Articles

Equilibria and Kinetics of the Reactions between Hydrogen Peroxide and Methyltrioxorhenium in Aqueous Perchloric Acid Solutions

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In aqueous solutions the colorless compounds CH_3ReO_3 (=MTO) and H_2O_2 form 1:1 and 1:2 adducts. The latter is yellow, with $\epsilon_{360} = 1.1 \times 10^3$ L mol^{-1} cm^{-1}. Peroxide binding to MTO shows cooperativity, as shown by the inversion of the usual order of binding constants. The stepwise equilibrium constants are $K_1 = 7.7$ L mol^{-1} and $K_2 = 145$ L mol^{-1} at 25 °C. The buildup of product, which occurs on the stopped-flow time scale at 9–680 mM H_2O_2, is fit by biexponential kinetics. The equilibria and rates are independent of $[H_3O^+]$ in the range 10^{-1}–10^{-3} M. The peroxide complexes decompose more rapidly at lower $[H_3O^+]$, particularly at pH > 3. Possible structures for 1:1 and 1:2 MOT–H_2O_2 adducts are presented and discussed.

Introduction

The title rhenium compound, first reported[1] in 1979 and now known as MTO, shows many fascinating aspects of reactivity. The most interesting and important are reactions in which MTO catalyzes the oxidations of various substrates. In a generic sense, this is represented by the following equation that depicts the donation of a single atom of oxygen from hydrogen peroxide to the oxidizable substrate S:

$$H_2O_2 + S \xrightarrow{\text{cat. MTO}} H_2O + SO$$

The substrates include alkenes, some alkynes, and certain ketones as reported by Herrmann *et al.*[2]

We are actively investigating the mechanism of selected oxidations catalyzed by MTO, and we shall shortly report the results in full experimental detail. In the course of these investigations we found it useful to study what interactions, if any, occur between MTO and hydrogen peroxide itself, in the absence of an oxidizable substrate. The first indiction of an appreciable interaction is the yellow coloration that develops nearly immediately after mixing the two colorless aqueous solutions of MTO and H_2O_2. Further investigation of these solutions showed that MTO and H_2O_2 form two "adducts", in 1:1 and 1:2 ratios. They are not formed irreversibly, but are in equilibrium with the constituents.

The equilibrium reactions are written in a stepwise fashion to facilitate the representation of the molecular steps in which A and **B** are formed as in eqs 1 and 2. It has proved convenient to

$$\text{MTO} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{A} + H_2O \quad K_1 = k_1/k_{-1} \qquad (1)$$

$$\text{A} + H_2O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{B} + H_2O \quad K_2 = k_2/k_{-2} \qquad (2)$$

indicate the formulas of the adducts as if they are the anhydrides, although that is not a conclusion that we can reach from the equilibrium data.

Experimental Section

Reagents. Methyltrioxorhenium, CH_3ReO_3, was prepared from the reaction of dirhenium heptoxide and tetramethyltin, as described in the literature.[3] It was separated from $(CH_3)_3SnOReO_3$, the other product, by vacuum sublimation and was further purified by recrystallization from methylene chloride/hexane. Its purity was checked by ^{1}H NMR (δ 2.6 ppm in $CDCl_3$),[1] IR (999 cm^{-1}, w, 965 cm^{-1}, vs, in CS_2),[4] and UV–vis (H_2O).[5]

Aqueous solutions of this white crystalline solid do not absorb in the visible region. Concentrations were determined spectrophotometrically at the absorption maxima in the UV, $\lambda_{max} = 239$ nm ($\epsilon = 1900$ L mol^{-1} cm^{-1}) and 270 nm (1300 L mol^{-1} cm^{-1}).[5]

Solutions of hydrogen peroxide were standardized iodometrically. Because compounds **A** and **B** are much more stable in acidic solutions than in neutral ones, most of the measurements were carried out in dilute aqueous perchloric acid. Apart from the stabilization of the products, acid shows no effect on the kinetics or thermodynamics of the reactions studied.

