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Organometallic Catalysis in Aqueous Solution: Oxygen Transfer to Bromide

James H. Espenson,* Oleg Pestovsky, Patrick Huston, and Stacy Staudt

Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Abstract: The reaction between hydrogen peroxide and bromide ions in aqueous acidic solutions, ordinarily very slow, is strongly catalyzed by CH_3ReO_3, a water-soluble organometallic oxide. The complex catalytic kinetics showed that the rate-controlling process consists of two steps: (1) reversible formation of the independently-known 1:1 and 2:1 adducts of hydrogen peroxide and methylrhenium trioxide (the formulas, including the water that had been shown to be coordinated, are $CH_3Re(O)_2(\eta^2\text{-}O_2)(H_2O)$ and $CH_3Re(O)(\eta^2\text{-}O_2)_2(H_2O)$) and (2) their reactions with bromide ions that yield HOBr. The rate constants for these steps were evaluated by several steady-state kinetic techniques. The HOBr intermediate reacts with Br^- to yield Br_2. When hydrogen peroxide was in excess, the reaction yielded oxygen instead of bromine. This can be accounted for by the reaction of HOBr with H_2O_2. The 2:1 peroxide–rhenium adduct, formed only at the higher concentrations of hydrogen peroxide, also reacts with bromide ions, but more slowly. Kinetic modeling by numerical techniques was used to provide verification of the reaction scheme. The various steps of peroxide activation consist of nucleophilic attack of bromide ions on peroxide ions that have become electrophilically activated by binding to the rhenium compound. The rhenium catalyst bears some resemblance to the enzyme vanadium bromoperoxidase.

Introduction

The search is underway for environmentally-acceptable reagents that effect desired chemical transformations, yet avoid unneeded byproducts (*e.g.*, salts) and certain solvents (*e.g.*, halocarbons). Aqueous media and catalytic reactions hold considerable promise.[1] One of the most promising reagents is hydrogen peroxide, since the excision from hydrogen peroxide of one O atom, transferring it to a substrate, gives this net effect:

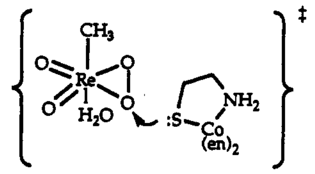
$$H_2O_2 + S \rightarrow H_2O + SO \qquad (1)$$

or

$$H_2O_2 \rightarrow H_2O + \{O\} \qquad (2)$$

To do this cleanly (without the byproducts of peroxide radical reactions) and efficiently (since the nonradical reactions of hydrogen peroxide are often very slow), a catalyst is needed to activate this particular mode of reactivity. Methylrhenium trioxide (CH_3ReO_3), sometimes referred to as MTO, is a promising catalyst. The combination of CH_3ReO_3 and H_2O_2 has been reported to effect a number of transformations of this general type, *e.g.*, alkenes to epoxides.[2] We recently reported[3] that the cobalt thiolate complex $(en)_2CoSCH_2CH_2NH_2^{2+}$ (here $CoSR^{2+}$) is oxidized by this combination to the sulfenato complex, then to the sulfinato by a mechanism in which the coordinated sulfur nucleophilically attacks the 1:1 peroxide–rhenium adduct.[4] The reactions and the first transition state can be diagrammed as[3]

$$\mathrm{CoSR}^{2+} \xrightarrow{H_2O_2/MTO} \mathrm{CoS(O)R}^{2+} \xrightarrow{H_2O_2/MTO} \mathrm{CoS(O)_2R}^{2+} \qquad (3)$$



The present study was undertaken to probe additional features of the catalytic capabilities of the CH_3ReO_3/H_2O_2 system, and to define the conditions where catalytic reactions of hydrogen peroxide can be utilized. We also sought to learn whether the mechanism deduced for $CoSR^{2+}$ applies more generally. Toward this end we chose to study aqueous bromide ions because they are chemically very different from $CoSR^{2+}$ and react at a nearly negligible rate with hydrogen peroxide in the absence of a catalyst.

We also anticipated that an intermediate would be involved in the catalytic reaction, quite possibly hypobromite ions, by analogy to the oxygen atom transfer process found for the $CoSR^{2+}$ system. If so, then it may be possible to detect HOBr by competing reactions. As it turned out, when hydrogen peroxide was in excess, one could record not only the catalytic formation of bromine but also the catalytic disproportionation of hydrogen peroxide. This was evidenced by the copious evolution of dioxygen. Disproportionation clearly occurs as a feature of the bromide mechanism since, without Br^-, oxygen was not evolved in solutions of hydrogen peroxide and CH_3ReO_3.

The system of CH_3ReO_3–H_2O_2 and the active catalysts formed in it resemble vanadium bromoperoxidase. This enzyme catalyzes the bromide–hydrogen peroxide reaction so as to brominate selected substrates and liberates oxygen as a consequence of the bromide-assisted disproportionation of hydrogen peroxide under appropriate conditions.[5-8] To explore this relation we examined the effect of the combination CH_3ReO_3–H_2O_2–Br^- on 2-chlo-

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rodimedone (5,5-dimethyl-2-chlorocyclohexa-1,3-dione), commonly used to calibrate the activity of bromoperoxidases.

Experimental Section

Materials. Methylrhenium trioxide was prepared from the reaction of dirhenium heptoxide with tetramethyltin[9] in the presence of perfluoroglutaric anhydride.[10] The product was purified first by sublimation, then by recrystallization from dichloromethane/hexane, and finally by another sublimation. Its purity was checked by IR, ^{1}H NMR, and UV–vis; the values found matched exactly those reported previously.[3,10-12]

The other compounds were reagent grade materials, used without purification: sodium bromide, hydrogen peroxide (30%), sodium perchlorate, and perchloric acid. The solutions were made up in high-purity water, obtained by passing laboratory distilled water through a Millipore-Q water purification system.

Kinetics. The principal method used was UV–visible spectrophotometry, since Br_2 buildup could be monitored easily at 452 nm, where the other species (and intermediates) are essentially transparent. This wavelength is an isosbestic point for Br_2 and Br_3^- (ϵ 108 L mol^{-1} cm^{-1}), making it convenient to derive the rate of concentration change from the rate of absorbance change without need to allow for a molar absorptivity that varied as a result of a shift in the position of equilibrium in the reaction $Br_2 + Br^- = Br_3^-$ over the range of concentrations used and as the reaction progressed. The reactions were carried out in quartz cuvettes of 1, 2, or 5 cm optical path, thermostated at 25.0 °C. In general air was not excluded from the reactions, since it was shown to have no effect. The reagent added last was either CH_3ReO_3 or H_2O_2. It proves less desirable, other than for special tests, to incubate these two before adding bromide ions, since the two peroxide–MTO compounds will then form prior to reaction. These compunds are adducts of H_2O_2 and CH_3ReO_3 in the ratios 1:1 (A, [$CH_3Re(O)_2(\eta^2\text{-}O_2)(H_2O)$]) and 2:1 (B, [$CH_3ReO(\eta^2\text{-}O_2)_2(H_2O)$]), which have been shown[13] to contain a strongly-coordinated water molecule. Indeed, A and B play important roles, but the kinetic data were more easily dealt with by avoiding the CH_3ReO_3-H_2O_2 interaction[3] prior to the initiation of the main reaction.

