Oxidation of Chloride Ions by Hydrogen Peroxide, Catalyzed by Methylrhenium Trioxide

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Methylrhenium trioxide, CH_3ReO_3, catalyzes the hydrogen peroxide oxidation of chloride ions in acidic aqueous solutions. The active catalytic species are the monoperoxo complex, $CH_3ReO_2(\eta^2\text{-}O_2)$, **A**, and the diperoxo complex, $CH_3ReO(\eta^2\text{-}O_2)_2(OH_2)$, **B**. At 25 °C in 1.0 M $HClO_4$ and $\mu = 2.0$ M the rate constants for the reactions of **A** and **B** with Cl^- were determined to be 0.059 ± 0.007 and 0.124 ± 0.005 L mol^{-1} s^{-1}, respectively, and both were approximately 10^5 times faster than the rate constant for the uncatalyzed reaction under similar conditions. Kinetic experiments employed the initial-rate method; reactions were monitored by following the consumption of monochlorodimedone (MCD) at $\lambda = 270$ nm. MCD reacts rapidly with the chloride ion oxidation product(s).

Introduction

The effectiveness of transition metal ion complexes as catalysts of hydrogen peroxide oxidations has been known for more than 50 years.[1,2] These catalyzed reactions have broad synthetic applications and are widely used in both organic and inorganic chemistry.[3,4] Hydrogen peroxide is an environmentally attractive oxidizing agent, since its reduction yields only water, by any standard a harmless byproduct. The rhenium compound can be used in very small quantities; indeed, Herrmann et al. have shown that it can be used as a supported catalyst on silica−alumina, although we did not attempt that here since our interest was in the homogeneous mechanism.

The synthesis of methylrhenium trioxide, CH_3ReO_3 (often referred to as MTO), was first reported in 1979.[5] Herrmann et al. first reported its use as a catalyst for hydrogen peroxide oxidations of a number of alkenes, alkynes, and ketones in 1991.[6] Since then studies of MTO as a catalyst for hydrogen peroxide oxidations of a wide range of compounds have been reported including the following: olefins;[7−9] a thiolatocobalt(III) complex;[10] organic sulfides;[11] anilines;[12] and triphenylphosphines, triphenylarsine, and triphenylstibine.[13] Attractive features of this catalyst include its ease of synthesis, its stability in air, its solubility and stability in both aqueous (low pH) and organic solvents, and its effectiveness as either a homogeneous or heterogeneous catalyst. In particular, its use in aqueous media holds promise as the basis for processes which are environmentally safer, cheaper, and sounder.

A number of kinetic studies focusing on the oxidation of bromide[14−19] and iodide[20,21] ions using hydrogen peroxide catalyzed by synthetic transition metal ion complexes have appeared in the literature in recent years. It is generally accepted that the major halogen product of these oxidations is an "X^+" species (at least formally) although uncertainty exists owing to the rapid equilibria between OX^-, HOX, X_2, and X_3^-. Little attention has been devoted, however, to the kinetics of the corresponding chloride ion oxidation. In this paper we report on the oxidation of chloride ion by hydrogen peroxide using methylrhenium trioxide as the catalyst.

Although hydroperoxo and μ-peroxo complexes are common, the η^2- (or side-on) peroxo complexes are the most frequently encountered transition metal peroxides[22] and are typically the catalytically active species in oxidation reactions. In the case of MTO, two different η^2-peroxo complexes exist in solution, specifically the monoperoxo complex, $CH_3ReO_2(\eta^2\text{-}O_2)$, **A**, and the diperoxo complex, $CH_3ReO(\eta^2\text{-}O_2)_2(OH_2)$, **B**, both of which are catalytically active. The speciation of MTO, **A**, and **B** in aqueous solution remains somewhat open to question, especially with regard to the presence of a coordinated water. The structure of MTO has been characterized by a variety of techniques in the gas phase, solid phase, and in organic solvents.[23] The results of all of these characterizations were consistent with C_{3v} molecular symmetry. Gas-phase electron diffraction yielded a pseudotetrahedral structure with all bond angles within 3.5° of the tetrahedral angle. Although the crystal structure of neither **A** nor **B** has been reported, the crystal structure of the diglyme adduct of **B** clearly exhibits a seven-

