Methyltrioxorhenium-Catalyzed Oxidation of a (Thiolato)cobalt(III) Complex by Hydrogen Peroxide

Patrick Huston, James H. Espenson,* and Andreja Bakac

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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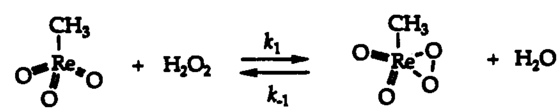
The oxidation of $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ by H_2O_2 is catalyzed by CH_3ReO_3. Studies of the kinetics and mechanism were carried out in aqueous solutions of dilute perchloric acid. The (thiolato)cobalt(III) complex is oxidized first to a sulfenato complex, $(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$, which is in turn more slowly oxidized to the sulfinato complex, $(en)_2Co(S(O)_2CH_2CH_2NH_2)^{2+}$. The two steps are well resolved in time, the second being some 1500 times slower than the first. Both steps fit the same kinetic pattern, which is consistent with a Michaelis–Menten scheme in which there are two substrates. This scheme involves the reversible formation of a 1:1 H_2O_2/CH_3ReO_3 adduct (**A**). The reversible formation of a 2:1 H_2O_2/CH_3ReO_3 adduct (**B**) also occurs, but it appears to be a dead-end process, in that **B**, if involved at all, is much less reactive than **A**. Rate constants were determined at 25 °C, $\mu = 0.10$ M ($HClO_4$), for the formation of the 1:1 H_2O_2/CH_3ReO_3 adduct A ($k_1 = 77 \pm 1$ L mol^{-1} s^{-1}) and its dissociation ($k_{-1} = 9.0 \pm 0.5$ s^{-1}) and for the oxidation by A of the thiolato complex, $(4.2 \pm 0.3) \times 10^5$ L mol^{-1} s^{-1}, and of the sulfenato complex, 265 ± 7 L mol^{-1} s^{-1}.

Introduction

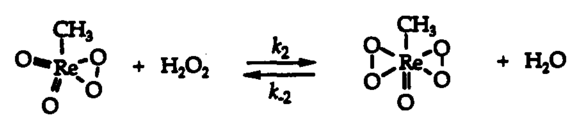
Peroxometal complexes have important applications in synthetic organic chemistry, particularly in olefin epoxidations[1] and in the synthesis of fine chemicals based on hydrogen peroxide.[2] Recently an organometallic oxide, methyltrioxorhenium(VII), sometimes referred to as MTO, was reported to be an excellent catalyst for olefin epoxidations by hydrogen peroxide.[3] This catalyst is soluble and stable in many solvents, including water, and is stable in aqueous solutions even at pH 0–3. It also has the advantage of being employable as either a homogeneous or a heterogeneous catalyst. The CH_3ReO_3/H_2O_2 system generates a very potent oxidant that is more kinetically competent than hydrogen peroxide itself. This mixture oxidizes even electron-poor olefins and simple gaseous olefins, and these reactions are catalytic in CH_3ReO_3 under many conditions. The mechanism suggested[3] for this epoxidation reaction involves a 2:1 peroxide–metal complex as the active species. We have concluded, however, that the active species for the oxidation of the cobalt thiolate and cobalt sulfenate substrates studied in this work is a 1:1 complex, not the 2:1 peroxide–rhenium complex. We have set out to characterize the CH_3ReO_3/H_2O_2 system kinetically, to identify the active species, and to determine the mechanism of the oxidation of various inorganic and organic substrates.

Hydrogen peroxide and methyltrioxorhenium form 1:1 and 2:1 complexes (eqs 1 and 2), which are denoted as **A**, the monoperoxo complex, and **B**, the diperoxo complex. These reactions are reversible, and are characterized by the stepwise equilibrium constants $K_1 = 7.7$ L mol^{-1} and $K_2 = 145$ L mol^{-1}.[4] In the chemical equilibria, complexes **A** and **B** are presented as anhydrides, although the current evidence for this is indirect.

It is not known which of the adducts (either or both) is the reactive species in catalytic reactions.[3] The simple fact that the 2:1 adduct does form is, in itself, insufficient evidence to establish that **B** is the active species. Since the reactions of methyltri-oxorhenium with hydrogen peroxide are reversible, it is entirely


(1)

A


(2)

B

possible that the active species involved in the oxidation of a given substrate is A, or even some other minor but highly reactive component. A study of the reaction kinetics can provide information about the active form of the catalyst; indeed in this respect kinetic studies are far more meaningful than the isolation and structural characterization of **A** or **B**, which were not undertaken.

To carry out this initial study, it was important to choose a substrate not because it necessarily represents an oxidation that is important to accomplish but so that its characteristics will allow the most definitive picture possible of the reaction mechanism. The qualities that we thus sought in a substrate for these initial studies with the CH_3ReO_3/H_2O_2 system included (1) an oxidation product whose buildup can be conveniently monitored by techniques that respond rapidly and quantitatively, (2) a reaction chemistry for the uncatalyzed process that is well-established and so slow in comparison to that of the process catalyzed by CH_3ReO_3 that no corrections are needed for the contribution of the uncatalyzed reaction, and (3) a reaction that is interesting and important in its own right.

The substrate that we have chosen is a particular (thiolato)-cobalt(III) complex, $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$. This complex is soluble in water. It is known to be oxidized slowly by hydrogen peroxide to form the (sulfenato)cobalt(III) complex (eq 3). In the chemical equations that characterize its reactions it will be abbreviated as $CoSR^{2+}$, since the five amine donors remain unchanged throughout. The uncatalyzed reaction occurs

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with a rate constant $k_3 = 1.36$ L mol^{-1} s^{-1} at pH 1.0.[5] The resulting sulfenato complex is also oxidized by H_2O_2. This occurs much more slowly than the oxidation of $CoSR^{2+}$ by H_2O_2, with $k_4 = 3.9 \times 10^{-4}$ L mol^{-1} s^{-1} at pH 1.0, to form the (sulfinato)cobalt(III) (eq 4).[6] The three cobalt(III) complexes are easily

$$CoSR^{2+} + H_2O_2 \xrightarrow{k_3} CoS(O)R^{2+} + H_2O \quad (3)$$

$$CoS(O)R^{2+} + H_2O_2 \xrightarrow{k_4} CoS(O)_2R^{2+} + H_2O \quad (4)$$

distinguished by differences in their UV–vis spectra.[5] It should be noted that the peroxide oxidation of this $CoSR^{2+}$ complex is catalyzed by molybdenum(VI) and tungsten(VI), which are electrophilic, high-oxidation-state materials.[7] The organorhenium oxide may well catalyze the reaction by a similar mechanism.