It was essential to determine the rate over a wide range of concentrations, to bring out each of the terms in a complicated rate law. In some situations, the rate of product buildup followed first-order kinetics: $Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)\exp(-k_\psi t)$. The determinations of k_ψ were repeated at different concentrations of each of the components within the range where first-order kinetics applied. In even more cases, however, the kinetic pattern was more complex. Typical of catalytic reactions, many of the determinations at low and intermediate [Br$^-$] started with a nearly zeroth-order dependence at the beginning, changing gradually to nearly first-order toward the end. The kinetic data for such situations are described by the Michaelis–Menten equation. Its integration yields a transcendental equation which has no closed-form solution for [Br_2] as a function of time. Two methods were used in these cases. In one, the initial rates, $v_i = (d[Br_2]/dt)_i$, were evaluated from the rates of absorbance change in the initial stages (3–10%) of the reaction. This family of rates, over a range of concentration variables, was then used to define the functional dependence of v_i on [Br$^-$], [H_2O_2], and [CH_3ReO_3].

A second method was also used, more as an occasional double-check at various of the concentration limits than a primary procedure. In this method, a nonlinear solution of the differential equations in the rate law was carried out, based on *all* of the chemical reactions believed to be involved. This solution was implemented with the program KINSIM,[14] which was used to calculate concentration–time profiles for many of the sets of starting concentrations used. The match between simulations and experiment was taken to infer the correctness of the kinetic model.

Oxygen evolution, signaling the catalytic decomposition of hydrogen peroxide, occurred in solutions containing CH_3ReO_3, H_2O_2, and Br$^-$ only when hydrogen peroxide was in stoichiometric excess over bromide ions. Oxygen evolution, too, was catalytic with respect to the organometallic oxide; oxygen buildup was followed with the use of an oxygen electrode, as described earlier,[15] usually on solutions that were initially anaerobic. The kinetic data were treated by the method of initial rates, with $(d[O_2]/dt)_i$ being determined by mathematical extrapolation.

Equilibrium Measurements. The interaction between CH_3ReO_3 and H_2O_2 results in the formation of 1:1 and 1:2 complexes (labeled, as before, as A and B).[4] The adoption of ionic strength 2.00 M required new equilibrium measurements on the interaction between CH_3ReO_3 and hydrogen peroxide, which were made by recording absorbances in the range 360–420 nm over a suitable range of concentrations. These data were fitted to the equation[4]

$$\bar{\epsilon} = \frac{\epsilon_0 + \epsilon_A K_1[H_2O_2] + \epsilon_B K_1 K_2 [H_2O_2]^2}{1 + K_1[H_2O_2] + K_1 K_2 [H_2O_2]^2} \qquad (4)$$

Results

Equilibrium Constants. The equilibria characterized in our earlier work are represented by two chemical equations. They depict the formation of the two adducts **A** and **B**, which are the respective 1:1 and 2:1 adducts of hydrogen peroxide and CH_3ReO_3. These equations also show rate constant labels and are numbered in a different sequence for more ready reference later.

$$H_2O_2 + CH_3ReO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3Re(O)_2(\eta^2\text{-}O_2)(H_2O) \qquad (I)$$

$$H_2O_2 + CH_3Re(O)_2(O_2)(H_2O) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H_2O + CH_3Re(O)(\eta^2\text{-}O_2)_2(H_2O) \qquad (II)$$

The new spectrophotometric determinations of K_1 and K_2 were carried out with 1.00 M perchloric acid, 1.00 M sodium perchlorate, 1.00 mM CH_3ReO_3, and variable [H_2O_2], 0.0200–0.500 M. The ionic strength was 2.00 M, the temperature was 25.0 °C; the spectra were recorded at wavelengths of 360, 380, 400, and 420 nm. The respective values of ϵ_{MTO} are 22, 6.4, 2.1, and 1.1 L mol^{-1} cm^{-1}. A global fit of the data to eq 4 gave ϵ_A = 730 ± 210, 560 ± 180, 335 ± 125, and 170 ± 75 L mol^{-1} cm^{-1} and ϵ_B = 1135 ± 5, 946 ± 4, 629 ± 3, and 330 ± 3 L mol^{-1} cm^{-1} at these wavelengths. (The ϵ_A values are relatively imprecise owing to the low [A] throughout.) The equilibrium constants are K_1 = 12.5 ± 0.9 L mol^{-1} and K_2 = 108 ± 17 L mol^{-1}. The values are not so different from those reported[4] at μ = 0.100 M, K_1 = 7.7 L mol^{-1}, and K_2 = 145 L mol^{-1}.

Kinetics Overview. The spontaneous reaction of bromide ions with H_2O_2 (eq 5) is quite slow (eq 6, at 25.0 °C and ionic strength 0.40 M).[16] Under a few of the conditions used in the catalyzed reaction it was necessary to correct for the rate of the uncatalyzed process, v_u. The constants in eq 6 are such that only the acid-dependent term was significant in this study.

$$H_2O_2 + 2Br^- + 2H^+ = Br_2 + 2H_2O \qquad (5)$$

$$v_u = \{3.8 \times 10^{-7} + (2.3 \times 10^{-4})[H^+]\}[H_2O_2][Br^-] \qquad (6)$$

Since the system we are describing is fairly complicated, it is helpful first to consider a partial reaction scheme that fits much of the kinetic data. There are two chemical reactions that describe the kinetics under most of the conditions. They consist of the reversible formation of A as in eq I and the reaction between A and Br$^-$, eq III, the additional water molelcule omitted. Under many of the circumstances used in these studies, this pair of

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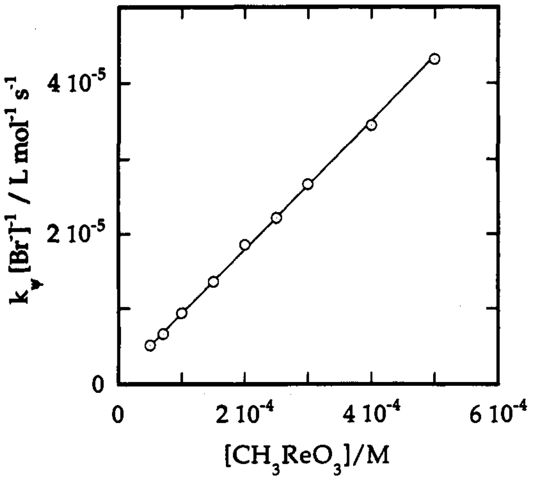

Figure 1. The first-order rate constants for bromine buildup vary linearly with the concentration of CH_3ReO_3. These data were taken at 1.00 M Br^- and 2.00 mM H_2O_2 at 25.0 °C, 1.00 M H^+, and 2.00 M ionic strength.

reactions constitutes a satisfactory description; we shall take up the exceptional cases later.

$$A + Br^- \xrightarrow{k_3} CH_3ReO_3 + OBr^- \qquad (III)$$

The rate equation was derived from these two reactions by means of the steady-state approximation for [A]. With the notation $[Re]_T = [CH_3ReO_3] + [A]$, the rate of the catalyzed reaction could be expressed as follows assuming that **B** does not react with Br^-:

$$v_c = \frac{d[Br_2]}{dt} = \frac{k_1k_3[Re]_T[Br^-][H_2O_2]}{k_{-1} + k_3[Br^-] + k_1[H_2O_2]} \qquad (7)$$

Kinetics at High [Br^-]. Inspection of eq 7 revealed that there are, at least in principle, concentrations of bromide ion high enough to reduce eq 7 to a simpler limiting form, with a rate that is independent of [Br^-]. The rate of the catalyzed reaction would then be given by

$$v_c = k_1[Re]_T[H_2O_2] \qquad (8)$$

Preliminary experiments indicated that bromide ion concentrations approaching 1 M would be needed to attain this limit (and thus the adoption of ionic strength 2.00 M). As it happens, these are the conditions where the uncatalyzed reaction cannot be neglected entirely. Thus the rate law expected is

$$v_{Br_2} = v_c + v_u = k_1[Re]_T[H_2O_2] + k_u[Br^-][H_2O_2][H^+] \qquad (9)$$

This is the equation for pseudo-first-order kinetics, with [H_2O_2] being the only time variable since both $[Re]_T$ and [Br^-] were constant in each of the experiments, but varied among them. Values of k_ψ were determined at $[H_2O_2]_0$ = 2.00 mM and [Br^-] = 1.00 M over a range of $[Re]_T$, 50–500 μM. They showed a linear dependence on $[Re]_T$, as predicted from eq 9. The data at 25.0 °C and μ = 2.00 M are depicted in Figure 1.