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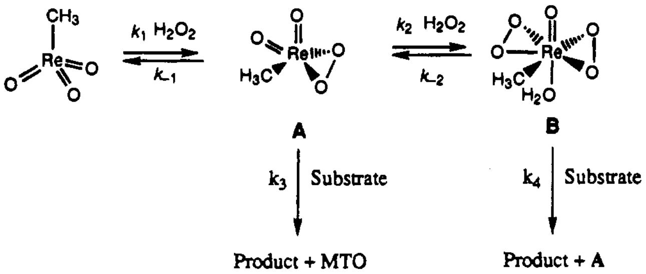
Scheme 1



coordinate rhenium atom: two η^2-peroxo ligands and a methyl group in equatorial positions, and an axial oxo ligand trans to a coordinated water molecule to which the diglyme is hydrogen bonded.[7] In addition, low temperature ^{1}H NMR spectra of **B** in THF-d_8 provide strong support for the presence of a coordinated water molecule in **B** itself.[24] The speciation of **A** in solution is far less certain although the ^{1}H NMR work mentioned above strongly suggests that **A** has no coordinated water molecule.

In a number of respects the MTO/H_2O_2/Cl^- system resembles the biochemical CPO/H_2O_2/Cl^- system (where CPO represents a chloroperoxidase). In both cases, the net general reaction in the presence of substrate (SH) is[25,26]

$$\mathrm{SH} + \mathrm{H_2O_2} + \mathrm{H^+} + \mathrm{Cl} \xrightarrow{\text{MTO or CPO}} \mathrm{SCl} + 2\mathrm{H_2O} \quad (1)$$

Furthermore in the absence of substrate, both MTO and chloroperoxidase react with H_2O_2 and Cl^- to produce singlet oxygen ($^1\Delta_g$).[27]

$$\mathrm{H_2O_2} + \mathrm{H^+} + \mathrm{Cl^-} \xrightarrow{\text{MTO or CPO}} \mathrm{HOCl} + \mathrm{H_2O} \quad (2)$$

$$\mathrm{H_2O_2} + \mathrm{HOCl} \rightarrow {}^1\mathrm{O_2} + \mathrm{H^+} + \mathrm{Cl^-} + \mathrm{H_2O}$$

The essential chemical features of a number of MTO-catalyzed oxidation reactions can be summarized as shown in Scheme 1. Reported values for the equilibrium constants under the conditions employed in this study are: $K_1 = k_1/k_{-1} = 16.1$ L mol^{-1} and $K_2 = k_2/k_{-2} = 132$ L mol^{-1}.[24] The rate constants k_1 and k_2 have also been reported as 42.2 L mol^{-1} s^{-1} and 5.2 L mol^{-1} s^{-1}, respectively.[16] Combining the latter with the former yields values for k_{-1} and k_{-2} of 2.62 s^{-1} and 0.039 s^{-1}.

The rate equation derived from Scheme 1 by applying the steady-state approximation is given in eq 3, where $[\mathrm{Re}]_T = [\mathrm{CH_3ReO_3}] + [\mathbf{A}] + [\mathbf{B}]$; note that the last two terms are not negligible in the steady state since MTO is present at catalytic levels.

$$v_C = \frac{k_1[\mathrm{Re}]_T[\mathrm{Cl^-}][\mathrm{H_2O_2}]\left\{k_3 + \dfrac{k_2k_4[\mathrm{H_2O_2}]}{k_4[\mathrm{Cl^-}] + k_{-2}}\right\}}{k_{-1} + k_3[\mathrm{Cl^-}] + k_1[\mathrm{H_2O_2}] + \dfrac{k_1k_2[\mathrm{H_2O_2}]^2}{k_4[\mathrm{Cl^-}] + k_{-2}}} \quad (3)$$

Experimental Section

Materials and Solutions. Methylrhenium trioxide was purchased from Aldrich Chemical Co.; one portion was purified by sublimation before use, a second portion was used as received (no distinguishable differences were observed). Aqueous stock solutions of this reagent were protected from light, stored at −5 °C, and used within 4 days. These solutions, typically with concentrations of 2−20 mM, were standardized daily spectrophotometrically (λ = 239 nm, ϵ = 1900 L mol^{-1} cm^{-1} and λ = 270 nm, ϵ = 1300 L mol^{-1} cm^{-1}).

2-Chloro-5,5-dimethyl-1,3-cyclohexanedione (monochlorodimedone or MCD) was purchased from Aldrich (98%) and used without further purification. The approximately 4 mM MCD stock solutions were standardized daily spectrophotometrically (λ = 270 nm, ϵ = 12 980 L mol^{-1} cm^{-1}). Lithium perchlorate was prepared by neutralizing lithium carbonate with perchloric acid followed by three recrystallizations from water. Reagent grade sodium chloride, perchloric acid, and 30% hydrogen peroxide were purchased from Fisher and used as received. The 30% hydrogen peroxide was standardized by iodometric titration.