Measurements. The equilibrium and kinetic determinations were based upon spectrophotometric experiments. The determinations of the equilibrium constants were made by scanning the UV spectrum of MTO solutions containing a sufficiently large excess of hydrogen peroxide such that the equilibrium value of $[H_2O_2]$ could be approximated as the starting concentration. Absorbance values were read at several wavelengths in the region 360–420 nm. The data were obtained with the use of a Shimadzu UV-2101PC spectrophotometer. The data analysis, including the nonlinear least-squares fitting, was carried out with the program KaleidaGraph.

The reactions are rather rapid, such that the first stage is complete in about 100 ms, and the complete system generally reaches equilibrium within a few seconds. Kinetic data were therefore obtained by use of a Sequential DX-17MV stopped-flow instrument purchased from Applied Photophysics Ltd. Experiments at low $[H_2O_2]$ were followed at 300 nm. Those at $[H_2O_2] > 0.1$ M were followed at 360 nm, where the yellow-colored 1:2 adduct **B** has an absorption maximum. These wavelengths were selected to optimize the conditions for the resolution of the separate kinetic steps; this was not really possible, however, as explained later.

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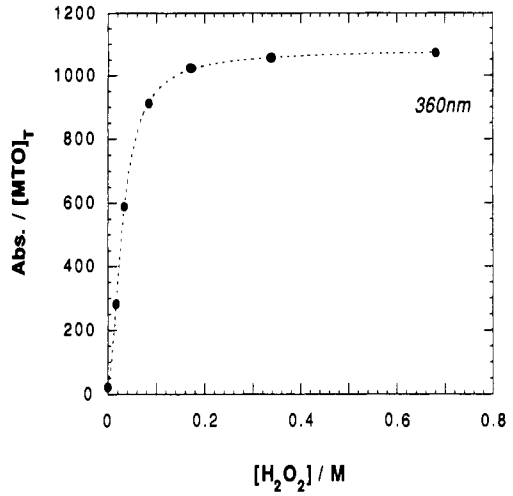


Figure 1. Plots of the absorbance at 360 nm of MTO–H_2O_2 solutions as a function of $[H_2O_2]$ at $[MTO]_T$ = 1.0 mM. The continued increase in absorbance out to very high ratios of peroxide to MTO show that at least one equilibrium reaction is occurring in this system.

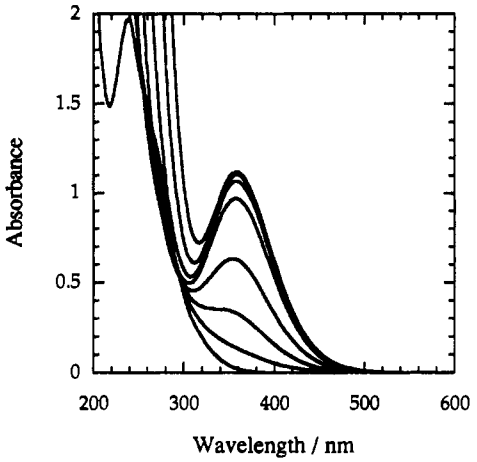


Figure 2. UV spectra of equilibrated MTO–H_2O_2 mixtures in 0.1 M perchloric acid at 25 °C. The total MTO concentration is 1.0 mM. Reading upward at 360 nm, the hydrogen peroxide concentrations are 0, 8.5, 17, 34, 85, 170, 340, and 680 mM. Approximate isosbestic points are seen at 319 and 289 nm at low hydrogen peroxide concentrations, but they are not maintained to higher concentrations.

Results

General Observations. The mixing of solutions of MTO and hydrogen peroxide results in a yellow color that is more intense at higher peroxide concentrations. The absorbance–concentration diagram is not that of a titration curve, however, in that the absorbance continues to rise as more peroxide is added, until finally a plateau is reached. This is illustrated in Figure 1.

The shape of the curve in Figure 1 suggests that the system is an equilibrating one. An analysis of the data on the basis of a single equilibrium was not successful, as seen from the UV spectral scans at various peroxide concentrations, Figure 2. Evidently more than one reaction occurs over the full range of $[H_2O_2]$, since the isosbestic points at 294 and 252 nm that exist at least approximately at the lower peroxide concentrations are not maintained over the entire concentration range. The higher $[H_2O_2]$ also contributes to the absorbance at the lower wavelengths.

