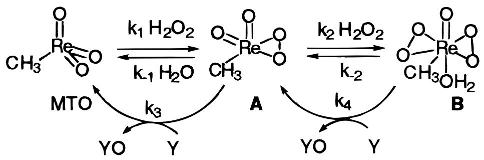
Scheme 1



those in the predecessor compound as the number of Re═O bonds is reduced at each stage.

Kinetic Data. Both initial rate and full time course analyses were employed to determine the kinetics. To determine initial rates, the absorbance−time data from spectrophotometric kinetics or the integrated intensities−time data from ^{1}H NMR kinetics were converted to concentration−time values. The initial rate for each experiment was obtained by fitting each curve to a polynomial function: $[Y]_t = [Y]_0 - m_1t - m_2t^2 - m_3t^3$ ... The value of parameter m_1 was taken as the initial reaction rate, v_i. Under some circumstances the reaction was first-order with respect to the thioketone concentration. In such cases the absorbance−time data were fitted to the equation

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)\exp(-k_\psi t) \quad (2)$$

Trapping of SO with Dienes. 4,4′-Difluorothiobenzophenone *S*-oxide (13 mM) and MTO (12 mM) were mixed in acetonitrile containing 0.1 M HOTf to stabilize the MTO.[17] Hydrogen peroxide (250 mM) was then added to the solution, followed immediately by 2,3-dimethyl-1,3-butadiene (100 mM). The reaction was monitored by ^{1}H NMR. After 1.5 h, 2,5-dihydro-3,4-dimethylthiophene-1-oxide (5.0 mM) was formed. This compound is the known product of the reaction between sulfur monoxide and the diene.[19] The detected spectrum matched that of the known compound: ^{1}H (CD_3CN) δ 3.85 (d, 2H), 3.61 (d, 2H), 1.77 (s, 6H). The remainder of the diene (46 mM) had been oxidized to diol products. MTO-catalyzed oxidations of dienes with hydrogen peroxide have been well-characterized.[20]

The same procedure using 4,4′-dimethoxythiobenzophenone and thiobenzophenone *S*-oxides with the same trapping reagent, 2,3-dimethyl-1,3-butadiene, was used. In these cases the same SO trapped product was obtained.

Results

Identification and Isolation of the Sulfines. The initially formed sulfines were identified by their UV−vis, ^{1}H NMR, and mass spectra in comparison with those of the known compounds.[7,8,11,14,15,21−28] These spectra and those of the starting thiones and final product ketones are given in the Supporting Information. The only exceptions to that are two of the sulfines, which have evidently not been previously reported. These are the previously unknown compounds $(p\text{-}FC_6H_4)_2CSO$ and $(m\text{-}CF_3C_6H_4)_2CSO$. The synthesis and isolation of those compounds has been reported separately.[29]

Kinetics of Thioketone Oxidation. Control experiments for reactions between thioketones and hydrogen peroxide, without MTO, proceeded more than 10^3 times more slowly than those measured with the catalyst present. Thus the uncatalyzed reaction can be neglected entirely. It was also shown that oxidation by atmospheric oxygen or photoactivation in laboratory light were not important. No effort was made to exclude either.

The typical ranges of concentrations used for kinetics experiments on thioketones in these studies were 0.01−0.1 mM thioketone, 0.1−1 mM hydrogen peroxide, and 1−100 μM MTO. The analysis of the kinetic data requires an examination of the general scheme by which MTO activates hydrogen peroxide. The general mechanism has now been established.[30−32] The reactions, shown in Scheme 1,[30] feature (a) conversion of MTO to two successive peroxorhenium complexes, (b) attack of substrate Y at an oxygen of the peroxo group, and (c) transfer of that oxygen to Y. This general picture requires a few refinements in special cases, as recently reviewed,[33] but it otherwise suffices quite well.