All aqueous solutions were prepared from high-purity water obtained by passing laboratory distilled water through a Millipore-Q reagent water system.

Kinetics. Nearly all of the kinetic experiments in this study employed the initial-rate method and UV−vis spectrophotometry. All solutions were aqueous and air was not excluded from the reaction mixtures. The acidity was maintained at 1.00 M with perchloric acid and the ionic strength was maintained at 2.00 M using lithium perchlorate. UV−vis spectral data were obtained using Shimadzu UV-2101PC and UV-3101PC spectrophotometers fitted with thermostated water-filled cuvette holders. Quartz cuvettes with an optical path length of 0.2 or 1.0 cm were used (the latter with far greater frequency). The consumption of MCD, owing to its rapid reaction with the Cl^- oxidation product(s), was monitored at λ = 270 nm (ϵ = 12 980 L mol^{-1} cm^{-1})—a few experiments employed λ = 280, 285, or 290 nm. Data were typically collected for only the first 1−10% of the reaction, and it proved immaterial whether Cl^- or H_2O_2 was added last. Reagent concentrations varied over the following ranges: [MTO] = 0.010−0.50 mM; [H_2O_2] = 0.10 mM to 1.0 M; [Cl^-] = 1.0 mM to 1.0 M; [MCD] = 0.025−0.50 mM.

Curve fitting and regression analyses were performed using the commercially available programs KaleidaGraph, GraFit, and PSI-Plot, as well as the Shimadzu UV-2101/3101PC Personal Spectroscopy Software package. All kinetic simulations were computed using the public-domain program KINSIM.[28] Initial slope values (dA_{270}/dt) were determined from kinetic trace data by using the Shimadzu software derivative function directly or by using the derivative of a polynomial fit to the data using GraFit.

Results

Monochlorodimedone (MCD) as a Kinetic Probe. Preliminary experiments suggested that the MTO/H_2O_2/Cl^- system behaved very much like the MTO/H_2O_2/Br^- system[16] except that the chloride ion oxidation steps (characterized by k_3 and k_4 in Scheme 1) are three to four orders of magnitude slower than the corresponding bromide oxidation steps. In addition, whereas the isosbestic point for the Br_2/Br_3^- equilibrium (λ = 452 nm, ϵ = 108 L mol^{-1} cm^{-1}) provided a convenient means for monitoring the buildup of Br_2 using UV−vis spectrophotometry, the corresponding isosbestic point for the Cl_2/Cl_3^- equilibrium (λ = 289 nm, ϵ = 27 L mol^{-1} cm^{-1})[29] could not be utilized in this manner owing to the small molar absorptivity combined with the interference of other absorbing species present in the reaction mixture.

Monochlorodimedone (MCD) is generally employed as the standard substrate for the determination of haloperoxidase enzyme activity.[30] Its wide use stems from its ability to undergo rapid and complete monochlorination or monobromination (see eq 4) and the ease with which it can be monitored using UV−vis spectroscopy. In acidic aqueous solutions MCD exists

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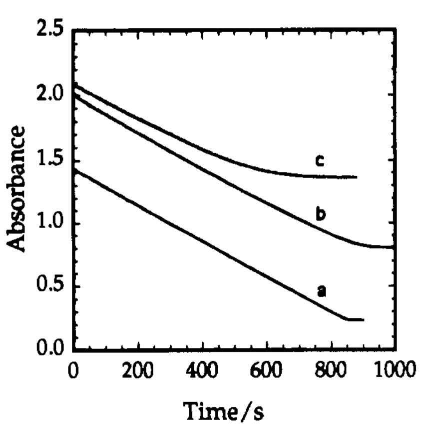
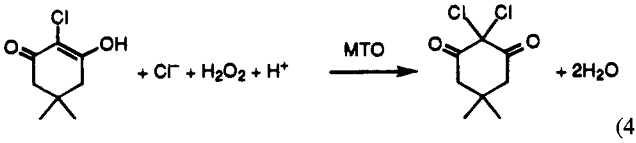


Figure 1. Experimental absorbance vs time data at 25 °C with pH = 0.0, μ = 2.0 M and path length = 1.0 cm. Conditions: (a) λ = 270 nm, $[Re]_T$ = 0.10 mM, $[Cl^-]$ = 0.10 M, $[H_2O_2]$ = 6.0 mM, [MCD] = 0.10 mM; (b) λ = 270 nm, $[Re]_T$ = 0.50 mM, $[Cl^-]$ = 1.0 mM, $[H_2O_2]$ = 0.10 M, [MCD] = 0.10 mM; (c) λ = 285 nm, $[Re]_T$ = 0.50 mM, $[Cl^-]$ = 0.030 M, $[H_2O_2]$ = 0.50 M, [MCD] = 0.10 mM.