Equilibrium Constants. It did not come entirely as a surprise to learn that more than one peroxide-containing species exists in these solutions. We state that, because of a claim in the literature[2] (without much reported evidence, however), that species with 1:1 and 1:2 ratios of MTO to hydrogen peroxide exist in such solutions. There is no guidance, however, as to the fact that these are equilibrium and not stoichiometric reactions, nor to the peroxide concentrations at which they are formed.

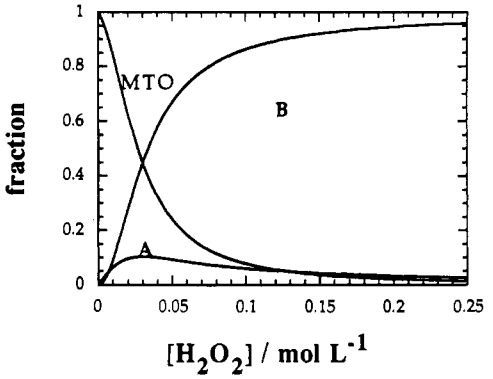


Figure 3. Calculated distribution curves showing the relative proportions of MTO, **A**, and **B** over the range of peroxide concentrations. These curves were calculated with the average values of K_1 and K_2 given in Table I.

The analysis was then carried out in terms of eqs 1 and 2, which featured the simultaneous formation of 1:1 (**A**) and 1:2 (**B**) compounds. That is, the absorbance changes at every wavelength were consistent with a two-reaction equilibrium model. Since both $[H_2O_2]$ and [MTO] contribute negligibly to the absorbance at $\lambda \geq 360$ nm, we can express the absorbance as

$$Abs = \epsilon_A[\mathbf{A}] + \epsilon_B[\mathbf{B}] \tag{3}$$

where the definitions are obvious and the species concentrations are the equilibrium ones. Substituting the equilibrium constant expressions from eqs 1 and 2, we obtain

$$\bar{\epsilon} = \frac{Abs}{[MTO]_T} = \frac{\epsilon_A K_1[H_2O_2] + \epsilon_B K_1 K_2[H_2O_2]^2}{1 + K_1[H_2O_2] + K_1K_2[H_2O_2]^2} \tag{4}$$

The data at each of several wavelengths were fit to this equation. The data were obtained over a range of concentrations of hydrogen peroxide of 0.009–0.680 M. To prove that there is no involvement of hydrogen ion in the reactions, this variant in concentration of hydrogen peroxide was carried out at 0.02, 0.05, 0.10, and 0.20 M $HClO_4$. A separate calculation was carried out at each wavelength and at each acid concentration. A given calculation provides from the nonlinear least-squares fit the values of ϵ_A and ϵ_B at the given wavelength and the equilibrium constants K_1 and K_2.

Table I presents the values that we calculated by this procedure. The values of K_1 and K_2 are the same over all of the variations, within experimental error, although the compartmentalized procedure we adopted tends to exaggerate the differences. This shows that the formulation in the two chemical equations is sufficient to describe the interactions in these solutions under the conditions examined. Indeed, the same constants are valid even at neutral pH, as suggested by matching spectral changes, except that less acidic solutions decompose relatively rapidly.

The binding constant for the second molecule of hydrogen peroxide is substantially larger than that for the first, being K_2 = 145 L mol^{-1} as compared to K_1 = 7.7 L mol^{-1}. This is an unusual finding, at least if we make reference to the widely-studied phenomenon of stepwise metal–ligand binding. Nearly always in such cases the strength of successive Lewis acid–base interactions weakens with the binding of the next base. The inversion of the order of binding that characterizes the interaction of MTO and hydrogen peroxide is referred to as *cooperativity*. The consequences of this will be taken up in the Discussion. The species distribution curves are relatively unusual in their shapes; the calculated curves are shown in Figure 3. At no concentration of hydrogen peroxide does the concentration of **A** attain more than 10% of the total. For this reason the absorption due to **A** in Figure 2 is small and the values of ϵ_A in Table I have rather substantial errors.