From the slope we obtain k_1 = 42.2 ± 0.4 L mol^{-1} s^{-1}. With this value, and that given above for K_1, k_{-1} = 3.4 s^{-1}. The intercept gives k_u = (5.2 ± 1.0) × 10^{-4} L^2 mol^{-2} s^{-1} at μ = 2.00 M, which is in fair agreement with 2.3 × 10^{-4} L^2 mol^{-2} s^{-1} from eq 6, which refers to μ = 0.4. A direct determination of k_u under these conditions by a different method (described later) gave k_u = (4.9 ± 0.3) × 10^{-4} L^2 mol^{-2} s^{-1} at μ = 2.00 M.

The value k_1 = 42.2 L mol^{-1} s^{-1} is modestly different from 77 L mol^{-1} s^{-1} at μ = 0.100 and 25.0 °C reported for $CoSR^{2+}$ in earlier studies.[4,5] To verify that the experiments for both systems were being correctly interpreted, we returned to the previously-studied complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$, repeating a comparable set of experiments at the higher ionic strength. This gave k_1 = 46.8 ± 4.5 L mol^{-1} s^{-1}. This is the same within the error as that for bromide ions, validating the assignment of the same (substrate-independent) reaction for both. A series of experiments was then carried out to evaluate k_1 at other hydrogen ion concentrations. This was done with the $CoSR^{2+}$ complex since the Br^- reaction becomes more complicated at lower [H^+], as described below. At 0.100 M H^+ and μ = 2.00 M, k_1 is 44.1 ± 1.0 L mol^{-1} s^{-1}, showing the absence of a pH effect between pH 0 and 1. Also, at μ = 1.00 M and 0.100 M H^+, an intermediate value was obtained: k_1 = 55.3 ± 1.5 L mol^{-1} s^{-1}.

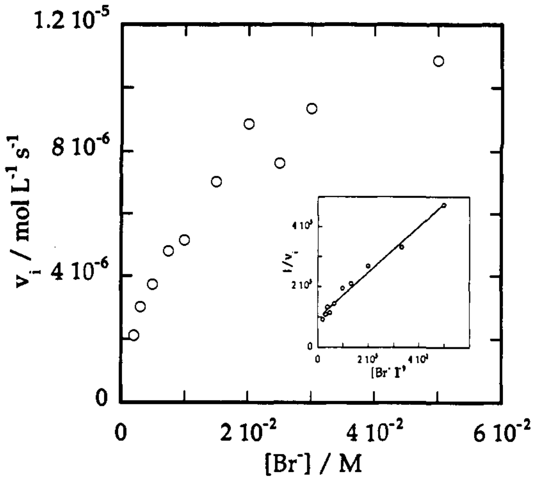

Figure 2. The initial rate of bromine formation in the MTO-catalyzed Br^-–H_2O_2 reaction, determined at constant concentrations of CH_3ReO_3 and H_2O_2, illustrating plateaus with the concentration of bromide ions, consistent with eq 7. Inset: the Lineweaver–Burk plot.

Kinetics with Variable [Br^-]. With 1.00 M $HClO_4$, and $NaClO_4$ to maintain μ = 2.00 M, a series of experiments was done with $[Re]_T$ = 0.100 mM and [H_2O_2] = 3.00 mM. In this series the concentration of bromide ions was varied from 2.00 to 50 mM. Under these conditions the buildup of Br_2 with time was not described by a simple kinetic equation, and so the method of initial rates was used. Values of $(v_{Br_2})_i$ over the first 5% of reaction were determined from the absorbance–time data. Figure 2 displays the plot of v_i against [Br^-], and illustrates the plateauing function of rate with concentration. The data are also shown in the Lineweaver–Burk formalism for reactions that follow the Michaelis–Menten equation by a plot of the inverse of the intial reaction rate against the inverse of the substrate concentration.

Kinetics with Variable [H_2O_2]. Kinetic measurements were also carried out with a constant [CH_3ReO_3] of 0.050 mM and a constant [Br^-] of 10.0 mM. The concentration of hydrogen peroxide was varied in the range of 50–200 mM. These data were also collected by the method of initial rates of Br_2 buildup, not only because the data did not follow any integrated equation, but also because oxygen evolution set in during the reaction. Bubble formation occurred late enough that it did not interfere with the measurement of the initial rate of bromine formation. Figure 3 displays the dependence of v_i on [H_2O_2].

Global Fit of the Rate of Br_2 Buildup. All the sets of kinetic data described to this point were subject to a single data fitting procedure, to demonstrate that eq 7 does, in fact, represent the variation of the reaction rate, and to provide the most reliable value of the rate constant k_3. To carry out this calculation, we used the nonlinear least-squares program GraFit, which allowed the simultaneous incorporation of several x-variables, there being three in this case. The 27 data points fit well, and gave k_3 = (3.34 ± 0.09) × 10^2 L mol^{-1} s^{-1}.

To display the quality of the fit, Figure 4 depicts the observed versus the calculated values of v_i. The three different sets of data

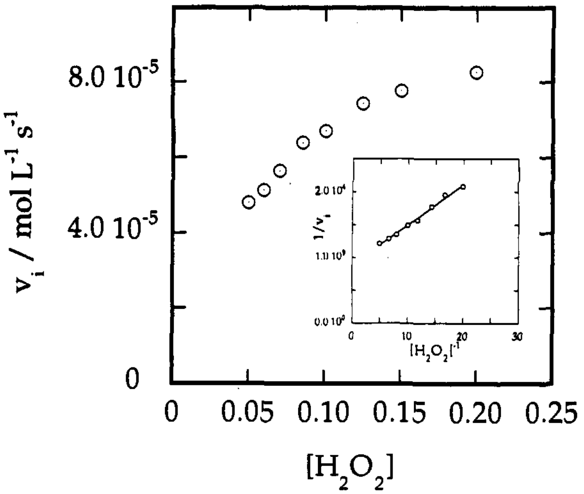

Figure 3. The variation of the initial reaction rate with hydrogen peroxide concentrations, determined at constant concentrations of CH_3ReO_3 (50 μM) and Br^- (10.0 mM). The plateauing function is consistent with the form given in eq 7. Inset: the Lineweaver–Burk plot.