almost entirely in the enol form.[31] ^1H NMR spectrometry revealed that MCD was converted quantitatively to 2,2-dichloro-5,5-dimethyl-1,3-cyclohexanedione when included in an MTO/H_2O_2/Cl^- reaction mixture.[32]



(4)

The molar absorptivity difference between MCD and Cl-MCD was found to be 12 100 L mol^{-1} cm^{-1} at pH = 0.0 and μ = 2.0 M. These features made MCD an attractive kinetic probe for this study. Use of MCD and the initial-rate method proved satisfactory throughout the range of reagent concentrations employed in this study.

The use of MCD as a kinetic probe assumed of course that essentially all of the chloride oxidation product(s) reacted rapidly with MCD, and that MCD was not consumed by any other reaction. In this regard, two concerns arose regarding alternative competing reaction pathways. First, since the reaction mixtures employed in this study were highly oxidizing the question of whether MCD itself might be oxidized was considered. It has been demonstrated that although MCD is oxidized to 3,3-dimethylglutaric acid by the MTO-H_2O_2 catalytic system, under the experimental conditions employed in our study the rate of this reaction is negligible compared to the reaction of MCD with the Cl^- oxidation product(s).[32]

A second concern was the known reaction of H_2O_2 and HOCl to produce singlet oxygen (eq 6). The kinetics and mechanism of this reaction were characterized by Makower and Bray[33] over 60 years ago. During our study, most of the MCD absorbance vs time kinetic traces were essentially linear (i.e., zeroth order) except near the very end of the descending portion of the trace where they displayed a slight curvature. However, at high concentrations of H_2O_2 ($\geq$0.25 M) this curvature became much more pronounced and extended over a much larger portion of the kinetic trace (see Figure 1).

Scheme 2 includes a number of reactions believed to be relevant to the competition between MCD and H_2O_2 for reaction with the chloride oxidation product(s).

Scheme 2

$$OCl^- + H^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} HOCl \tag{5}$$

$$HOCl + H_2O_2 \xrightarrow{k_6} {}^1O_2 + H^+ + Cl^- + H_2O \tag{6}$$

$${}^1O_2 \xrightarrow{k_7} {}^3O_2 \tag{7}$$

$$HOCl + H^+ + Cl^- \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} H_2O + Cl_2 \tag{8}$$

$$MCD + Cl_2 \xrightarrow{k_9} ClMCD + HCl \tag{9}$$

$$MCD + HOCl \xrightarrow{k_{10}} ClMCD + H_2O \tag{10}$$

Kinetic simulations using the program KINSIM demonstrated that combining the reactions of Scheme 1, Scheme 2, and eq 12 (below) did indeed produce kinetic traces with pronounced curvature for reaction mixtures with high concentrations of H_2O_2. Literature values for k_6, k_7, k_8, k_{-8}, and k_{10} were assumed.[33,35-37] Given the acidity of our reaction mixtures (pH = 0.0), the limited acid strength of HOCl (pK_a = 7.40),[34] and the very rapid rate of OCl^- protonation under these conditions, the HOCl was assumed to be entirely associated. Although no value for k_9 was located in the literature, it has been reported that this reaction is too fast to be studied by stopped-flow techniques.[37] As we progressively increased the value of k_9 used in our simulations the curvature of the simulated kinetic traces decreased since the effect of the competing reaction pathway (eqs 6 and 7) became less pronounced. However, the simulations tended to exaggerate the severity of the curvature of the kinetic traces even when k_9 was increased to a value which assumed that eq 9 was essentially diffusion controlled.

We considered the possibility that perhaps singlet oxygen reacted with MCD (eq 11). If present, this reaction would lessen the effect of the competing reaction pathway (eqs 6 and 7) and our omission of this reaction from the simulation scheme could perhaps account for the exaggerated curvature of the simulated kinetic traces at high H_2O_2 concentrations. Methylene blue is a known photosensitizer for the production of singlet oxygen from triplet oxygen.[38] Two aqueous solutions of MCD (0.1 mM) and methylene blue (6.0 μM)—one flushed with argon, the other with oxygen—were exposed at 0 °C to light which included wavelengths known to be absorbed by methylene blue. After 30 min of exposure, the UV—vis spectra of the two solutions revealed that the MCD remained unchanged in the solution flushed with argon but was essentially absent from the solution flushed with oxygen. This experiment was qualitative only, and no attempt was made to determine k_{11}. This established, however, that in principle eq 11 could be an additional pathway for the consumption of MCD in our experiments. The rapid decay of singlet oxygen to triplet