Values for ϵ_B at each of the wavelengths were also determined independently at pH 1. This was done by taking the spectrum

Table I. Equilibrium Constants for the Formation of Compounds A and B According to Reactions 1 and 2

$[H_3O^+]$/M	λ/nm	K_1/L mol^{-1}	K_2/L mol^{-1}	ϵ_A/L mol^{-1} cm^{-1}	ϵ_B/L mol^{-1} cm^{-1}	ϵ_B/L mol^{-1} cm^{-1} [a]
0.02	360	8.9 ± 1.2	136 ± 18	140	1084	
0.05	360	7.3 ± 0.5	144 ± 9	500	1097	
	380	6.0 ± 0.5	166 ± 12	380	921	
	400	7.3 ± 1.2	141 ± 18	140	616	
	420	6.9 ± 1.6	147 ± 27	80	343	
0.10	360	9.6 ± 1.7	115 ± 16	480	1018	1124
	380	8.5 ± 1.5	124 ± 18	350	858	942
	400	8.2 ± 1.6	128 ± 19	170	571	640
	420	8.4 ± 1.1	126 ± 13	100	318	348
0.20	360	7.7 ± 3.0	156 ± 46	380	1063	
	380	7.5 ± 3.3	160 ± 53	120	900	
	400	7.2 ± 2.9	167 ± 51	20	599	
	420	6.4 ± 3.7	178 ± 79	40	332	
		av 7.7	av 145			

[a] Independent determinations of ϵ_B in 0.50 M H_2O_2 and (3.2–8.0) × 10^{-4} M CH_3ReO_3.

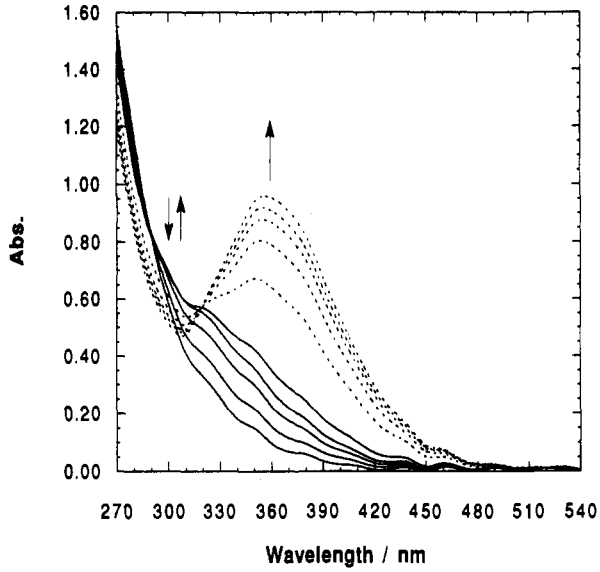


Figure 4. Reconstructed spectral changes during the reaction of MTO (1.0 mM) and H_2O_2 (0.2 mM) in 0.1 M aqueous perchloric acid. The solid lines show the spectra at short times: reading upward at 360 nm, the times are 0.025, 0.050, 0.10, 0.20, and 0.50 ms. The subsequent changes are given by the dashed lines; they were recorded at 2.5, 4.5, 6.5, 8.5, and 20.5 s.

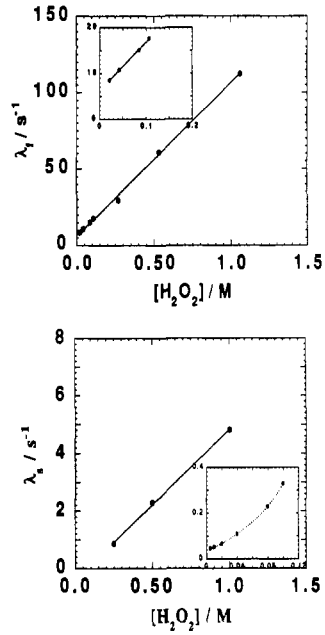


Figure 5. Plots showing the dependences of the fast (top) and slow relaxation times from eqs 5 and 6 on the concentration of hydrogen peroxide. The insets show the values in the limit of low $[H_2O_2]$.

of solutions containing 0.50 M H_2O_2 and (3.2–8.0) × 10^{-4} M MTO. Under these conditions (low pH) solutions of **B** are quite stable, allowing accurate determinations of ϵ_B. The average values obtained are also listed in Table I.