The kinetic data for the thioketones could be analyzed by accounting for only the left-hand loop in Scheme 1. That is so because these experiments were carried at low $[H_2O_2]$, where any contribution from **B** can be ignored. Under these circumstances the rate of the reaction takes the form

$$v = \frac{k_1k_3[H_2O_2][Y][Re]_T}{k_{-1} + k_3[Y] + k_1[H_2O_2]} \cong \frac{k_1k_3[H_2O_2][Y][Re]_T}{k_{-1} + k_3[Y]} \quad (3)$$

in which $[Re]_T$ stands for the total rhenium concentration. Under the conditions used for the thioketones, the $k_1[H_2O_2]$ denominator term was entirely negligible. The expression for the reaction rate in eq 3 states that the variation of the initial rate with the concentration of the thioketone will take the form of a rectangular hyperbola, with the rate attaining a thioketone-independent plateau at high concentrations. The same is true for values of k_ψ as a function of $[R_2CS]$. These experiments were carried out with $(p\text{-}MeOC_6H_4)_2C{=}S$ and with thiocamphor. Data for both compounds are displayed in Figure 1. From both experiments, the value $k_1 = 15.5 \pm 0.6$ L mol^{-1} s^{-1} was obtained. Given $K_1 = 91$ L mol^{-1} from ^{1}H NMR experiments cited previously, we obtain the value $k_{-1} = 0.17$ s^{-1}. Such determinations were needed to substantiate the model and establish values of k_1 and k_{-1} in this medium, but the kinetic data at the plateau provided no new data and no information about the reaction of the thioketone itself.

In most of the determinations, therefore, the thioketone concentration was kept deliberately low, such that eq 3 could be simplified even further by dropping the k_3 term in the denominator. The initial rate could then be accurately represented by

$$v_i = K_1k_3[R_2C{=}S]_0[H_2O_2]_0[Re]_T \quad (4)$$

The test of this kinetic equation is presented in Figure

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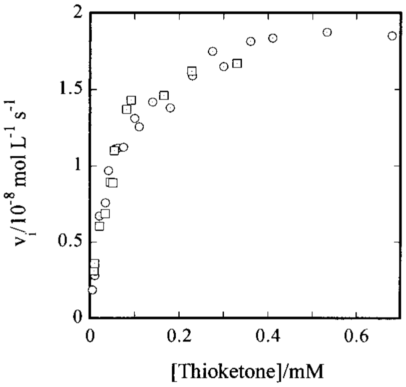


Figure 1. Kinetic data for the oxidation of thioketones to sulfines by hydrogen peroxide with MTO as a catalyst. The initial rates at constant catalyst and hydrogen peroxide concentrations describe a rectangular hyperbola against the concentration of the thioketone. Data were acquired in aqueous acetonitrile (1:4) at 25 °C. Values are shown for $(4\text{-MeOC}_6H_4)_2$-CS (squares) and for thiocamphor (circles).

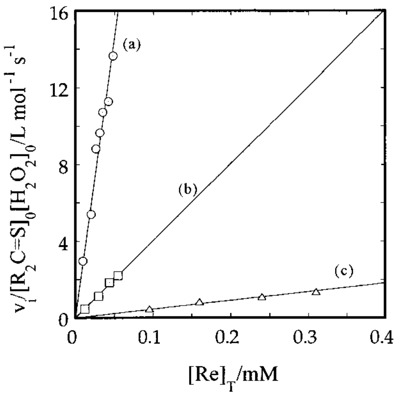


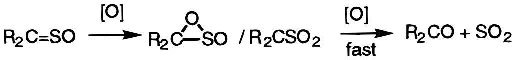
Figure 2. Kinetics of oxidation of thiobenzophenones by hydrogen peroxide. The y-axis displays the initial rate divided by $[Ar_2CS]_0[H_2O_2]_0$. This quantity is directly proportional to $[Re]_T$, in accord with eq 4. Data, acquired in aqueous acetonitrile (1:4) at 25 °C, are shown for $(p\text{-XC}_6H_4)_2CS$, with X = CH_3O (a), CH_3 (b), and Cl (c).