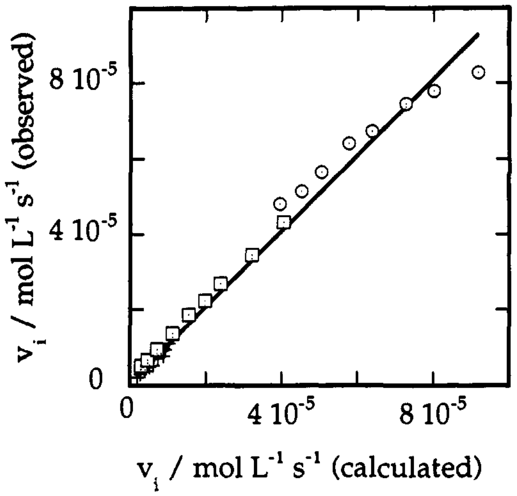

Figure 4. The initial rates of bromine formation from the three different variations presented in Figures 1–3 plotted against those calculated from a least-squares global fit of all the data to eq 7. The symbols refer to the variation of CH_3ReO_3 (+), Br^- (□), and H_2O_2 (○).

are shown with different symbols, to show that, individually, the agreement is quite satisfactory. The greatest deviations are for the set with the circled points, these being the experiments at high [H_2O_2] where O_2 evolution may interfere and where, as yet, no allowance has been made for the possible reactions involving **B**.

Catalyzed Disproportionation of Hydrogen Peroxide. Oxygen evolution was observed in experiments with CH_3ReO_3 in which hydrogen peroxide was in excess over bromide ions. Oxygen was produced much more slowly than bromine at the start, but its rate rose after the steady level of [Br_2] had been formed. No oxygen was evolved when either CH_3ReO_3 or bromide was absent. The ternary mixture of Br^-, H_2O_2 (excess), and CH_3ReO_3 evolved much more oxygen than would correspond to the initial concentration of bromide ions.

Oxygen was also evolved when hydrogen peroxide was added to a solution of bromine. As O_2 was released, the concentration of Br_2 fell to a low level. These phenomena really reflect the same happening, since O_2 was evolved in both instances from the independently-known[17] reaction V of Br^- with HOBr (which in both instances resulted from the facile hydrolysis of bromine,[18] reaction IV):

$$HOBr + Br^- + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} Br_2 + H_2O \qquad \text{(IV)}$$

$$HOBr + H_2O_2 \xrightarrow{k_5} O_2 + Br^- + H_3O^+ \qquad \text{(V)}$$

The value of k_5 given in the literature was determined under somewhat different conditions and by a different technique; the reported value[17] is 5.8×10^4 L mol^{-1} s^{-1}. This rate constant was redetermined under our conditions by monitoring the initial rate of [Br_2] decrease. With the steady-state approximation for [HOBr], the rate is given by

$$-\frac{d[Br_2]}{dt} = \frac{k_5 k_{-4}}{k_4} \frac{[Br_2][H_2O_2]}{[Br^-][H^+]} \qquad (10)$$

These experiments had 10.0 mM Br^-, 100 mM H_2O_2, and 1.00, 1.50, 2.00, and 2.50 mM Br_2 at pH 0 and μ = 2.00 M. Given the rate constants for reaction IV,[18] this treatment yields $k_5 = (1.82 \pm 0.09) \times 10^4$ L mol^{-1} s^{-1}. Other experiments were done to show that neither **A** nor **B** reacts with H_2O_2.

In all the experiments described, the rates at which HOBr was formed and consumed were equal, by virtue of the steady-state requirements. This was probed further in the following experiments. The initial rate of bromine formation was determined in a series of such experiments with varying [H^+] at μ = 2.00 M. The other concentrations were the same in each: 50 μM CH_3ReO_3, 10.0 mM Br^-, and 100 mM H_2O_2. The rate of Br_2 production was less at lower [H^+], values of v_i / 10^{-5} mol L^{-1} s^{-1} being 6.70 (1.00 M H^+), 5.46 (0.10 M), and 2.97 (0.020 M). This trend with [H^+] can be explained by noting that $[HOBr]_{ss}$ was higher at lower [H^+], thus increasing the rate of formation of oxygen *after the induction period had passed*. Since the kinetics requires that the sum of the rates of oxygen and bromine formation be a constant under these (and most other) conditions, bromine formation was clearly disfavored as a consequence. By the same token, however, the *initial* rate of oxygen evolution should have risen at lower [H^+], which it did.

Measurements of d[O_2]/dt after the point at which [Br_2] reached its final level were carried out under these conditions: 3.0 μM CH_3ReO_3, 1.00 mM Br^-, and 50.0 mM H_2O_2 at [H^+] = 1.00, 0.100, and 0.0100 M. The rate was nearly invariant at 2.1×10^{-7} mol L^{-1} s^{-1}, independent of [H^+]. This amounts to 62% of the rate at which HOBr is produced. Thus a substantial portion of the intermediate was *eventually* diverted toward oxygen under these conditions.

The formation of Br_2 was also monitored in these three experiments, two of which, at [H^+] = 1.00 and 0.100 M, are depicted in Figure 5. The reaction at pH 0 produced 44 μM Br_2 at the end, about 9% of theoretical. The same at pH 1 produced only 1% of the theoretical quantity, and none was found at pH 2.

Another experiment used different hydrogen peroxide concentrations (50 and 100 mM), again with 3 μM CH_3ReO_3 and 1.00 mM Br^- at 1.00 M H^+. More Br_2 was formed at the lower peroxide concentration, consistent with the competition between reactions IV and V.

These reactions provided a basis for the determination of k_u at pH 0 and ionic strength 2.00 M, with these initial concentrations: 1.00 mM Br^-, 21.4 mM Br_2, and 154 mM H_2O_2. The bromine level fell with time until its equilibrium value was obtained. Since $[Br_2]_{eq}$ follows from the steady-state condition for [HOBr], it can be expressed by eq 11:

$$k_u[H_2O_2][Br^-] = k_5[H_2O_2]\left\{\frac{k_{-4}[Br_2]}{k_4[H^+]^2[Br^-]}\right\} \qquad (11)$$

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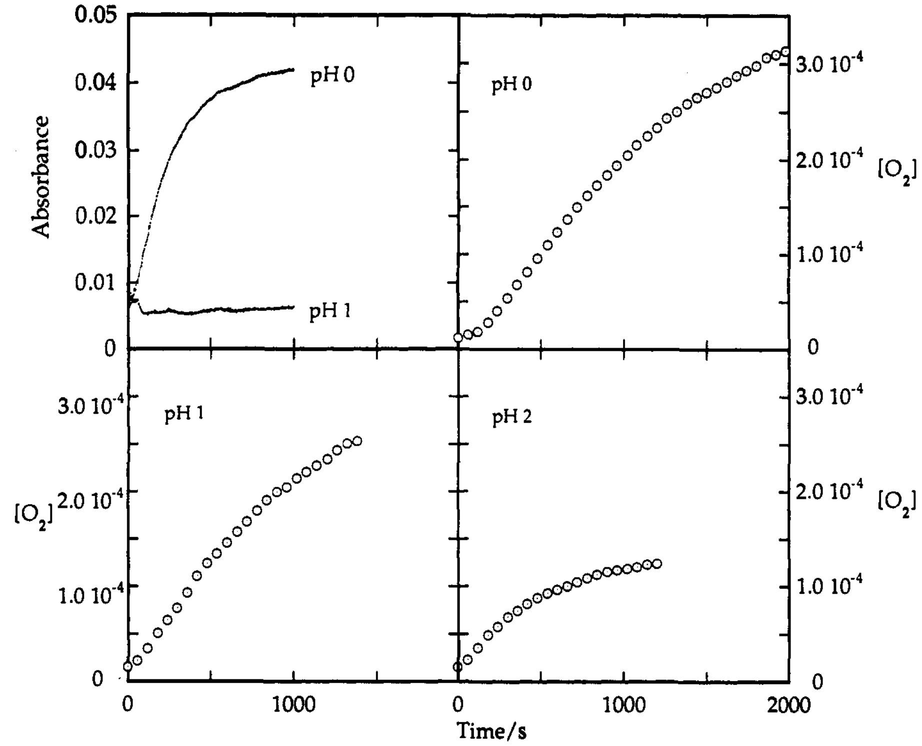