$$MCD + {}^1O_2 \xrightarrow{k_{11}} products \tag{11}$$

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oxygen ($\tau = 4.2 \pm 0.2\ \mu s$)[35] and the low concentrations of MCD employed in our experiments (typically 10^{-4} M) required that k_{11} approach the diffusion-controlled limit in order for eq 11 to successfully compete with eq 7 (i.e., $k_{11}[MCD] \approx (1/\tau) = 2.4 \times 10^5\ s^{-1}$). The reactions of singlet oxygen with β-diketones have been reported in the literature, although MCD was not included in the study.[39] The reactions were described as sluggish in the absence of a fluoride catalyst, and even with this catalyst and substrate concentrations suitable for synthetic studies, the reaction times were measured in hours. Although the presence of the chlorine atom in MCD might serve to enhance the rate of its reaction with singlet oxygen, our study did not firmly establish that eq 11 plays a significant role in the MCD reaction scheme (i.e., Scheme 2).

Empirically we observed that whether the H_2O_2 concentration was high or low, the limiting slopes of our kinetic traces yielded initial rates which were consistent with the same model (Scheme 1) and rate constants (k_3 and k_4), and hence MCD did serve as a suitable kinetic probe throughout our study. Principally for this reason we decided not pursue further the exact nature of the MCD consumption scheme. The uncertainties surrounding the exact nature of the "Cl^+" reaction product(s) and the complexities of aqueous chlorine chemistry also contributed to this decision. (For the analogous enzyme-catalyzed oxidation of Cl^- and subsequent MCD chlorination, the exact nature of the chlorine intermediate has has not been established, and the mechanism of the chlorination of MCD is still an open question.[40-42])

The Uncatalyzed Reaction. The uncatalyzed oxidation of Cl^- by H_2O_2 has long been known. The reaction proceeds by two independent pathways as reflected in the rate law (eq 13, at 25 °C and $\mu = 0.40$ M).[43] Although a higher ionic strength

$$H_2O_2 + 2Cl^- + 2H^+ = Cl_2 + 2H_2O \qquad (12)$$

$$v_u = \{1.8 \times 10^{-9} + (8.3 \times 10^{-7})[H^+]\}[H_2O_2][Cl^-] \qquad (13)$$

($\mu = 2.0$ M) was employed in our study, eq 13 was used to apply corrections to our observed initial reaction rates wherever warranted.

Kinetics with Fast Prior Equilibria. It is apparent from Scheme 1 that if the MTO/**A**/**B** equilibria are fast compared to the reactions of **A** and **B** with chloride, then the rate law for substrate oxidation can be written as

$$v = (k_3[\mathbf{A}]_{eq} + k_4[\mathbf{B}]_{eq})[Cl^-] = k_\psi[Cl^-] \qquad (14)$$

such that

$$k_\psi = k_3[\mathbf{A}]_{eq} + k_4[\mathbf{B}]_{eq} \qquad (15)$$

The necessary conditions for these fast prior equilibria are

$$k_1[H_2O_2] + k_{-1} \gg k_3[Cl^-] \qquad k_2[H_2O] + k_{-2} \gg k_4[Cl^-] \qquad (16)$$

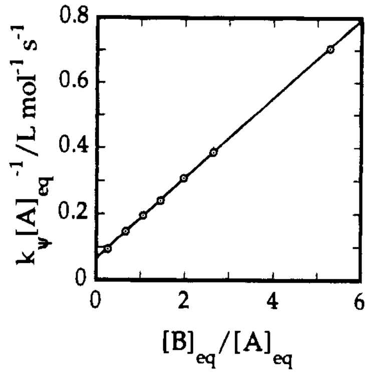

Figure 2. Plot of $k_\psi/[\mathbf{A}]_{eq}$ vs $[\mathbf{B}]_{eq}/[\mathbf{A}]_{eq}$ for the oxidation of Cl^- with [MTO] = 0.10 mM, $[Cl^-] = 0.024-0.100$ M, and $[H_2O_2] = 0.002-0.040$ M. The least-squares fit has intercept $k_3 = 0.0646 \pm 0.0015$ L mol^{-1} s^{-1} and slope $k_4 = 0.1214 \pm 0.0006$ L mol^{-1} s^{-1}.