Table 1. Kinetic Data for the MTO-Catalyzed Oxidation of Thiobenzophenones $(XC_6H_4)_2C{=}S$ and Sulfines $(XC_6H_4)_2C{=}S{=}O$ by Hydrogen Peroxide

X	thioketones k_3 (L mol^{-1} s^{-1})(25 °C)	sulfines k_4 (L mol^{-1} s^{-1})(22.5 °C)
p-NMe$_2$	$(9.2 \pm 0.4) \times 10^3$	$(1.93 \pm 0.12) \times 10^1$
p-OMe	$(3.3 \pm 0.1) \times 10^3$	$(3.00 \pm 0.08) \times 10^{-1}$
p-Me	$(4.5 \pm 0.1) \times 10^2$	$(5.46 \pm 0.13) \times 10^{-2}$
H	$(9.0 \pm 0.1) \times 10^1$	$(2.02 \pm 0.07) \times 10^{-2}$
p-F		$(3.03 \pm 0.16) \times 10^{-2}$
p-Cl	$(5.2 \pm 0.1) \times 10^1$	$(2.71 \pm 0.09) \times 10^{-2}$
p-Br		$(2.90 \pm 0.06) \times 10^{-2}$
m-CF$_3$		$(3.37 \pm 0.12) \times 10^{-2}$
m-NO$_2$	$(5.4 \pm 0.3) \times 10^0$	$(1.06 \pm 0.01) \times 10^{-1}$
thiocamphor	$(3.0 \pm 0.1) \times 10^3$	

2, which displays plots of $v_i/[Y]_0[H_2O_2]_0$ against $[Re]_T$ for three substrates. The values of k_3 for these compounds and for others are summarized in Table 1.

Kinetics of Sulfine Oxidation. The next step of oxidation converts the sulfine to a sultine and/or a sulfene:



(5)

These reactions occur rather more slowly. To conduct the kinetics measurements, the thioketones were first treated with 1.0 equiv of hydrogen peroxide, in the presence of MTO. The conversion to the sulfine was shown by ^{1}H NMR in each case to be quantitative, within the precision of the measurement. Additional hydrogen peroxide was then added to provide $[H_2O_2]/[Ar_2CSO] \geq 20$. The disappearance of the sulfine was monitored by ^{1}H NMR, because the absorbance changes were not suitable. The overall concentration ranges in these experiments were 2–20 mM sulfine, 0.2–0.5 M H_2O_2, and 0.1–10 mM MTO.

The conditions under which a thioketone is oxidized give reactions with a typical lifetime of ~10 min; under similar conditions the resulting sulfine requires 670 h. The addition of the electronegative oxygen atom to the sulfur greatly reduces the rate of a subsequent oxidation.

Higher peroxide concentrations were used for the sulfines to avoid a prolonged reaction time. This change means that the simplified kinetic treatment given above will not suffice, because **B** now attains a high concentration and contributes to the overall catalysis. With all the reactions in Scheme 1, the rate law takes the form

$$-\frac{d[Y]}{dt} = \frac{k_1k_3[Re]_T[H_2O_2][Y] + \dfrac{k_1k_2k_4[Re]_T[Y][H_2O_2]^2}{k_4[Y] + k_{-2}}}{k_{-1} + k_3[Y] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_4[Y] + k_{-2}}} \qquad (6)$$

At these high peroxide concentrations, however, a different simplification is valid. This provides a form that is an accurate representation under the circumstances:

$$v = k_4[R_2CSO][Re]_T \qquad (7)$$

To check this equation, tests were carried out to affirm the first-order dependence on sulfine concentration, the first-order dependence on the total MTO concentration (see Figure 3), and the absence of a kinetic term in the hydrogen peroxide concentration, which was varied without effect in the range 0.2–0.5 M. The values of k_4 determined for the sulfines by this procedure are summarized in Table 1.