Figure 5. Different measurements on the same experiment are shown. The initial concentrations were 3.0 μM CH_3ReO_3, 1.00 mM Br^-, and 50.0 mM H_2O_2. The absorbance of bromine rises promptly. Although O_2 evolution precludes accurate absorbance readings at longer times, the final level of $[Br_2]$ at pH 0 is only 9% of $[Br^-]_0/2$ and <1% at pH 1. Oxygen evolution is characterized by an induction period, which is most prominent at pH 0, following which $[O_2]$ rises more rapidly to concentrations much greater than those of bromine.

The measurement of $[Br_2]$ provided one value, and $[Br^-]$ followed from the mass balance. The value of $[H_2O_2]$ canceled, which is fortunate since its disproportionation began to occur over this time. With $k_4 = 1.1 \times 10^2\ s^{-1}$, $k_{-4} = 2.0 \times 10^{10}\ L^2\ mol^{-2}\ s^{-1}$, and $k_5 = 1.82 \times 10^4\ L\ mol^{-1}\ s^{-1}$, we obtained $k_u = (4.9 \pm 0.3) \times 10^{-4}\ L\ mol^{-1}\ s^{-1}$ at $\mu = 2.00$ M and 25.0 °C.

The Kinetic Role of B. Since **B**, like **A**, contains η^2-peroxo ligands, it is reasonable to seek evidence as to whether it, too, reacts with bromide ions as in reaction VI.

$$\mathbf{B} + \mathrm{Br}^- \xrightarrow{k_6} \mathbf{A} + \mathrm{OBr}^- \qquad \text{(VI)}$$

The first evidence for the involvement of **B** was an experiment at $\mu = 2.00$ M and 1.00 M H^+ containing 1.00 mM Br^- and 3.0 μM CH_3ReO_3. Following the injection of 50 mM hydrogen peroxide, after 1200 s, 0.044 mM Br_2 and *ca.* 0.25 mM O_2 were found. These values were much higher than those calculated on the basis of all the other reactions cited to this point, save VI, which was therefore introduced to explain this. Over a longer time, a rise in this $[O_2]$ plateau was found without a measureable change in $[Br_2]$.

Two stopped-flow experiments with these concentrations were carried out: 100 mM Br^-, 0.100 mM CH_3ReO_3, and 384 mM H_2O_2. They differed only as to the order of mixing in the stopped-flow instrument. In one, a solution of the first two was mixed with the peroxide; in the other, the second two were first incubated and then mixed with the bromide ions. Both kinetic traces for the buildup of bromine were the same. If **B** did not react with Br^-, then there would have been an induction period in the buildup of bromine, during which the rate would be governed by the rate at which **B** reverts to **A** or $k_{-2} \sim 0.020$–$0.04\ s^{-1}$. On the other hand, if **B** shows a direct reaction with bromide ions, no delay would be evident. The results are given in Figure 6, which compares these experiments to the calculations for each case—with and without prior incubation, and with and without allowance for reaction VI. Very clearly, **B** does react with Br^-.

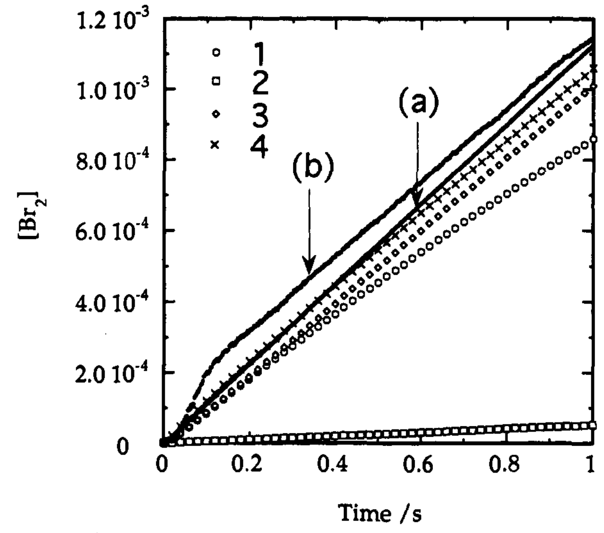


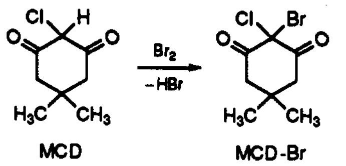
Figure 6. Kinetic data from two stopped-flow experiments, with $[Br^-]_0 = 100$ mM, $[Re]_T = 0.100$ mM, and $[H_2O_2] = 384$ mM, with (a) and without (b) prior incubation of CH_3ReO_3 and H_2O_2, as explained more fully in the text. These two essentially coincide. Also shown are four lines depicting the theoretical bromine buildup curves, as follows: (1) without incubation, $k_6 = 0$; (2) with incubation, $k_6 = 0$; (3) without incubation, $k_6 = 90\ L\ mol^{-1}\ s^{-1}$; and (4) with incubation $k_6 = 90\ L\ mol^{-1}\ s^{-1}$. This established the requirement for reaction VI.

The direct determination of k_6 was carried out in experiments with 10, 15, and 20 mM Br^-, 0.099 mM CH_3ReO_3, and 384 mM H_2O_2. The high peroxide concentration made VI the only reaction to determine the bromine buildup in the early stages. The absorbance at 358 nm contained contributions only from Br_2/Br_3^- ($\epsilon \sim 100\ L\ mol^{-1}\ cm^{-1}$) and **B** ($\epsilon$ 1140 $L\ mol^{-1}\ cm^{-1}$). Because of this, the absorbance initially decreased with time, and the initial rate of Br_2 buildup was calculated as (d Abs/dt)/(100–1140). These absorbance values, although not terribly precise owing to the very small absorbance change and the subsequent reactions, gave $k_6 = 89 \pm 14$ L mol^{-1} s^{-1}, if we assumed that only the one reaction contributed, which is not exactly correct in that it assigns all the offsetting changes in absorbance to a single reaction involving **B**. This rate constant was therefore determined with better precision using 2-chlorodimedone as described below.

In these experiments 97% of the total rhenium was initially present as **B** with minor amounts of **A**, 2%, and of uncomplexed CH_3ReO_3, <1%. Clearly, then, the initially-formed bromine arose nearly exclusively from the reaction of **B**. But let us inquire what happened once this small quantity of **B** was largely exhausted, being converted to **A** in reaction VI. More bromine was then formed following this point, as evidenced by the absorbance–time profile at 358 nm reaching a minimum and then beginning to rise. At this point, **A** redistributed itself between these alternatives: reaction with H_2O_2 to form **B** again, or reaction with Br^- to produce HOBr. The first has a rate constant given by $k_2[H_2O_2]$ or *ca.* 1 s^{-1}, and the second at 20 mM Br^- is given by $k_3[Br]$ or *ca.* 13 s^{-1}. Most of the subsequent buildup of bromine, past the fast initial stage in which **B** was consumed by Br^-, occurred by way of **A** and Br^-. The concentrations of both **A** and CH_3ReO_3 were sustained at steady-state levels that are much *higher* than those governed by the CH_3ReO_3–**A**–**B** equilibria I and II.