A series of seven experiments was carried out with $[Re]_T$ = 0.10 mM, $[Cl^-] = 0.024-0.10$ M, and $[H_2O_2] = 2.0-40$ mM. For all of these experiments the left-hand members of eq 16 exceeded the right-hand members by a factor of at least 17 (assuming previously reported values for k_1, k_{-1}, k_2, and k_{-2} and using k_3 and k_4 values determined independently herein). For each experiment the contribution of the uncatalyzed reaction was determined (using eq 13) to be less than 1% of the experimental initial rate, and hence no corrections were applied.

The observed rate constants, k_ψ, were calculated from the initial rates, $k_\psi = v_i/[Cl^-]$, and $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$ values were calculated from $[Re]_T$ and $[H_2O_2]$ using eqs 17 and 18 with

$$[\mathbf{A}]_{eq} = \frac{K_1[H_2O_2][Re]_T}{1 + K_1[H_2O_2] + K_1K_2[H_2O_2]^2} \qquad (17)$$

$$[\mathbf{B}]_{eq} = \frac{K_1K_2[H_2O_2]^2[Re]_T}{1 + K_1[H_2O_2] + K_1K_2[H_2O_2]^2} \qquad (18)$$

equilibrium constants $K_1 = 16.1$ L mol^{-1} and $K_2 = 132$ L mol^{-1}. Equation 15 then provided the basis for a multivariate linear regression analysis using the program GraFit with dependent variable k_ψ and independent variables $[\mathbf{A}]_{eq}$ and $[\mathbf{B}]_{eq}$. This analysis yielded $k_3 = 0.0663 \pm 0.0012$ L mol^{-1} s^{-1} and $k_4 = 0.1209 \pm 0.0004$ L mol^{-1} s^{-1}.

An alternative analysis of these data employed eq 19, obtained by dividing eq 15 by $[\mathbf{A}]_{eq}$. A plot of $k_\psi/[\mathbf{A}]_{eq}$ vs $[\mathbf{B}]_{eq}/[\mathbf{A}]_{eq}$

$$\frac{k\psi}{[\mathbf{A}]_{eq}} = k_3 + k_4\frac{[\mathbf{B}]_{eq}}{[\mathbf{A}]_{eq}} \qquad (19)$$

yielded a straight line with intercept $k_3 = 0.0646 \pm 0.0015$ L mol^{-1} s^{-1} and slope $k_4 = 0.1214 \pm 0.0006$ L mol^{-1} s^{-1} (see Figure 2). The analysis based on eq 15 is the preferable one; that based on eq 19, although it leads to a graph suitable for a visual examination of the data, suffers from statistical unreliability since it mixes dependent and independent variables on the ordinate.

Kinetics at High $[H_2O_2]$. Owing to the large value of K_2 (132 L mol^{-1}), at sufficiently high $[H_2O_2]$ the concentration of **A** is small compared to that of **B**. Also, preliminary experiments indicated that the magnitudes of k_3 and k_4 were comparable. Hence at high $[H_2O_2]$ the rate of Cl^- oxidation by **A** is insignificant compared to the rate of Cl^- oxidation by **B**, i.e., $k_3[\mathbf{A}] \ll k_4[\mathbf{B}]$. Furthermore, at high $[H_2O_2]$ the MTO/**A**/**B** equilibrium is fast compared to the reaction of **B** with Cl^- and thus eq 3 reduces to eq 20. Under these conditions the

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$$v = k_4[\mathbf{B}][\mathrm{Cl}^-] \qquad (20)$$

concentration of **B** remains essentially constant and can be readily calculated using eq 18.

Including replicates, 24 experiments met the criterion of $[H_2O_2] \geq 0.1$ M. The ranges of reagent concentrations were as follows: $[\mathrm{Re}]_T = 0.0125-0.50$ mM, $[\mathrm{Cl}^-] = 1.0$ mM-0.50 M, and $[H_2O_2] = 0.10-1.0$ M. Owing to the high $[H_2O_2]$ values used in these experiments, the initial rates were corrected (using eq 13) for the rate of the uncatalyzed reaction. For each experiment, k_4 was determined by solving eq 20. The mean value of k_4 obtained from the 24 experiments was 0.1215 ± 0.0032 L mol^{-1} s^{-1}.