The oxidation of metal thiolate complexes may lead to a convenient method for the synthesis of organic sulfoxides, disulfides, or sulfinic acids. Sulfenic acids are known to be intermediates in a number of organic reactions[6] and may be involved in the oxidation of some protein thiol groups.[8] These reactions may also be related to the poisoning of catalysts which contain metal sulfides.

It is the purpose of this research to characterize the stoichiometry and products of the reactions catalyzed by CH_3ReO_3, to study the reaction kinetics, and from them to formulate a plausible mechanism. We also sought to test these postulates by experiments that would probe the intermediates that may intervene and the ways in which they can react.

Experimental Section

Materials. The solvent used in this study was in-house distilled and deionized water passed through a Millipore-Q purification system. Perchloric acid (Fisher) and hydrogen peroxide (Mallinckrodt) were used as received. Hydrogen peroxide was standardized by iodometric titration on the same day it was used.

Methyltrioxorhenium, CH_3ReO_3, was prepared according to two literature methods. The first method involved direct reaction of dirhenium heptaoxide with tetramethyltin.[9] In the second method dirhenium heptaoxide was mixed with perfluoroglutaric anhydride followed by reaction with tetramethyltin. This latter method was more efficient, forming CH_3ReO_3 in much higher yields.[10] CH_3ReO_3 was purified by sublimation and then dissolved in the minimum amount of dichloromethane; the pure compound was obtained as needlelike crystals with the slow addition of hexane. Purity was checked by IR (999 (w), 965 cm^{-1} (vs); in CS_2),[11] ^{1}H NMR (δ 2.6 ppm; in $CDCl_3$),[12] and UV–vis (239 nm (ϵ 1900 L mol^{-1} cm^{-1}), 270 nm (1300 L mol^{-1} cm^{-1})).[13] Stock solutions of CH_3ReO_3, typically 10^{-4} M, were prepared in water, protected from light, and stored at −5 °C for no more than 2 weeks before use. The concentrations of these solutions were determined spectrophotometrically before each use and were found to be stable over this time.

(2-Mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, was prepared according to the method of Nosco and Deutsch[14] and was recrystallized from water. Stock solution concentrations were determined spectrophotometrically at 282 nm (ϵ 13 800 L mol^{-1} cm^{-1}), 370 nm, sh (ϵ 283 L mol^{-1} cm^{-1}), 482 nm (ϵ 138 L mol^{-1} cm^{-1}), and 600 nm, sh (ϵ 41.4 L mol^{-1} cm^{-1}).[15] Solutions of the sufenato complex, $(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$, were prepared by the reaction of the thiolate complex with hydrogen peroxide prior to the addition of MTO.

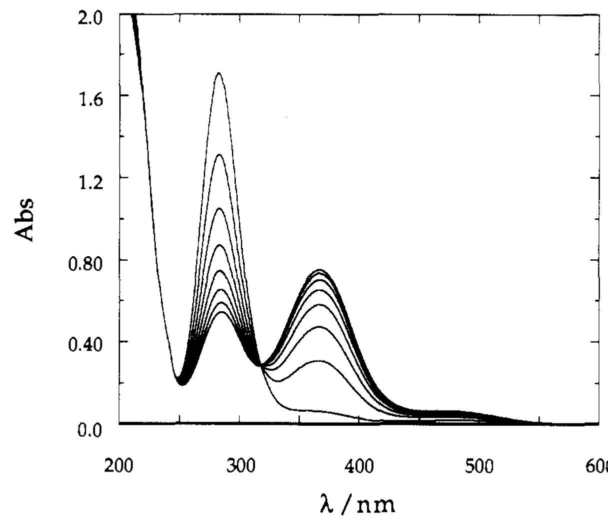

Figure 1. Spectral changes at 10-min intervals for the oxidation of 1.3×10^{-4} M $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ with 4.8×10^{-4} M H_2O_2 in the presence of 0.2 μM CH_3ReO_3 at pH 1.0. At these concentrations, the contributions to the spectra of CH_3ReO_3 and of **A** are negligible; so would be the absorbance of **B**, but as explained in the text, **B** never accumulates while the catalytic reaction is in progress.

Kinetic Studies. Reaction mixtures were prepared with the last reagent added being H_2O_2 (usually) or CH_3ReO_3 (sometimes). This order proved immaterial. Except for a special demonstration presented later, however, the cobalt complex was never the last reagent added. This procedure was necessary to avoid the occurrence of reaction 2, which is otherwise immaterial.

Kinetic studies were carried out by use of a Shimadzu UV-2101PC spectrophotometer and a Sequential DX-17MV stopped-flow instrument from Applied Photophysics Ltd. Kinetic studies were carried out by monitoring the loss of the thiolato complex at 282 nm (ϵ 13 800 L mol^{-1} cm^{-1}) or formation of the sulfenato complex at its absorption maximum, 365 nm (ϵ 6700 L mol^{-1} cm^{-1}).[6] The kinetic data at both wavelengths were in complete agreement. When higher concentrations of $CoSR^{2+}$ were required, the reaction was monitored at longer wavelengths (400–430 nm). A typical set of repetitive reaction spectra for the oxidation of the thiolato complex are displayed in Figure 1. The kinetic studies of the second reaction stage, for the oxidation of $CoS(O)R^{2+}$, were carried out by monitoring the loss of the sulfenato complex at 365 nm or the buildup of the sulfinato complex, $CoS(O)_2R^{2+}$, at 288 nm (ϵ 14 200 L mol^{-1} cm^{-1}). All of the kinetic studies were conducted at 25.0 ± 0.2 °C and ionic strength 0.10 M, maintained with perchloric acid. Some data were obtained by following the absorbance for the full time course of the reaction, and others, by monitoring only the initial stage, from which the initial reaction rate was calculated. All of the kinetic parameters were independent of the wavelengths at which measurements were made for both stages of the reactions, and for the different types of rate measurements made, as described subsequently.