It is for this reason, along with its inherently greater reactivity toward bromide ions, that **A** carried most of the reaction. The notable point is this: Although **B** is nearly as reactive as **A** in transferring oxygen to bromide, much of the **B** was soon depleted, not to be readily replenished since $k_2[H_2O_2]$ was small relative to $k_3[Br^-]$. Thus most of the reaction beyond this point occurred by way of **A**, which was originally distinctly in the minority, being 2.3% of $[Re]_T$ at the outset. This compares to $[A]_{ss} \cong 45\%$ during the active catalytic cycle for bromine production. Once the point at which the higher steady-state concentration of **A** was reached, the calculated *steady-state* percentages at 20.0 mM Br^- are these: 25% CH_3ReO_3, 45% **A**, and 29% **B**.

2-Chlorodimedone as a Kinetic Probe for the Buildup of Bromine. 5,5-Dimethyl-2-chlorocyclohexa-1,3-dione (2-chlorodimedone or MCD) is known to react readily with a variety of brominating species such as bromine or hypobromous acid:



(12)

The large difference in extinction coefficients between MCD and MCD-Br allowed us to use MCD as a kinetic probe for bromine formation.[7] At pH 0 and $\mu = 2.00$ M the difference in extinction coefficients at 270 nm is 12 800 L mol^{-1} cm^{-1}, which is different from the reported value[6] because of the different pH. Figure 7 represents a typical kinetic trace for the CH_3ReO_3–H_2O_2–Br^-–MCD system with an excess of Br^-. The consumption of MCD may be seen in the first part of the kinetic trace (negative slope). The second part (positive slope) shows formation of Br_2–Br_3^-. The specific activity of CH_3ReO_3 in this reaction is 6 μM MCD min^{-1} mg^{-1} of MTO (pH 0, $\mu = 2.00$ M, 1 mM H_2O_2, 10 mM Br^-, 94 μM MCD), on the scale on which bromoperoxidase activity is usually expressed.

To determine the rate over a wide range of concentrations, a set of experiments with low concentrations of Br^- and a high concentration of H_2O_2 was carried out using MCD. The conditions were pH 0, $\mu = 2.00$ M, [Re] = 100 μM, $[H_2O_2]$ = 10 mM, $[Br^-]$ = 70–250 μM, and [MCD] = 100 μM. No oxygen bubbles were observed during the consumption of MCD. The six data points obtained were used for fitting the data as described later.

The unique properties of MCD allowed the design of a new set of experiments to determine k_6 directly with much better precision. Under these conditions—pH 0, $\mu = 2.00$ M, [Re] = 0.5–1 mM, $[H_2O_2]$ = 100 mM, $[Br^-]$ = 10 mM and [MCD] = 30 μM—the reaction rate law should obey a pseudo-first-order rate law. The rate is $v = [Br^-](k_3[A] + k_6[B])$ with a pseudo-first-order rate constant given by $k_\psi = k_3[A] + k_6[B]$ because the reactions of **A** and **B** with Br^- do not affect the equilibrium under these conditions. Because of the equilibrium between **A** and **B**, it was possible to express the concentration of **A** in terms of concentration of **B**: $[A] = [B]K_2^{-1}[H_2O_2]^{-1}$ so that $k_\psi = [B](k_3 K_2^{-1}[H_2O_2]^{-1} + k_6)$. The data obtained when the reaction was monitored at 290 nm followed accurate first-order kinetic traces. The pseudo-first-order rate constants were plotted against the concentration of **B**, and after correction for the reaction of **A**, the slope of the line gave $k_6 = 190 \pm 17$ L mol^{-1} s^{-1} .

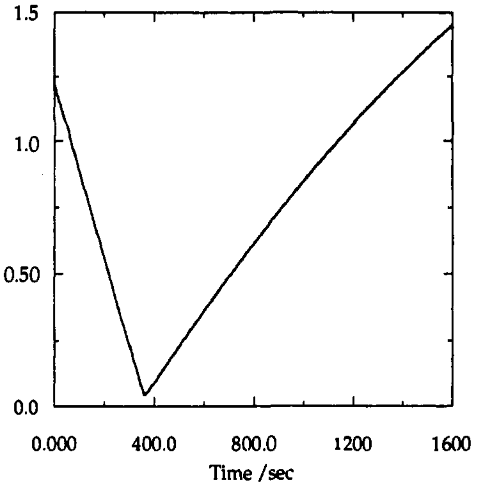
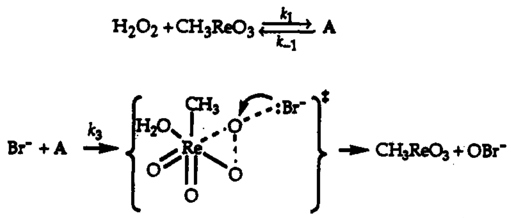


Figure 7. The kinetic trace for the MTO–H_2O_2–Br^-–MCD system with an excess of Br^-, with [Re] = 10 μM, $[H_2O_2]$ = 1 mM, $[Br^-]$ = 10 mM, and [MCD] = 94 μM. The left part of the trace (before 370 s) shows the consumption of MCD. After ca. 370 s, no MCD was left in the solution and the formation of Br_2–Br_3^- began.

Scheme 1



Discussion

The Rate-Controlling Step. Scheme 1 shows the two steps that lead ultimately to the products by way of BrO^-/HOBr. As far as the kinetics goes, however, the rate constant for bromine formation does not depend on the much faster reactions of HOBr.

The rate equation that results from Scheme 1 is given in eq 7. An abbreviated derivation is as follows. Since Br_2 is formed in a subsequent and very rapid reaction, its rate of Br_2 formation is the rate of the k_3 step. Thus,