Kinetics at High $[\mathrm{Cl}^-]/[H_2O_2]$ Ratios. Under conditions of high $[\mathrm{Cl}^-]$ and low $[H_2O_2]$, the reaction of the monoperoxo complex **A** with H_2O_2 to form **B** is much slower than the reaction of **A** with Cl^- to form product and consequently eq 3 reduces to eq 21. A series of 10 experiments was completed

$$v = K_1k_3[\mathrm{Re}]_T[\mathrm{Cl}^-][H_2O_2] \qquad (21)$$

with $[\mathrm{Re}]_T = 0.20-0.50$ mM, $[\mathrm{Cl}^-] = 0.40-1.0$ M, and $[H_2O_2] = 0.10-1.0$ mM; in each case $[\mathrm{Cl}^-]$ exceeded $[H_2O_2]$ by at least a factor of 1000. For each experiment the contribution of the uncatalyzed reaction was determined (using eq 13) to be less than one percent of the measured rate and hence no corrections were made. Using GraFit and eq 21 with $K_1 = 16.1$ L mol^{-1}, the application of nonlinear regression analysis to the data from these experiments yielded $k_3 = 0.0508 \pm 0.0011$ L mol^{-1} s^{-1}.

Global Fit to All Kinetic Data. Following completion of all kinetic experiments, a global fitting of eq 3 to all of the data was performed using the program PSI-Plot and the Marquardt–Levenburg algorithm. The rate constants k_1, k_{-1}, k_2, and k_{-2} were fixed at the literature values noted in the Introduction. This fitting included 78 experiments (21 being replicates) which covered the following concentration ranges: $[\mathrm{Re}]_T = 0.010-0.50$ mM; $[H_2O_2] = 0.10$ mM to 1.0 M; $[\mathrm{Cl}^-] = 1.0$ mM to 1.0 M. For 16 of the 78 experiments the contribution of the uncatalyzed reaction to the observed initial rate exceeded 5% and hence all of the observed initial rates were corrected using eq 13. The results of this fitting yielded $k_3 = 0.0562 \pm 0.0061$ L mol^{-1} s^{-1} and $k_4 = 0.1305 \pm 0.0049$ L mol^{-1} s^{-1}. (Using uncorrected rather than corrected initial rates altered the resultant values for k_3 and k_4 by less than 3%.) Figure 3 provides a measure of the quality of the global fit by displaying a graph of the experimental initial rates plotted vs the calculated initial rates. The fact that the points all lie close to the 45° line means that the experimental data fit this model. It should be remarked that this method of displaying the fit between data and model allows the incorporation of all 78 points on one two-dimensional graph.

Discussion

Reactivity of A and B. The results of this study clearly support the view that both the monoperoxo complex **A**, $CH_3ReO_2(\eta^2\text{-}O_2)$, and the diperoxo complex **B**, $CH_3ReO(\eta^2\text{-}O_2)_2(OH_2)$, are catalytically active, and indeed have reactivities that are comparable. This conclusion is consistent with the results of the analogous MTO/H_2O_2/Br^- study[16] and a number of other MTO catalyzed hydrogen peroxide oxidation studies using a variety of substrates.[9,11-13] Insofar as we are aware, only the MTO-catalyzed oxidation of $(\mathrm{en})_2\mathrm{Co}(SCH_2CH_2NH_2)^{2+}$ yielded results inconsistent with this pattern.[10] In that case only **A** was found to possess catalytic activity. For dimethylaniline, **A** is much more reactive than **B**.[12]

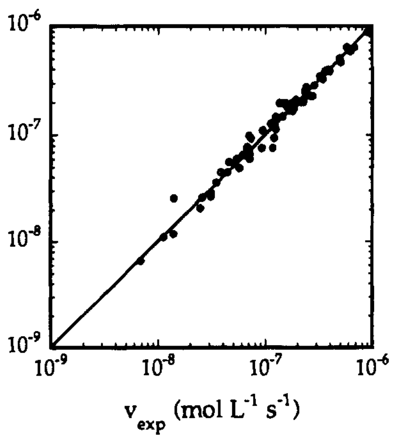

Figure 3. Plot of v_{calc}, the initial rate calculated using eq 3 and the best fit values for k_3 and k_4, vs v_{exp}, the experimental initial rate. The values of $k_1 = 42.2$ L mol^{-1} s^{-1}, $k_{-1} = 2.62$ s^{-1}, $k_2 = 5.2$ L mol^{-1} s^{-1}, and $k_{-2} = 0.039$ s^{-1} in eq 3 were fixed. The best fit values for k_3 and k_4 were, 0.0562 ± 0.0031 L mol^{-1} s^{-1} and 0.1305 ± 0.0049 L mol^{-1} s^{-1}, respectively. This global fitting included data from 78 experiments. The plot is shown on a log–log scale to allow the full range of variations to be seen.