The oxidation of sulfines to ketones may proceed through a sultine or sulfene intermediate, as written in eq 5, or in some other manner. It had been suggested previously, in the oxidation of sulfines with monoperphthalic acid[8] and perbenzoic acid,[7] that the second oxygen was added to the C=S double bond. Theoretical calculations showed that the sultine intermediate so obtained was more stable than its isomer, the sulfene. It was further suggested that the sultine would rapidly eliminate the ketone, forming sulfur monoxide.[7,8,34,35]

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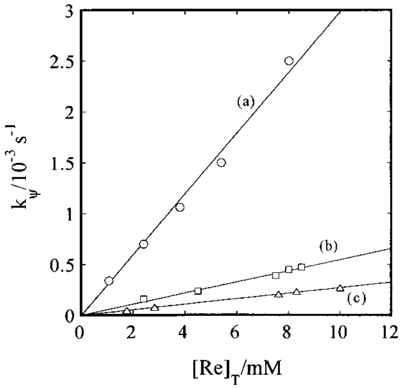
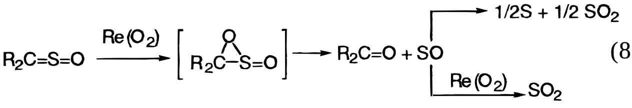


Figure 3. Values of the pseudo-first-order rate constants in aqueous acetonitrile (1:4) at 22.5 °C for the oxidation of thiobenzophenone oxides are a linear function of $[Re]_T$, in agreement with eq 7. Values are shown for $(p\text{-}XC_6H_4)_2CSO$, for X = CH_3O (a), CH_3 (b), and Cl (c).

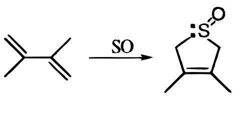
That sulfur monoxide could disproportionate, and it was the previous basis for suggesting the sultine. The oxidation of SO by peroxorhenium complexes seems more probable in this medium; no elemental sulfur was found in our experiments.



(8)

Close attention was therefore paid to the NMR spectra taken during the course of this reaction. Signals from the thioketone, sulfine, and ketone were easily detected. No signal corresponding to a sultine (or sulfene) was detected. Because no intermediate or any other new species was observed, it can be concluded that the subsequent step(s) must be much more rapid than the first.

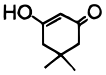
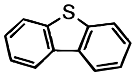
Trapping of Sulfur Monoxide. Sultine formation was not proved by trapping the sulfur monoxide released; evidence for it was the formation of elemental sulfur, suggested to come from SO disproportionation.[7,8] Elemental sulfur was not seen in the present study because even if it was formed under these conditions, it would be oxidized very quickly to sulfur dioxide. To establish this mechanism, experiments were done to trap SO from the oxidation of sulfines. Dienes were known to be able to react with SO fast enough that SO could be trapped as thiophene 1-oxides.[19] Thus 2,3-dimethyl-1,3-butadiene was put into the reaction mixture to trap the SO produced from sulfine oxidation (eq 9). Because dienes



(9)

can also be oxidized by MTO/H_2O_2 and in some cases react faster than sulfines, an excess of sulfines was used to increase the rate of oxidation of sulfines. 4,4′-Difluoro-,4,4′-dimethoxythiobenzophenone and thiobenzophenone sulfines were used, and even though part of the dienes were lost to oxidation, the SO trapped product 2,5-dihydro-3,4-dimethylthiophene 1-oxide was still detected by ^{1}H NMR up to 10% yield based on diene. Because so much diene was oxidized, a better basis is to examine the fate of sulfur monoxide; 100% of it was trapped, about 40% being detected as the product of eq 9 and the balance as its oxidation product.