Kinetic simulations were carried out to match the observed kinetic curves to those for certain reaction models. This was necessary because the associated differential equations were not soluble in closed form under some concentration conditions, and numerical methods had to be employed. This was carried out with the program KINSIM,[16] which uses the Runge–Kutta and Gear methods to generate concentration–time profiles for any scheme, given the rate constants and starting concentrations. Experimental spectrophotometric data were fitted using the program Spectracalc or were converted to files for a Macintosh computer and fitted with the program Kaleidalgraph.

Results

Preliminary Experiments. It was shown that CH_3ReO_3 does indeed catalyze the oxidation of this (thiolato)cobalt(III) complex

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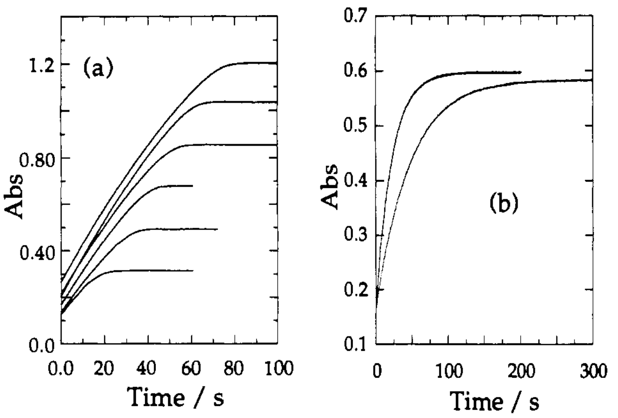


Figure 2. (a) Kinetic traces at 365 nm. Conditions: 25.0 °C, 0.10 M $HClO_4$, 5.6 × 10^{-6} M CH_3ReO_3, 5.0 mM H_2O_2, (0.2–1.8) × 10^{-4} M $(en)_2Co(SCH_2CH_2NH_2)^{2+}$. (b) First-order traces obtained at 365 nm. Conditions: 25.0 °C, 0.10 M $HClO_4$, 1.0 × 10^{-3} M $CoSR^{2+}$, 9.6 × 10^{-5} M H_2O_2, 2.6 × 10^{-4} M CH_3ReO_3 (lower trace) or 5.7 × 10^{-4} M CH_3ReO_3 (upper trace).

($CoSR^{2+}$). When H_2O_2 was added to a solution of $CoSR^{2+}$ in the presence or absence of CH_3ReO_3, the UV–visible spectrum showed the loss of the thiolate at 282 nm and the concurrent buildup of the initial cobalt sulfenate product having an absorption maximum at 365 nm. These changes during the rhenium-catalyzed reaction are shown in Figure 1. The second stage was studied on a slower time scale. It was characterized by the disappearance of the absorption spectrum of the sulfenato complex at 365 nm as it was further oxidized to the sulfinato complex, $CoS(O)_2R^{2+}$, whose buildup was quantitative according to the absorbance change at 288 nm. The two stages are so well separated in time that in each stage the appropriate isosbestic points are maintained throughout. They were found at 318 nm during the first stage and at 323 nm during the second. The absorbance changes were directly proportional to the concentration changes of the limiting reagent (H_2O_2 or $CoSR^{2+}$) and were precisely those required by a 1:1 stoichiometry, with and without the catalyst.

The Uncatalyzed Reaction. The reaction in the absence of CH_3ReO_3 was re-examined under pseudo-first-order conditions (1.0 mM H_2O_2 and 0.10 mM $CoSR^{2+}$) at pH 1.0. The absorbance increases observed at 365 nm followed precise first-order kinetics. Under these conditions, the first stage of the reaction reached completion within 1 h. The second-order rate constant we obtained for the uncatalyzed reaction at pH 1.0 is 1.34 L mol^{-1} s^{-1}, in agreement with the reported value[5] of 1.36 L mol^{-1} s^{-1} under similar conditions. The second stage does not interfere, since it is very much slower.

Catalysis by CH_3ReO_3: Excess Peroxide. Under the same conditions, but with 50 μM CH_3ReO_3, the appearance of the kinetic trace was dramatically different. The reaction was now much faster, being complete in 15 s. The reaction appears approximately zeroth-order during the initial part of the reaction and approximately first-order toward the end of the reaction. This is illustrated in Figure 2a for a series of experiments at variable [$CoSR^{2+}$]. Also, the order of the reaction with respect to the concentration of $CoSR^{2+}$, the limiting reagent in this series, increases with increasing [H_2O_2]. At extremely high concentrations of H_2O_2 (4 M), the traces do ultimately attain a limit that is approximately first-order with respect to [$CoSR^{2+}$].

These observations as well as the results described below lead us to suggest a Michaelis–Menten mechanism that involves the two substrates, $CoSR^{2+}$ and H_2O_2 (eqs 1 and 5). Under conditions where eq 2 is unimportant (*i.e.*, when [**B**] is negligible), which is realized at low [H_2O_2],[4,17] this mechanism leads to the rate law given by eq 6. That is, as will be shown later, **A** is the reactive

$$CH_3Re(O)_2(O_2) + CoSR^{2+} \xrightarrow{k_5} CH_3ReO_3 + CoS(O)R^{2+} \quad (5)$$

$$\frac{d[CoS(O)R^{2+}]}{dt} = \frac{k_5[Re]_T[H_2O_2][CoSR^{2+}]}{\frac{k_{-1} + k_5[CoSR^{2+}]}{k_1} + [H_2O_2]} \quad (6)$$

form of the catalyst. When the main reaction is carried out, **B** never forms until the supply of $CoSR^{2+}$ has been exhausted. This point is implicit in the kinetic treatment that will be developed in the subsequent section. The notation $[Re]_T$ is used to symbolize the total CH_3ReO_3 concentration: $[Re]_T = [CH_3ReO_3] + [A]$. The proportion of each form depends on the concentrations of $CoSR^{2+}$ and H_2O_2 present at any point during the course of the reaction. These are the concentrations that govern the steady-state proportions of the two forms in which the rhenium exists during the reaction.