Kinetics. In view of the inversion in the order of the K's, it was not possible to study the kinetics of one reaction under conditions where the other did not contribute. Even at relatively low $[H_2O_2]$ there is an appreciable contribution from both reactions. The biexponential absorbance-time traces taken at different wavelengths were used, along with the computer programs supplied with the stopped-flow instrumentation, to construct spectra at various times during the reaction. This is displayed in Figure 4. At short times (<0.5 s), isosbestic points are preserved at 289 and 319 nm, but these are lost at longer times, as shown.

The absorbance–time curves were fit to two exponentials, whose rate constants we label λ_f and λ_s. If we postulate that eqs 1 and 2 describe the kinetics as well, the biexponential fit is to be expected if the system is irreversible (*i.e.*, if $k_{-2} \sim 0$, which will hold at all of the $[H_2O_2]$ used, given the values of K_1 and K_2) and if $[H_2O_2]_0 \gg [MTO]_0$ such that $[H_2O_2]$ is constant in each run. On the basis of this model, the rate constants are

$$\lambda_s = {}^1/_2(p - q) \qquad (5)$$

$$\lambda_f = {}^1/_2(p + q) \qquad (6)$$

where $p = (k_1 + k_2)[H_2O_2] + k_{-1}$ and $q = (p^2 - 4k_1k_2[H_2O_2]^2)^{1/2}$. The functional dependences of λ_s and λ_f on $[H_2O_2]$ are thus complicated. Graphs of these composite rate constants are shown in Figure 5. This analysis fits the data, but the nature of these functions is such that the rate constants cannot be determined to high precision. We find $k_1 = 80$ L mol^{-1} s^{-1}, $k_{-1} = 10$ s^{-1}, and $k_2 \sim 5.2$ L mol^{-1} s^{-1}. This gives $k_{-2} = k_2/K_2 \sim 0.04$ s^{-1}.

Stability of the Peroxide Adducts. Solutions containing equilibrated A and B decompose slowly, as indicated by the decay of the yellow color. The parent MTO remains stable in aqueous solution under conditions where A and B decompose. This decomposition is pH-dependent, being much faster at higher pH. Figure 6 shows the decay of absorbance at 360 nm at different acid concentrations.

The initial reaction rate was evaluated from the early part of each curve. The dependence of the initial rate on the acid concentration is quite dramatic, as shown in Figure 7. Also, the decomposition rate is a mild function of $[H_2O_2]$. For example, the rate goes through a maximum, being roughly twice as high at 0.040 M H_2O_2 as it is at 0.01 or 0.2 M H_2O_2 (data not shown). This decomposition process was initially thought to be disproportionation of hydrogen peroxide, catalyzed by the rhenium

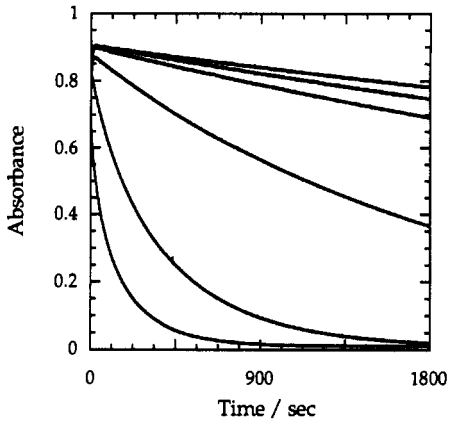


Figure 6. Absorbance–time traces showing the increasing rate of decomposition of complexes **A** and **B** as pH is increased. The solutions contained 1.0 mM MTO and 85 mM H_2O_2 at pH 0.7, 1.0, 1.3, 2.0, 3.0, and 7.0. The absorbances were recorded at 360 nm for 90-min time periods.