Table 2. Comparisons of the Rate Constants k_3 for A and k_4 for B in Their Reactions with Different Substrates

substrate	k_3 (L mol^{-1} s^{-1})^a	k_4/k_3^{a}	ref
PhSMe	2.65×10^3	0.36	37
Ph_2S	1.18×10^2	0.27	37
PPh_3	7.3×10^5	3.0	48
$P(C_6F_5)_3$	1.30×10^3	2.7	48
trans-PhCH=CHOMe	14.2	0.90	49
trans-PhCH=CHMe	0.51	0.43	49
Cl$^-$	5.6×10^{-2}	2.3	50
Br$^-$	3.5×10^2	0.49	51
	0.19	0.58	52
	10.2	2.1	53

^{a} From the original references compiled in ref 33.

Discussion

The most important issue to be dealt with is the comparison of the mechanism for thioketones versus sulfines. A seeming complication is that the experiments yielded values of k_3 for the one but k_4 for the other. In fact, this need be of no concern. For numerous substrates both rate constants have been determined. Relatively little variation has been found. The summary of rate constants in Table 2 makes this point very clearly. There is, indeed, one exception, but that refers to the case of allyl alcohols, where hydrogen bonding with **B** plays a special role.[36] With this justification, in what follows the values will be discussed interchangeably.

In earlier studies, the electronic structure of the transition state has been probed by the selection of different substrates. For example, phosphines and sulfides have been studied. With compounds Ar_3P and ArSMe, certain adjustments can be made that will alter the electron density at the accepting atom without causing an important structural change. In these particular cases, the introduction of substituents in meta or para positions provides a useful indicator. A substituent that is electron-attracting relative to H decreases the rate constant and vice versa. When correlated by Hammett's equation, the values are $\rho = -0.63$ (PAr_3) and -0.98 (ArSMe).

So it is with thioketones. The experimental rate constants for $Ar_2C{=}S$ were analyzed for the effect of substituent X by a plot of $\log(k_3^X/k_3^H)$ versus $2\sigma_X$. These points define a linear relation, Figure 4, and afford the reaction constant $\rho = -1.12 \pm 0.16$ ($r = 0.962$). If the somewhat deviant value for X = CH_3O is omitted, then $\rho = -1.06 \pm 0.07$ ($r = 0.994$). The value is comparable to values obtained in other oxidations of thiobenzophenones: $\rho = -0.88$ for perbenzoic acid[7] and $\rho = -0.75$ for *N*-sulfonyloxaziridines.[21]

The data for the thioketones reinforce the already-established depiction of the transition state. The negative reaction constant signifies that positive charge has accumulated in the transition state. The high-valent rhenium center, an electropositive Lewis acidic center,

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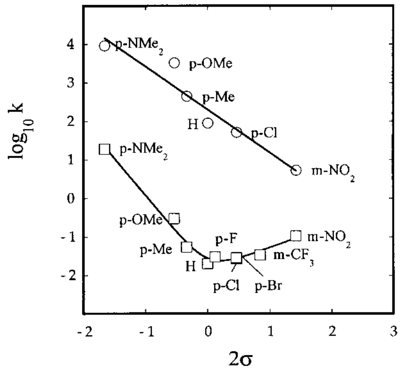


Figure 4. Hammett correlations of log *k* against 2σ for the MTO-catalyzed oxidations of thiobenzophenones (upper) and thiobenzophenone *S*-oxides (sulfines, lower).

polarizes the peroxide ion coordinated to it. Thus the peroxo oxygens are less electron-rich than those in hydrogen peroxide itself. As a result, nucleophilic centers attack at the peroxo oxygen directly, a point that has been affirmed by ^{18}O labeling.[37]

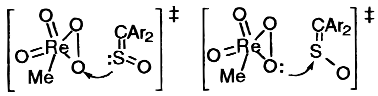
Against this background, the kinetic data for the oxidation of the sulfines form a marked contrast. The Hammett plot, also displayed in Figure 4, shows distinct curvature. Indeed, further compounds were prepared at both extremes of σ to establish that the upward curvature was experimentally and statistically valid over a wide variation.