That this rate equation follows from the chemical reaction scheme proposed, eqs 1 and 5, will be shown in this derivation. The assumption will be made (later to be justified by the fit to the kinetic data and the derived constants) that the concentration of the reactive molecule **A** obeys the steady-state approximation. The rate of the reaction is given by

$$\frac{d[CoS(O)R^{2+}]}{dt} = k_5[CoSR^{2+}][CH_3Re(O)_2(O_2)] \quad (7)$$

The steady-state approximation can be used to obtain the expression for $[CH_3Re(O)_2(O_2)]$:

$$[CH_3Re(O)_2(O_2)]_{ss} = \frac{k_1[CH_3ReO_3][H_2O_2]}{k_{-1} + k_5[CoSR^{2+}]} \quad (8)$$

In terms of $[Re]_T$, the expression for the intermediate becomes

$$[CH_3Re(O)_2(O_2)]_{ss} = \frac{[Re]_T[H_2O_2]}{\frac{k_{-1} + k_5[CoSR^{2+}]}{k_1} + [H_2O_2]} \quad (9)$$

Upon substitution into eq 7, this gives, for the total reaction rate, the expression written in eq 6. Many experiments were required to establish that this is the correct form and that it applies over a wide range of each of the concentrations. The different confirming experiments that were performed are outlined in the next several sections.

Catalysis by CH_3ReO_3: Excess $CoSR^{2+}$. An extensive set of determinations was carried out at low concentrations of H_2O_2, such that the term containing [H_2O_2] in the denominator of eq 6 is entirely negligible. Some of these experiments employed high concentrations of $CoSR^{2+}$; this was done in an effort to make $k_5[CoSR^{2+}] \gg k_{-1}$. In that limit, the rate law simplifies to the form given in eq 10, which is first-order with respect to the concentration of H_2O_2, the limiting reagent. The expression is

$$\frac{d[CoS(O)R^{2+}]}{dt} = k_1[Re]_T[H_2O_2] \quad (10)$$

With CH_3ReO_3 present, along with 1.0 × 10^{-3} M $CoSR^{2+}$ and 9.6 × 10^{-5} M H_2O_2, first-order kinetic traces were obtained, indicating that eq 10 is valid at these concentrations. The data

(17) The experiments were performed by the addition of either H_2O_2 or CH_3ReO_3 last, making reaction 2 unimportant for kinetic reasons. However, when the overall reaction was sufficiently slow that k_2 could be significant, the low concentration of H_2O_2 meant that there were very little **A** and almost no **B** formed, even at equilibrium.

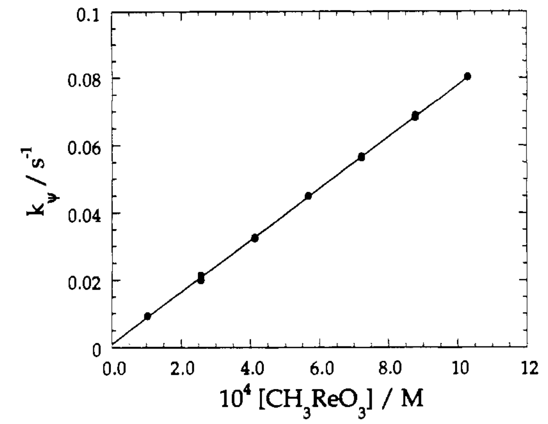


Figure 3. Plot of the observed first-order rate constants for the oxidation of $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ (1.0×10^{-3} M) by H_2O_2 (9.6×10^{-5} M) at 25.0 °C and pH 1.0 ($HClO_4$) showing linear variation with the total catalyst concentration. The slope of this line corresponds to $k_1 = 77 \pm 1$ L mol^{-1} s^{-1}.

from typical experiments are illustrated by Figure 2b. The pseudo-first-order rate constant was evaluated from each experiment by nonlinear fitting of the absorbance–time curves to the standard equation:

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)e^{-k_\psi t} \qquad (11)$$

In a series of such experiments, changes in the initial concentrations of H_2O_2 and $CoSR^{2+}$ had no effect. In these same experiments, the initial concentration of the catalyst was varied over the range 10^{-4}–10^{-3} M. The values of k_ψ are directly proportional to $[Re]_T$, as eq 10 suggests. A plot of the values of the experimental rate constant versus $[Re]_T$ is given in Figure 3. The slope of this line gives the value of $k_1 = 77 \pm 1$ L mol^{-1} s^{-1} at 25.0 °C in water with $\mu = [H_3O^+] = 0.10$ M.

Catalysis by CH_3ReO_3: Initial-Rate Methods. From eq 6 it can be seen that the conditions needed to obtain the most information about k_{-1} would be those with low $[H_2O_2]$ and with varied $[CoSR^{2+}]$ in the region where k_{-1} and $k_5[CoSR^{2+}]$ are comparable. These conditions were satisfied in a series of experiments with 1.3×10^{-4} M H_2O_2, 4.7×10^{-6} M CH_3ReO_3, and $(1–16) \times 10^{-4}$ M $CoSR^{2+}$. Under these conditions, the kinetic curves obtained were not first-order.

In view of this, the most convenient method to study the reaction kinetics is the initial-rate method, as is often the case with ordinary Michaelis–Menten kinetics. The reason, of course, is that the full kinetic equation under these concentration conditions is a transcendental equation that does not have a closed-form solution for concentration (or absorbance) as a function of time. Kinetic simulations were later performed to show that the appearance of the absorbance–time profiles (tending from zeroth-order to first-order from start to finish) is correctly accounted for by reactions 1 and 5.