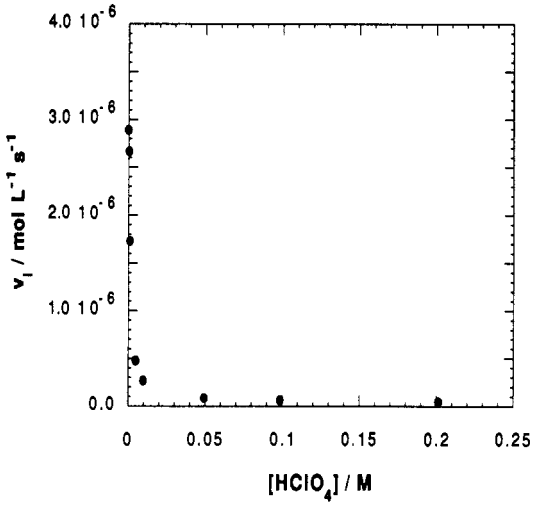
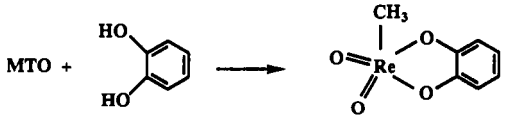


Figure 7. Plot of the initial rate of decomposition of complexes **A** and **B** as a function of the concentration of acid. The low rates at >0.05 M H_3O^+ are still much larger than the decomposition of MTO itself.

complexes present. However, this was ruled out by the failure to observe oxygen formation, even at high $[H_2O_2]$ (0.50 M).

Discussion

The notion that an organo(trioxo)rhenium compound would interact with an oxygen atom donor finds credence in the reported interaction of MTO with catechols.[6] This reaction produces the intensely purple-colored product of the following reaction:



(7)

Then, too, metal–oxo complexes in high oxidation states are known to react with hydrogen peroxide to yield peroxo complexes. Among them, we can cite the reactions of chromates, vanadates, molybdates, tungstates, titanates, and so on. In typical reactions we show the formation of TiO_2^{2+},[7] $Mo(O)(O_2)_2$,[8] and $V(O)(O_2)^+$:[9]

$$TiO^{2+} + H_2O_2 \rightarrow TiO_2^{2+} + H_2O \quad (8)$$

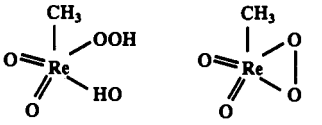
$$HMoO_3^+ + 2H_2O_2 \rightarrow MoO(O_2)_2 + H^+ + 2H_2O \quad (9)$$

$$VO_2^+ + H_2O_2 \rightarrow VO(O_2)^+ + H_2O$$

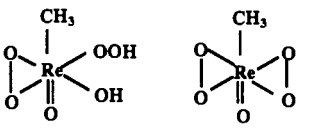
$$VO(O_2)^+ + H_2O_2 \rightarrow VO(O)_2^- + 2H^+ \quad (10)$$

The chemical interactions that one might suggest between CH_3ReO_3 and H_2O_2 can be based on those found for other high-valent metal–oxo species. In suggesting the specifics about the species that might be formed, it is important to note that the degree of hydration in an aqueous solution is of necessity undefined. In the first instance, this means that we do not really know whether MTO exists as such in aqueous solution, or whether the solvent acts as a Lewis base as in the formulations $CH_3ReO_3(H_2O)_n$ (n = 1 or 2). In the gas phase, MTO is a pseudotetrahedral molecule.[4] The MTO molecules that have been crystallized from solution are typified by CH_3ReO_3(quinuclidine).[10] In this species an axial position is occupied by the base, with an approximately trigonal planar ReO_3 unit. Also, MTO forms similar adducts with chloride ions,[11] both the pseudo trigonal bipyramid with one chloride and the pseudooctahedron with two.

Since the degree of hydration is uncertain, *any* of following structures may contain coordinated water molecules other than those shown. The 1:1 adduct **A** may thus be formulated as either of the following:



For the 1:2 adduct, **B**, similar species with structural formulas that represent both η^1-hydroperoxo and η^2-peroxo possibilities for the ligands can be suggested. As with **A**, the equilibrium data cannot distinguish between them, in that they differ by only a molecule of solvent. The suggested species for **B**, ignoring the possibility of yet further undisclosed hydration, are thus



It is likely that **B** has at least one η^2-peroxide and possibly two. This species has been reported to exhibit an IR band at 872 cm^{-1} in diethyl ether which is typical for η^2-peroxo complexes.[2]