$$\frac{d[Br_2]}{dt} = k_3[A][Br^-] \qquad (13)$$

The steady-state approximation for [A] is the solution of the equation

$$\frac{d[A]}{dt} = k_1[CH_3ReO_3][H_2O_2] - k_{-1}[A][Br^-] = 0 \quad (14)$$

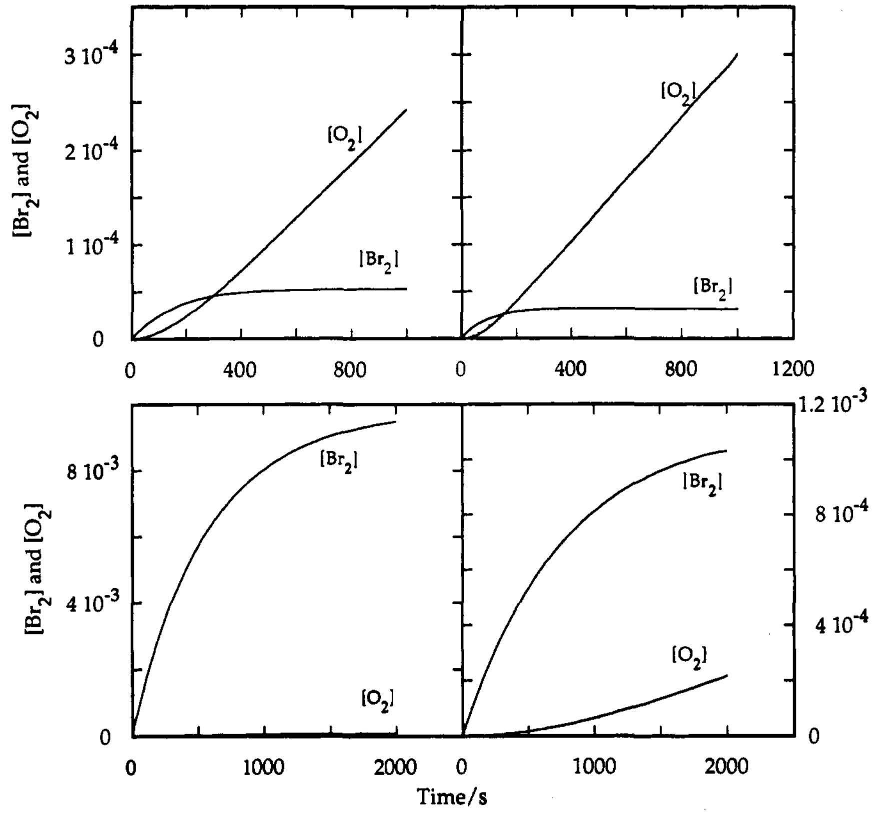


Figure 8. The calculated buildup of bromine and oxygen, as obtained by application of the simulation program KINSIM.[14] The upper part had 1.00 mM Br^-, 3.0 μM CH_3ReO_3, 1.00 M H^+, and ionic strength 2.00 M; $[H_2O_2]$ was 50 mM (left) and 100 mM (right). The lower yield of bromine at higher peroxide is noteworthy. The lower part had 50 mM CH_3ReO_3, 1.00 M H^+, and ionic strength 2.00 M at $[H_2O_2]$ = 10.0 mM, $[Br^-]$ = 50.0 mM (left), and $[H_2O_2]$ = $[Br^-]$ = 3.00 mM (right).

Solving for [A], and incorporating the mass balance expression $[Re]_T = [CH_3ReO_3] + [A]$, gives the following expression for $[A]_{ss}$, which combines with eq 13 to yield eq 7.

$$[A]_{SS} = \frac{k_1[Re]_T[H_2O_2]}{k_{-1} + k_3[Br^-] + k_1[H_2O_2]} \qquad (15)$$

Each of the three concentrations was varied over a wide range to establish the individual reaction orders. This was essential, since a system as complicated as this has several limiting forms in the different concentration ranges. The apparent reaction orders with respect to both $[H_2O_2]$ and $[Br^-]$ are fractional at the midpoint of the variation, tending from a first-order dependence at a low concentration of each to a zeroth-order dependence as the rate plateaus at a higher concentration. In this system the rate begins to plateau above *ca.* 0.50 M Br^- and above *ca.* 0.15 M H_2O_2. This is what is represented in Figures 2, 3, and 8.

The rate-controlling step is an S_N2 displacement. The nucleophile Br^- attacks a peroxide oxygen of A, since Br_2 is formed in a subsequent and very rapid reaction, displacing CH_3ReO_3. The rate constant for this step is $k_3 = 3.4 \times 10^2$ L mol^{-1} s^{-1}. By way of comparison, the following rate constants (analogous to k_3) were determined[3] for the complexes $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ and $(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$: 4.2×10^5 and 2.7×10^2 L mol^{-1} s^{-1} at 25.0 °C. This comparison indicates that toward A bromide ions and the cationic (sulfenato)cobalt complex are nucleophiles of comparable reactivity, but that both are much less nucleophilic than the (thiolato)cobalt complex. There is, of course, a strong resemblance between the nucleophilic displacement proposed for the reaction of A and bromide ions and that previously established for the reaction of hydrogen peroxide and bromide ions, eq 5. It is just that A is so much more reactive toward bromide ions than hydrogen peroxide is.[19] The electrophilic activation realized by coordination of peroxide to the rhenium compound is $>10^6$, given as the ratio of k_3 to k_u at 1 M H^+.

The Fate of the OBr⁻/HOBr Intermediate. An induction period preceding the timed formation of bromine was not evident, implying that the intermediate reacts very rapidly. This is consistent with the known chemistry of hypobromous acid in acidic solutions containing bromide ions. A very fast reaction occurs, eq IV, characterized by the rate constant $k_4 = 2 \times 10^{10}$ L^2 mol^{-2} s^{-1}.[18]

$$Br^- + HOBr + H^+ \xrightarrow{k_4} Br_2 + H_2O \qquad (IV)$$

This suggested that HOBr is the intermediate leading to bromine, but was not direct proof of it. When the MTO-catalyzed oxidation of bromide ions was carried out with excess hydrogen peroxide, oxygen was evolved. This means that HOBr is being diverted from its normal course, which arises from an independently-known[17] reaction:

$$HOBr + H_2O_2 \xrightarrow{k_5} O_2 + Br^- + H_3O^+ \qquad (V)$$

Proposing V as the only reaction leading to O_2 is consistent with the necessary criteria: (a) bromine is favored at very high $[H^+]$ and oxygen at lower $[H^+]$, in that reaction IV shows a direct dependence on $[H^+]$, whereas V is acid independent; (b) oxygen is favored at high $[H_2O_2]$, bromine at high $[Br^-]$; (c) the oxygen-forming reaction regenerates the bromide ions used in reaction III to form HOBr, and oxygen evolution could continue

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[18] Eigen, M. ; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.

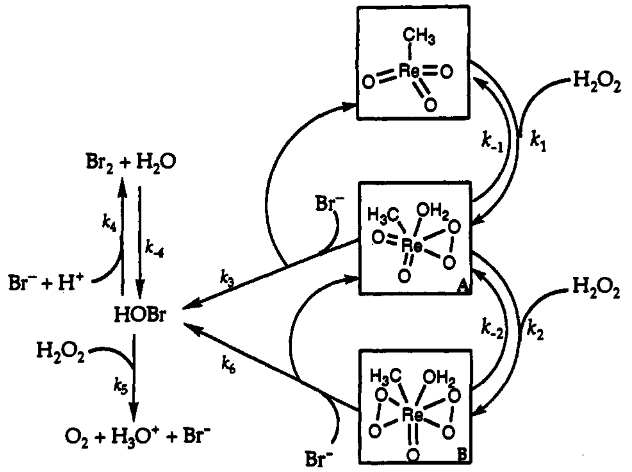
[19] For electrophilic and nucleophilic mechanisms of peroxide reactions, see: Curci, R.; Edwards, J. O. In *Catalytic Reactions with Hydrogen Peroxide as Oxidant*; Strukul, G., Ed.; Kluwer Academic Press: Dordrecht, 1993; pp 53–57.

Table 1. Summary of Reactions and Rate Constants[a]

	reaction	k_f/L mol^{-1} s^{-1}	k_r/s^{-1}	ref
I.	$CH_3ReO_3 + H_2O_2 \rightleftarrows A + H_2O$	42.2	3.4	this work
II.	$A + H_2O_2 \rightleftarrows B + H_2O$	5.2	0.04	4
III.	$A + Br^- \rightarrow CH_3ReO_3 + BrO^-$	3.5×10^2		this work
VI.	$B + Br^- \rightarrow A + BrO^-$	1.9×10^2		this work
IV.	$HOBr + H^+ + Br^- \rightleftarrows Br_2 + H_2O$	2×10^{10} [b]	1.1×10^2	17
V.	$HOBr + H_2O_2 \rightarrow O_2 + Br^- + H^+ + H_2O$	1.8×10^4		this work[c]

[a] In aqueous solution at 25 °C and μ = 2.00 M. [b] Units are L^2 mol^{-2} s^{-1}. [c] Compared to $k_6 = 5.8 \times 10^4$ L mol^{-1} s^{-1} under different conditions (ref 18).