The initial rate was corrected for the uncatalyzed contribution, although the correction was small and in every case ≤10% of the total rate. The plot of the initial rate versus $[CoSR^{2+}]$ is given in Figure 4, according to eq 6. In the limit of high $[CoSR^{2+}]$, the initial rate should reach a plateau that gives the already-determined value of k_1. Visual inspection of Figure 4 (left) confirms this.

So that too many parameters are not simultaneously varied, the best value of k_{-1} can be obtained by fitting these data to eq 6. In this calculation, the value for k_1 was fixed at 77 L mol^{-1} s^{-1}, as given in the preceding section, and k_5 at 4.2×10^5 L mol^{-1} s^{-1}, as given below.[18] This led to a value of $k_{-1} = 9.0 \pm 0.5$ s^{-1} at 25.0 °C at $\mu = 0.10$ M.

(18) The data sets employed to determine values for k_{-1} and k_5 were fitted iteratively to determine the best values for these rate constants.

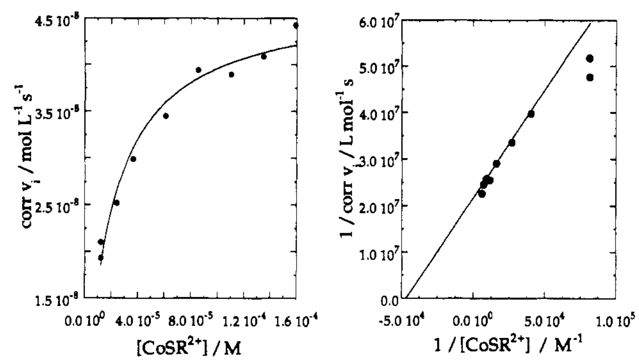


Figure 4. Variation of the initial rate of reaction, corrected for the uncatalyzed contribution, with $[(en)_2Co(SCH_2CH_2NH_2)^{2+}]$. The curve is a fit of these data to the rate law (eq 6) applicable when **[B]** is negligible. Conditions: 25.0 °C, 0.10 M $HClO_4$, 4.7×10^{-6} M CH_3ReO_3, 1.3×10^{-4} M H_2O_2. The right-hand diagram presents the same data in the traditional Lineweaver-Burke style, while is useful for a picture but not for a reliable statistical analysis. The line shown is not the fit to the double-reciprocal function but the fit to the nonlinear form in the left-hand plot.

The conditions required to determine k_5 are also those in which k_{-1} and $k_5[CoSR^{2+}]$ are comparable. Given the estimates of these quantities, this should be true at $CoSR^{2+}$ concentrations of the order 10^{-5} M. Two initial-rate studies were performed to determine a value for k_5. Both were carried out at low $[H_2O_2]$, so that the amount of CH_3ReO_3 present in form **B** would be negligible. In one series of experiments, $[Re]_T$ was varied from 0 to 18×10^{-6} M in the presence of 5.2×10^{-5} M $CoSR^{2+}$ and 9.7×10^{-5} M H_2O_2. The dependence of the initial rate, v_i, on $[Re]_T$ is linear as expected from eq 6. The extrapolated intercept from this plot has a value that does correspond to the initial rate of the uncatalyzed reaction[5] under these conditions. The data were fitted to eq 6, fixing values of k_1 and k_{-1}.[18] This yielded a value of $k_5 = (4.3 \pm 0.3) \times 10^5$ L mol^{-1} s^{-1}.

A second series of experiments was carried out with 6.0×10^{-6} M CH_3ReO_3 and 4.5×10^{-5} M $CoSR^{2+}$, varying $[H_2O_2]$ in the range $(0.5–5.0) \times 10^{-4}$ M. A plot of v_i vs $[H_2O_2]$ was linear at this low $[H_2O_2]$, where the denominator term in eq 6 that contains the peroxide concentration is small. These data were also fitted to eq 6, as described above, yielding a value of $k_5 = (4.2 \pm 0.2) \times 10^5$ L mol^{-1} s^{-1} at 25.0 °C and $\mu = 0.10$ M.

Incubated CH_3ReO_3 and H_2O_2. Consider that **A** may truly be the active species and **B** either much less active or inactive. This can be established by kinetics experiments under conditions where much of the rhenium is present from the outset in the form of **B**. That is, these experiments have CH_3ReO_3 and H_2O_2 equilibrated at high $[H_2O_2]$. The initial rate, upon addition of substrate, would then be slower, reflecting the slow conversion of **B** to **A** (0.04 s^{-1}),[4] as compared to the control experiment in which prior equilibration of the rhenium–peroxide complexes had not occurred. This was tested by changing the order of mixing of the reactants at high $[H_2O_2]$.

Figure 5 shows two kinetic traces obtained under the following conditions: 1.36 M H_2O_2, 4.6 μM CH_3ReO_3, and 47 μM $CoSR^{2+}$. In one of the experiments, CH_3ReO_3 and H_2O_2 were allowed to equilibrate in one syringe of the stopped-flow apparatus, so that nearly all of the rhenium was present in the form of **B** at the moment it was mixed with the solution in the syringe containing $CoSR^{2+}$ (both syringes also contained 0.1 M perchloric acid). In the second experiment, the rhenium and cobalt complexes (which do not react with one another) were in one syringe and hydrogen peroxide was in the other; each again contained 0.1 M perchloric acid. The rate of product buildup is significantly lower in the first case than in the second, when H_2O_2 was added last. All other experiments were ordinarily conducted without prior mixing of CH_3ReO_3 and H_2O_2.