It has been reported that only the **B** form of MTO is catalytically active,[6-8] however, it appears that the experimental conditions employed in the reported studies precluded observation of the reactivity of the monoperoxo species **A**. A high H_2O_2 concentration coupled with a large value for K_2 results in $[\mathbf{B}] \gg [\mathbf{A}]$; consequently even if the reactivities of **A** and **B** are comparable the rate of reaction of substrate with **A** will be negligible compared to that with **B**. In short, the observation that $k_4[\mathbf{B}] \gg k_3[\mathbf{A}]$ does not allow one to conclude that $k_4 \gg k_3$. In none of the systems examined to date has it been found that **B** is a catalyst and **A** is not.

The reactivity of both mono- and diperoxo transition metal complexes in halide oxidations is not unique to MTO. The catalytic activity of both the monoperoxo, $VO(O_2)^+$, and diperoxo, $VO(O_2)_2^-$, vanadium(V) complexes toward the oxidation of halide ions has been reported by Butler and colleagues[14] using bromide and Secco[20] using iodide. Remarkably, the bromide reaction involves not $OV(O_2)^+$ or $OV(O_2)_2^-$, the direct analogs of **A** and **B**, but $(OV)_2(O_2)_3$, the divanadium compound formed by their combination.[14b] As such, the value of this system as a precedent for the current work may be limited.

A number of transition metal catalyzed peroxidative halogenation reactions have been reported in which only one peroxo species was observed to react. Meister and Butler[18] examined the molybdenum(VI) and tungsten(VI) catalysis of bromide oxidation by hydrogen peroxide. They observed the peroxidation of bromide by the diperoxo species only. Reynolds and co-workers[19] studied the oxidation of bromide by the oxalatomolybdenum(VI) complex and likewise concluded that only the diperoxo species reacted. In both of these cases, however, the authors recognized that their experimental conditions dictated only very small concentrations of monoperoxo species. Thompson and co-workers[44,45] have shown that the monoperoxo to diperoxo equilibria for these complexes are characterized by equilibrium constants in excess of 10^6 M^{-1}. Ironically, a report[21] on the kinetics and mechanism of the molybdenum(VI) catalysis of iodide oxidation by hydrogen peroxide proposed that the active species is H_2MoO_5, presumably a monoperoxo species.

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In addition, Butler and co-workers[15] examined the oxidation of bromide by the peroxides of two vanadium(V) tridentate-Schiff base complexes and Pecoraro and co-workers[17] studied the oxidation of bromide and iodide using a tetradentate ligated oxoperoxovanadium(V) complex. Both investigators proposed that the catalytically active species was the monoperoxo species, but in neither case was evidence for the existence of a diperoxo species even obtained; quite probably formation of the diperoxo species was precluded for steric and/or electronic reasons given the spatial and coordination requirements of the rather large tri- and tetradentate ligands.

In summary, our observation that both the monoperoxo and diperoxo forms of MTO are catalytically active toward the oxidation of chloride is not inconsistent with other published reports of peroxometal halide oxidations.

Chloride vs Bromide Reactivity. Not unexpectedly the hydrogen peroxide oxidation of Cl^-, catalyzed by MTO, was found to be much slower than that of the corresponding reaction for Br^-. At 25 °C with $[H^+] = 1.0$ M and $\mu = 2.0$ M, the rate constants of the halide oxidation steps are as follows: for Cl^-, $k_3 = 0.06$ L mol^{-1} s^{-1} and $k_4 = 0.12$ L mol^{-1} s^{-1}, while for Br^-, $k_3 = 350$ L mol^{-1} s^{-1} and $k_4 = 190$ L mol^{-1} s^{-1}.[16] These values imply that **A** is 5.9×10^3 times more reactive with Br^- than with Cl^-, and that **B** is 1.5×10^3 times more reactive with Br^- than with Cl^-. By comparison, for the uncatalyzed reactions of H_2O_2 with Br^- and Cl^- at 25 °C with $[H^+] = 1.0$ M and $\mu = 0.4$ M, the Br^- oxidation occurs only 290 times faster than the Cl^- oxidation.[43]

If one views the halide oxidation steps as S_N2 displacements, i.e., the attack of a nucleophilic halide ion on a peroxidic oxygen atom, then the greater effectiveness of **A** and **B** in catalyzing the oxidation of Br^- is not surprising. The greater nucleophilicity of Br^- compared to Cl^- in S_N2 reactions is widely recognized by organic chemists and is attributed to the greater polarizability, lower electronegativity, and smaller solvation energy of the bromide ion.[46]

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