Curvature in a Hammett plot signals a certain complexity in the mechanism. By the laws of adding exponentials, concave curvature implicates two pathways in parallel, whereas convex curvature is consistent with alternative rate-controlling steps along a single pathway.[38,39] The first of these options is indicated by these results.

Just as with the thioketones, those sulfines that have electron-donating substituents increase in rate, with log *k* varying linearly with σ. The left-hand portion of the Hammett plot for the sulfines is as steep as the line for the thioketones and perhaps steeper. This is reasonable in that the sulfine, with an oxygen atom reducing electron density on the sulfur, makes the C=S=O group of the sulfine more electropositive than the C=S group of the thioketone. The sulfine rates are lower, but their sensitivity to substituents is somewhat greater.

The Hammett plot reverses in slope for substituents with large σ values. This has not been seen before for the oxidations of aromatic thiones or sulfines with other oxidizing reagents.[21,33,38] Substituents that are electron-attracting cause a lesser rate diminution and then a rate increase. This effect can be explained in terms of a model in which the direction of electron flow in the transition state has been reversed. This can be explained by the change of the mode of peroxide activation from electrophilic at negative σ values to nucleophilic at positive σ values. The "normal" case—found for thioketones and for most other reagents and for those sulfines with electron-donating substituents—features the nucleophilic reagent attacking the peroxo oxygen. One says that peroxide has been activated electrophilically. On the other hand, peroxides are inherently nucleophilic. Substrates with substituents that are sufficiently electron-attracting can be so attacked.

The suggested transition states are shown in these diagrams:



Whether the changeover will actually be found in any reaction series cannot be specified in advance. The matter clearly depends not only on the peroxorhenium species, common to any series, but also on the nature of the reaction partner. The sulfine, unlike the sulfide and many others, at least invites both alternatives. To our knowledge, this is the first instance of a mechanistic feature in the MTO activation of peroxide. The phenomenon has been recorded previously, however. Perhaps the closest analogy to these results is provided by the oxidation of ArSCH$_3$ by a peroxotitanium complex.[40] In MTO−peroxide chemistry, the only previous example of the nucleophilic activation of peroxide appears to be in Baeyer−Villiger reactions.[41] Examples elsewhere include the OsO$_4$-catalyzed oxidation of *trans*-cinnamic acids by chloramine-T and -B[42,43] and by pyridinium chlorochromate;[44] oxidation of benzyl alcohols by quinolinium dichromate;[45] oxidation of styrenes by dioxoruthenium(VI) porphyrins[46] and quarternary ammonium permanganates.[47]

Thioketones are oxidized so much more rapidly than sulfines that the product of the first stage can be produced with but little subsequent oxidation. To do so, thioketone and peroxide were reacted in 1:1 quantities with a catalytic amount of MTO. Some of the reactions were monitored by ^{1}H NMR. The spectra showed the reaction was efficient, reaching completion in (typically) 5 min.

Some interferences were checked by adding each of the substances cyclohexene, PhNMe$_2$, Me$_2$SO, and Me$_2$CO. This material was added prior to MTO/H$_2$O$_2$. The yield of the sulfine was determined by ^{1}H NMR. With these reagents no loss of sulfine was noted.

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The addition of $NaHCO_3$ stopped the reaction entirely. This is a general phenomenon for MTO−peroxide chemistry, which comes about by the base-catalyzed decomposition of **A** and **B**. (Actually, this occurs by the reaction of HOO^- with MTO).[17] This mode of decomposition is so efficient that nonacidified solutions of MTO and H_2O_2 will not long survive intact.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-9625349). Some experiments were conducted with the use of the facilities of the Ames Laboratory. We are grateful to Prof. William S. Jenks for helpful discussions and thermochemical values.

Supporting Information Available: ^1H NMR chemical shifts for substituted thiobenzophenones, $(XC_6H_4)_2C{=}S$, their corresponding sulfines and ketones. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990621E