The lower rate found when the $CH_3ReO_3/H_2O_2/$**A**/**B** system is preequilibrated is further indication that **B** is not the active

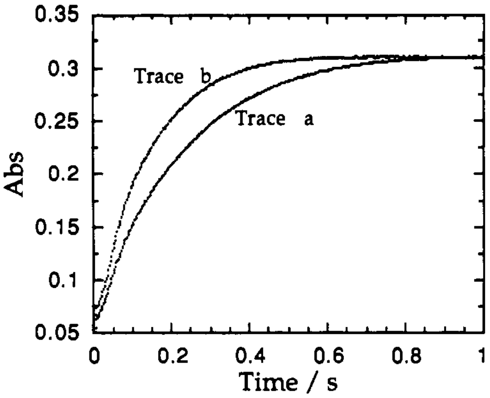


Figure 5. Kinetic traces obtained at 365 nm for the oxidation of $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ with H_2O_2 catalyzed by CH_3ReO_3. Conditions: 25.0 °C, 0.10 M $HClO_4$, 1.36 M H_2O_2, 4.7×10^{-5} M $CoSR^{2+}$, 4.6×10^{-6} M CH_3ReO_3. Trace a was obtained when CH_3ReO_3 and H_2O_2 were allowed to equilibrate before addition of $CoSR^{2+}$. Trace b was obtained when H_2O_2 was added last.

form of the catalyst. At low concentrations of H_2O_2, the order of addition of the three components should (and does) make no difference, because the amount of **B** at equilibrium is very small under these conditions. To put it another way, **B** is not present in any of the kinetics experiments, except this special one, at a significant concentration, because the reactive species **A** is diverted back to CH_3ReO_3 by reaction with a cobalt substrate before any of it can be converted to **B** by reaction with hydrogen peroxide.

Rate Dependences on $[H_3O^+]$. The effect of acid was investigated in the range 0.001–0.10 M $HClO_4$, ionic strength being maintained at 0.1 M with $LiClO_4$. There was no effect on the observed rate constant in this pH range. The same was true under all of the different concentration conditions and ratios examined; we conclude that none of the reactions was pH-dependent in this range. Indeed, some experiments were carried out in the range pH 4–7, and as far as could be discerned, the same was true there, except that the catalyst system was somewhat less stable near neutral pH.

Second-Stage Oxidation. The slower reaction involves the oxidation of the sulfenato complex to the (sulfinato)cobalt(III) ion as shown in eq 12. This stage was characterized by the loss

$$CH_3Re(O)_2(O_2) + CoS(O)R^{2+} \xrightarrow{k_{12}} CH_3ReO_3 + CoS(O)_2R^{2+} \quad (12)$$

of the absorption bands at 365 and 470 nm as the sulfenato complex reacts, along with an increase in absorbance at 288 nm due to the formation of the sulfinato complex. The kinetic behavior was similar to that of the first stage of the oxidation. With excess H_2O_2 present, the kinetic traces were again non-first-order and the rate depended on both $[CH_3ReO_3]$ and $[H_2O_2]$.

We shall initially assume that eqs 1 and 12 constitute the reaction scheme. By the method given earlier, the rate law is given by eq 13. This assumes that $[H_2O_2]$ is sufficiently low that insignificant amounts of **B** are formed which can of course be true if **A** is indeed the active catalyst.

$$\frac{d[CoS(O)_2R^{2+}]}{dt} = \frac{k_{12}[Re]_T[H_2O_2][CoS(O)R^{2+}]}{\dfrac{k_{-1} + k_{12}[CoS(O)R^{2+}]}{k_1} + [H_2O_2]} \quad (13)$$

A value for k_{12} was determined by the initial-rate method. With $[H_2O_2] = 5.0$ mM, $[CoSR^{2+}] = 0.10$ mM, and $[CH_3ReO_3] = 0.1$–1.0 mM, v_i is directly proportional to $[CH_3ReO_3]$, as predicted by eq 13. The contribution due to the uncatalyzed reaction is negligible under these conditions. The values established above for k_1 and k_{-1} were used in fitting the data to eq 13. The value for k_{12} was found to be 265 ± 7 L mol^{-1} s^{-1}.

According to this mechanism, the same values for k_1 and k_{-1} should be obtained for both stages of the oxidation reaction. However, because k_{12} is relatively small, it is not possible to use concentrations of $CoSR^{2+}$ that are sufficiently high to make k_{-1} and $k_{12}[CoSR^{2+}]$ comparable. Therefore, at the low concentrations of $[H_2O_2]$ necessary to keep [**B**] negligible, only the ratio k_1/k_{-1} may be determined for the second stage (eq 14).

$$\frac{d[CoS(O)_2R^{2+}]}{dt} = \frac{k_1k_{12}}{k_{-1}}[CH_3ReO_3][H_2O_2][CoS(O)R^{2+}] \quad (14)$$

With $[H_2O_2] = 0.32$ mM and $[CoS(O)R^{2+}] = 2.15$ mM, initial rates were measured over a range of $[CH_3ReO_3] = 0.14$–1.5 mM. From these determinations the value of k_1/k_{-1} was determined to be 7.7 ± 0.5 L mol^{-1}.

Integrity of the Catalyst. Several tests were run to examine how stable the catalyst remains under the reaction conditions and how stable it is after effecting many turnovers. These tests were done at the lowest rhenium concentrations useful to be the most stringent ones possible. A 24 μM solution of CH_3ReO_3 in 0.1 M perchloric acid showed negligible (<1%) decomposition over 5 h if protected from light. Two experiments were done to explore its stability after its catalytic action. This was done with 5 mM $CoSR^{2+}$, 0.1 mM H_2O_2, and 0.2 mM CH_3ReO_3 in 0.10 M perchloric acid. Following this, the catalytic activity of the residual solution remained at *ca.* 90% of the original, irrespective of whether the second and identical portion of hydrogen peroxide was added immediately or was added after a 1-h wait.

Discussion

The absorbance–time recordings in experiments using excess H_2O_2 have a time-dependent (*i.e.*, concentration-dependent) order with respect to the concentration of the (thiolato)cobalt(III) complex. This and the observation that the reaction rate saturates at the higher concentrations of the cobalt complex led us to suggest a Michaelis–Menten rate law. The dependences are both qualitatively and quantitatively consistent with this formulation, as shown by the satisfactory fits of the data to this model. Since this is often the kinetic form taken by catalytic reactions, it comes as no surprise that it holds for this system as well.