Scheme 2



until the peroxide was exhausted, since the process is catalytic in bromide also; and (d) oxygen and bromine are formed competitively—the rate-controlling process remains the same, only the reactivity ratio changes in a way that depends on the concentrations.

Nonetheless, reaction V seems at first not to be an acceptable explanation for the oxygen evolution process, in that its rate appears to be way too low for it to be competitive with IV under any of the circumstances. We shall now compare the relative rates of V and IV, and ask under which set of circumstances they are comparable, as when $v_{IV} = v_V$, or $k_4[Br^-][H^+] = k_5[H_2O_2]$. Even at typically lower $[Br^-]$ ($\approx 10^{-4}$ M) and lower $[H^+]$ ($\approx 10^{-2}$ M), the establishment of this condition would require that $[H_2O_2]$ be well above 1 M. Clearly, reaction IV is so strongly favored over reaction V that the latter seems inadequate to explain the present observations in a numerical sense, despite its conceptual fit.

Small though the reactivity ratio is, it must be considered in light of the reverse of reaction IV, which is very rapid, with $k_{-4} = 1.1 \times 10^2$ s^{-1}. In effect reaction IV is instantly equilibrated on the time scale in which Br_2 and O_2 are formed. The hydrolysis of bromine regenerates HOBr repetitively; each time this happens a very small proportion of it is converted irreversibly to oxygen, in accord with the reactivity ratio. After a great many cycles through the scheme, *all* of the peroxide is eventually converted to oxygen. Oxygen formation, according to this scheme, is thus favored in principle and in practice by high peroxide and low bromine concentrations.

The Role of the 2:1 Adduct B. The kinetic equations have been formulated with A as the (only) species that reacts with Br^-, but we have demonstrated that there are conditions where B was effective as well. This was most prevalent at high $[H_2O_2]$, when it and CH_3ReO_3 were mixed prior to the addition of bromide ions. The involvement of B in a reaction like that of A is not implausible, in that two rhenium complexes, both bearing η^2-peroxo ligands, should not differ intrinsically in their reactivity, other than by certain numerical differences.

The finding that B is somewhat less reactive than A (k_6 = 190 L mol^{-1} s^{-1} versus k_3 = 334 L mol^{-1} s^{-1}) is consistent with the nucleophilic attack of bromide ions on the η^2-peroxide ligands. The compound with two such peroxides is clearly less electrophilically activated, and a diminution of reactivity can thus be understood.

The reactions of A and their pseudo-first-order rate constants are the following: release of peroxide (k_{-1} = 3.4 s^{-1}), reaction with bromide ions ($k_3[Br^-] = (3.5 \times 10^2)[Br^-]$ s^{-1}), and addition of a second peroxide to produce **B** ($k_2[H_2O_2] = 5.2[H_2O_2]$ s^{-1}). From these values we can see that the formation of B is unimportant relative to the others, except at high $[H_2O_2]$ and at very high ratios of $[H_2O_2]$ to $[Br^-]$. Under those conditions, however, oxygen evolution becomes important.

The one set of conditions under which B will certainly enter the picture is when it is present at the outset. This is realized by incubation of CH_3ReO_3 and H_2O_2 prior to the introduction of Br^-. To avoid the complications arising from **B**, most of the time experiments were not done that way, and hydrogen peroxide was the last reagent added. When peroxide was added prior to Br^-, however, we found that **B** was consumed early in the reaction with an initial small burst of bromine. A subsequent and larger quantity of bromine was recorded, as if the mixing order had been the ordinary one. In these experiments, after most of the bromine had formed, oxygen was produced.

The rate constant for the reaction of **B** and Br^- was estimated from a set of experiments given earlier, with 0.5–1 mM CH_3ReO_3, 100 mM H_2O_2, and 10^{-5} M Br^- using MCD as a kinetic probe. The plot of k_ψ against [**B**] corrected for known reactions of A gave k_6 = 190 ± 17 L mol^{-1} s^{-1}.

A full derivation of the rate equation, including reactions I, II, III, and VI, gave this expression for the rate of bromine formation. It is the counterpart of eq 7, except that now the involvement of **B** is included. The solution, obtained by the steady-state procedure outlined previously, is

$$v_c = \frac{d[Br_2]}{dt} = \frac{k_1[MTO][Br^-][H_2O_2]\left\{k_3 + \dfrac{k_2k_6[H_2O_2]}{k_6[Br^-] + k_{-2}}\right\}}{k_{-1} + k_3[Br^-] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_6[Br^-] + k_{-2}}} \tag{16}$$

When all 36 data points were used to refine k_3 and k_6 simultaneously, consistent values were obtained: k_3 = 350 ± 10 L mol^{-1} s^{-1} and k_6 = 185 ± 12 L mol^{-1} s^{-1}. This agrees very well with the value k_6 = 190 ± 17 L mol^{-1} s^{-1} obtained from direct measurement with dimedone.

The Disappearance of Bromine. The bromine formed in this system, under the (usual) conditions of excess bromide ions, remained stable in the solution. The balance of events determined the final levels of Br_2 and O_2 as given by the competition between reactions IV and V. According to this, once we incorporated reaction I that preceded this and generated A, then the sequence of reactions I, III, and V amounted to a scheme for the disproportionation of hydrogen peroxide, jointly catalyzed by rhenium and bromide:

$$2H_2O_2 \xrightarrow{\text{cat. MTO, Br}^-} O_2 + 2H_2O \qquad (17)$$

KINSIM Modeling. The differential rate equations representing reactions I–VI were solved simultaneously by numerical integration with KINSIM, since neither $[Br_2]$ nor $[O_2]$ could be expressed in closed form. Over the different ranges of the concentrations, curves of rather different shapes were found. In every case they matched the experimental data. A sampling of them is given in Figure 8, which shows in the upper part the low yield of bromine, which became lower as $[H_2O_2]$ increased, owing to the onset of oxygen formation. The induction period in oxygen buildup is quite evident. The lower part shows simulations for experiments with higher ratios of bromine to peroxide. The Michaelis–Menten shape of the bromine buildup curves is evident. Most notable is that in this pair, unlike the other, bromine formation is dominant, and $[Br_2]$ rises to nearly its theoretical maximum, $[Br^-]_0/2$.

Conclusions. The optimal values of the rate constants for the various reactions that constitute the overall scheme have been summarized in Table 1. The catalysis of the oxidation of bromide ions by hydrogen peroxide is efficiently carried out by methylrhenium trioxide. Like other substrates whose catalytic oxidation is effected by the CH_3ReO_3/H_2O_2 system, the immediate fate of the bromide ions is to acquire a single oxygen atom, being converted to $BrO^-/HOBr$. The subsequent reactions of this intermediate yield bromine or oxygen, depending on the concentration conditions. If run under conditions where bromine is formed first, then it may largely be lost at the expense of the subsequent formation of oxygen. Scheme 2 diagrams all of the catalytic scheme.

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