Clearly, the binding of a second molecule of hydrogen peroxide is favored thermodynamically over the first. If the sequence were simply one Lewis base added and then another, we might anticipate either a comparable affinity for each, or a diminished affinity for the second, the Lewis acid center having expended at least some of its acidity upon binding the first peroxide. It is as if the structure of the first adduct **A** is so altered to allow it to "bind" a second peroxide more tightly than the first. In fact, **A** contains one less electron donating oxo ligand than MTO, favoring the addition of a second peroxide. This inversion in the usual order of binding constants occurs for other d^0 metal ions as well. For example, the first and second binding constants for V(V) with H_2O_2 are 3×10^3 M^{-1} and 1.7×10^5 M^{-1} (pH 6.7).[12]

Kinetics of Formation of A and B. Hydrogen peroxide may react more rapidly in the first step than in the second because in the first step it adds to an oxo-only complex. Addition of H_2O_2 to **A**, on the other hand, may be inhibited kinetically because of

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the preexisting η^2-O_2^{2-} group. Until the exact molecular structures are known, however, further comment would be too speculative.

The reversibility of this system makes it difficult to draw conclusions about the active species in reactions catalyzed by MTO. More information about the structures of **A** and **B** would be useful, if one of these species were shown to be active. However, according to the present results **A** is never present at more than 10% of the total rhenium and is likely to be strongly solvated, making its isolation and further characterization extremely difficult. Isolation of complex **B** is much more likely, as it is possible to obtain solutions that contain virtually all of the rhenium in the form of **B**. In fact, a previous study included the titration of the diperoxo complex with substrate as evidence that **B** is the active species.[2] However, a reversible system such as this requires a kinetic study with substrate present to determine the composition of the active species.

The kinetics of the catalytic reactions, currently in progress, may also provide further numerical details on reactions 1 and 2. There may be fewer complications in the presence of oxidizable substrate, depending on how the catalytically-active form(s) of MTO react. For example, if the peroxide-containing forms of MTO are drawn off into a reactive catalytic cycle, then the reverse steps may not be of importance. If so, the values of the rate constants may later be obtained to better accuracy than those provisionally reported here.

The cooperativity manifest in the equilibrium constants is clearly not a consequence of the second rate constant for binding being much larger than the first. The reverse is in fact true, and $k_1 > k_2$. Cooperativity arises from the reverse rates, since we find $k_{-2} \ll k_{-1}$. Whether this should be taken to imply intrinsically different molecular structures for **A** and **B** (e.g. η^1 and η^2, as suggested by a reviewer) remains unclear at this stage. We hope that further studies of chemical reactivity, currently in progress, will settle the matter.

Decomposition. Over a long period of time, hours or longer depending on the pH, the yellow-colored mixtures of **A** and **B** fade to colorless mixtures. We have examined briefly how quickly this occurs, since it relates to the utility of catalytically active MTO–peroxide mixtures. We have not, however, examined the chemical aspects of this reaction. The results suggest that the catalytic system is most useful at low pH and is not useful in basic media.

Concluding Remarks. This work has demonstrated that MTO forms 1:1 and 1:2 adducts with hydrogen peroxide. We have suggested possible structures for them. These studies can resolve the thermodynamic binding constants for the successive interactions, and point to a striking *cooperativity*, in that the second hydrogen peroxide has a markedly higher binding constant than the first. However, the data do not reveal whether the 1:1 adduct **A** has monodentate HOO^- and HO^- ligands, or a chelated O_2^{2-}. From the previous IR data reported it is logical to presume that the 1:2 adduct **B** is the bis(η^2-peroxo) species $CH_3Re(O)(O_2)_2$. Another issue of structural uncertainty relates to the extent to which further hydration of both **A** and **B** occurs.

One final thought, indeed a precaution, is in order. The unequivocal demonstration that peroxide-containing species are formed as a result of the interaction of MTO with hydrogen peroxide does *not* show that any one of these adducts is the catalytically-featured intermediate in any of the oxidation reactions catalyzed by MTO. It is conceivable that these species, which certainly exist, are but mere bystanders in the catalysis. Further work on this question and others related to the catalytic reactions is in progress.

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