It is independently known[4] that CH_3ReO_3 reversibly forms adducts with H_2O_2. This points to a mechanism in which the product of either eq 1 or eq 2, or both, is involved in the catalytic cycle. That is, the 1:1 or the 2:1 compound formed from the hydrogen peroxide–methyltrioxorhenium interaction might be the catalytically active species. One of these steps represented by eq 1 or eq 2 is thus analogous to that in which the Michaelis–Menten complex forms. From the kinetic profile alone one cannot specify which of the species **A** or **B** acts as the reactive Michaelis–Menten complex. Other reasoning must be developed to advance the argument further.

The experimentally-determined rate law has the form given by eq 6, in which there is a denominator term containing $[CoSR^{2+}]$ as well as one containing $[H_2O_2]$. Therefore, this is a two-substrate system in its kinetic form, as it obviously is in its chemistry. Thus, the second step involves the reaction of one of the peroxide–rhenium compounds (**A** or **B**) with $CoSR^{2+}$, as depicted by eq 5 for the oxidation of the (thiolato)cobalt(III) ion and by eq 12 for the oxidation of the (sulfenato)cobalt(III) ion.

The value calculated for K_1 from the kinetic results of the first stage of the oxidation is $k_1/k_{-1} = 8.6$ L mol^{-1}, and that for the second stage is $k_1/k_{-1} = 7.7$ L mol^{-1}. These values are in agreement with the value of $K_1 = 7.7$ L mol^{-1} found in a direct study of the equilibrium.[4]

The form of the rate law given by eq 6 would also be consistent with an alternative mechanism in which the substrates enter the sequence in the opposite order. The scheme thus suggested is as shown in eqs 15 and 16. In this scheme Cat may be CH_3ReO_3

$$\mathrm{Cat} + \mathrm{CoSR}^{2+} \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} [\mathrm{Cat,CoSR}^{2+}] \quad (15)$$

$$[\mathrm{Cat,CoSR}^{2+}] + \mathrm{H_2O_2} \xrightarrow{k_{16}} \mathrm{Cat} + \mathrm{CoS(O)R}^{2+} + \mathrm{H_2O} \quad (16)$$

itself, but this is unlikely, because spectroscopic tests indicated no interaction between CH_3ReO_3 and $CoSR^{2+}$ that would be required by eq 15 were Cat = CH_3ReO_3. More likely, therefore, Cat represents either **A** or **B**.

This leads to a rate law of the same form as established experimentally, as shown in eq 17. It has the same form as eq

$$\frac{d[\mathrm{CoS(O)R}^{2+}]}{dt} = \frac{k_{15}[\mathrm{Re}]_T[\mathrm{H_2O_2}][\mathrm{CoSR}^{2+}]}{\dfrac{k_{-15} + k_{15}[\mathrm{CoSR}^{2+}]}{k_{16}} + [\mathrm{H_2O_2}]} \quad (17)$$

6 except that k_{15} replaces k_5, k_{-15} replaces k_{-1}, and k_1 becomes k_{16}. On the basis of our values for k_5 and k_{-1}, the equilibrium of eq 15 would be shifted far to the right ($K_{15} = 4.7 \times 10^4$ L mol^{-1}). However, there was no evidence in the UV–vis or ^{1}H NMR spectra of any complex formation during the reaction. For both the (thiolato)- and the (sulfenato)cobalt(III) oxidation reactions there were well-defined isosbestic points, suggesting that no such intermediate forms at a concentration sufficient to satisfy the requirement of this alternative mechanism, which was thus rejected.

At low concentrations of H_2O_2, and in the presence of excess $CoSR^{2+}$, the reaction is first-order with respect to $[H_2O_2]$. This indicates that the active species, at least under these conditions, is complex **A**, formed from 1 equiv of hydrogen peroxide. Were **B** the only or major active species, the reaction should be second-order in $[H_2O_2]$.

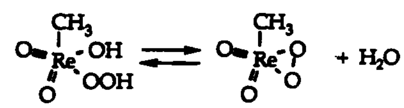
When the reaction was studied at much higher $[H_2O_2]$ (2 M or higher), the kinetics of both thiolate and sulfenate oxidations became approximately first-order with respect to the concentration of the limiting reagent, the respective cobalt substrate. This should be clear from the forms of eqs 6 and 13, both of which approach a limiting form $v = k[\mathrm{Co}][\mathrm{Re}]_T$ under the conditions where $[H_2O_2]$ is so high that it is the only important term in the denominator of the rate law.

But under these conditions, a significant amount of **B** is formed during the reaction and is present as soon as the equilibrium in eq 2, a comparatively fast process, has been attained. This leads to a much more complicated form of the rate law, if the steady-state approximation is applied to [**A**], rather than the prior-equilibrium approximation being applied to [**A**] and [**B**]. The steady-state approximation is valid because, as it turns out, **A** is so reactive toward the substrates that it (and **B**) never attain their equilibrium values. This was confirmed by kinetic simulations, in which the program KINSIM[16] was employed. The calculated concentrations of CH_3ReO_3 and **A** change significantly with respect to total rhenium present, when CH_3ReO_3 and H_2O_2 are *not* allowed to equilibrate before the addition of $CoSR^{2+}$. Thus, the prior-equilibrium approximation is invalid under these conditions.

Hydrogen peroxide is generally thought to react with reducing nucleophiles by an S_N2 mechanism.[19] Since coordinated sulfur has been shown to be very nucleophilic,[6,20] the mechanism of oxidation of the (thiolato)cobalt(III) complex by H_2O_2 was assumed to be nucleophilic attack by coordinated sulfur on the O–O peroxide bond.[5,21] It is reasonable that the same type of nucleophilic attack by the coordinated sulfur occurs in the CH_3ReO_3-catalyzed reaction. That is, the sulfur atom of the cobalt complexes attacks the oxygen of the coordinated peroxide ion of **A**.

The mechanism that we propose involves the formation of a 1:1 H_2O_2/CH_3ReO_3 adduct, **A**, which then reacts with $CoSR^{2+}$. Thus, catalysis must be due to the interaction of the electron-poor rhenium complex with H_2O_2, making it more susceptible to nucleophilic attack. In fact the activation of peroxide upon coordination to rhenium(VII) is remarkable. For the first stage, $k_5/k_{uncat} = 3.1 \times 10^5$, and for the second stage, $k_{12}/k_{uncat} = 6.8 \times 10^5$. Such a strong activation means that there must be significant structural and/or electronic changes in the peroxide upon coordination.

The actual structure of **A** in aqueous solution is not known for certain. Two possibilities (**A1** and **A2**) are shown here, ignoring any additionally coordinated water molecules:



(18)

A1 **A2**

A reasonable catalytic cycle can be written with either **A1** or **A2** as the active species. After transferring an oxygen atom, **A1** would presumably need to lose H_2O to re-form CH_3ReO_3 and complete the cycle. Also, movement of a hydrogen is required for **A1**. Structure **A1** is an inorganic hydroperoxide, where the difference from H_2O_2 is that the unit $CH_3ReO_2(OH)$ is substituted for one hydrogen. Coordination of hydrogen peroxide to this high-valent rhenium center should make the peroxidic oxygens more electrophilic than they are in free hydrogen peroxide.[22] After all, Re^{VII} is a stronger Lewis acid than H^+. However, the effect on the reactivity seems much too great to be attributed to an inductive effect such as this. For two molecules with OOH groups to differ in reactivity by $>10^5$ times would require a remarkable and we think unreasonable degree of activation by induction. For this reason we are inclined to discount the catalytic effectiveness of **A1**.

Structure **A2**, that has an η^2-peroxo group, seems a more reasonable suggestion for the active species. The η^2-peroxo group can strongly donate electron density to the metal, making the peroxide oxygen atoms more susceptible to nucleophilic attack. Indirect evidence suggests that η^2-peroxo complexes exist in solution.[23] The most convincing indirect evidence may be the difference in the abilities of H_2O_2 and *t*-BuOOH to bind with $OM(OR)_3$ complexes. For example, $OV(OC_2H_5)_3$ binds H_2O_2 10^3 times more strongly than *t*-BuOOH.[24] Chromium(VI), molybdenum(VI), and titanium(IV) also have high values of formation constants for H_2O_2 complexes.[25] This suggests that the ability of H_2O_2 to act as a bidentate ligand allows much stronger binding. This may also be the case with CH_3ReO_3,

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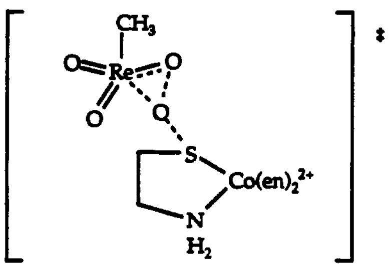
Table I. Summary of Rate Constants for the Oxidation of $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ and $(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$

	k/L mol^{-1} s^{-1}	
oxidant	reacn with $CoSR^{2+}$	reacn with $CoS(O)R^{2+}$
H_2O_2[a]	1.36	3.9×10^{-4}
$MoO(OH)(O_2)_2^-$ [b]	2.4×10^3	6.6
$MoO(O_2)_2$[b]	1.91×10^4	30.8
$WO(OH)(O_2)_2^-$ [b]	3.7×10^4	120
$WO(O_2)_2$[b]	3.7×10^5	980
$CH_3Re(O)_2(O_2)$[c]	$(4.2 \pm 0.3) \times 10^5$	265 ± 7

[a] At pH 1.0; ref 5. [b] Reference 20. [c] This work; at 25 °C and in 0.10 M $HClO_4$.

which does not activate t-BuOOH.[3] We suggest the following structure for the transition state:



The question remains: why is **A** active and **B** is not, or at least why is **B** much less active? In eq 2, **B** is written as the anhydride, but again the degree of hydration must be left undefined. It is possible that one or both of the η^2-peroxo ligands is hydrated (to hydroxo and hydroperoxo ligands). In any of these cases it should be considered that the rhenium center in **A** is better able to accept electron density from the peroxo ligand than the metal center in **B**. This may be because **A** contains one more oxo ligand than **B**, which has a second peroxo (or hydroperoxo) ligand instead. It also may be noted that **A** is likely to be more sterically accessible than **B**.

The oxidation of $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ by H_2O_2 is also known to be catalyzed by oxo diperoxo complexes of molybdenum(VI) and tungsten(VI).[8,26] These results are compared with the work reported here in Table I. The trend in the ability of metals to activate peroxide is Mo < W ≈ Re, keeping in mind that these molybdenum(VI) and tungsten(VI) complexes do not contain a methyl group like the rhenium(VII). In the Mo(VI)- and W(VI)-catalyzed oxidation of $CoSR^{2+}$, as well as in the Mo(VI)-catalyzed oxidations of S(IV) and I^-, it is the diperoxo complexes that are the active species.[26-28] The monoperoxo complexes are believed to be inactive, but no explanation was offered for this. It may be that the monoperoxo complexes of W(VI) and Mo(VI) are hydrated to the hydroxo and hydroperoxo groups, possibly rendering them inactive. In the case of the V(V)-catalyzed oxidations of sulfides and alkenes by H_2O_2, it is the monoperoxovanadium(V) complex that acts as the oxidizing agent, the diperoxo complex being much less active.[29]

Conditions in this study were adjusted to obtain the optimal kinetic parameters. In particular, we sought to make $v_{cat} \gg v_{uncat}$, so that a correction for the uncatalyzed process need not be made. This often meant the use of CH_3ReO_3 concentrations that were not much lower than those of the substrates. However, to show that CH_3ReO_3 is a highly efficient catalyst, we used concentrations of $CoSR^{2+}$ and H_2O_2 that were > 10^3 times that of CH_3ReO_3. As best we could tell, most of the CH_3ReO_3 remained at the end, capable of carrying out many further catalytic cycles.

Acknowledgment. This research was supported at Ames Laboratory by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82.

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