

Reduction and Oxidation of Hydroperoxo Rhodium(III) Complexes by Halides and Hypobromous Acid

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Oxygen atom transfer from *trans*-L(H₂O)RhOOH²⁺ {L = [14]aneN₄ (L¹), *meso*-Me₆[14]aneN₄ (L²), and (NH₃)₄} to iodide takes place according to the rate law $-d[L(H_2O)RhOOH^{2+}]/dt = k_I[L(H_2O)RhOOH^{2+}][I^-][H^+]$. At 0.10 M ionic strength and 25 °C, the rate constant $k_I/M^{-2} s^{-1}$ has values of 8.8×10^3 [L = (NH₃)₄], 536 (L¹), and 530 (L²). The final products are LRh(H₂O)₂³⁺ and I₂/I₃⁻. The (NH₃)₄(H₂O)RhOOH²⁺/Br⁻ reaction also exhibits mixed third-order kinetics with $k_{Br} \approx 1.8 M^{-2} s^{-1}$ at high concentrations of acid (close to 1 M) and bromide (close to 0.1 M) and an ionic strength of 1.0 M. Under these conditions, Br₂/Br₃⁻ is produced in stoichiometric amounts. As the concentrations of acid and bromide decrease, the reaction begins to generate O₂ at the expense of Br₂, until the limit at which [H⁺] ≤ 0.10 M and [Br⁻] ≤ 0.010 M, when Br₂/Br₃⁻ is no longer observed and O₂ is produced quantitatively. At this limit, the loss of (NH₃)₄(H₂O)RhOOH²⁺ is about twice as fast as it is at the high [H⁺] and [Br⁻] extreme, and the stoichiometry is 2(NH₃)₄(H₂O)RhOOH²⁺ → 2(NH₃)₄(H₂O)RhOH²⁺ + O₂; i.e., the reaction has turned into the bromide-catalyzed disproportionation of coordinated hydroperoxide. In the proposed mechanism, the hydrolysis of the initially formed Br₂ produces HOBr, the active oxidant for the second equivalent of (NH₃)₄(H₂O)RhOOH²⁺. The rate constant k_{HOBr} for the HOBr/(NH₃)₄(H₂O)RhOOH²⁺ reaction is $2.9 \times 10^8 M^{-1} s^{-1}$.

Introduction

Coordination of H₂O₂ to high-valent transition metal centers results in electrophilic activation of the peroxide. Such an enhancement in reactivity explains the role played by peroxometal compounds in a number of biological oxidations, including those catalyzed by haloperoxidases^{1–3} and some reactions of commercial significance.^{4,5} In such compounds, the peroxide has a side-on geometry, and the metal is typically in its highest oxidation state, i.e., V(V), Cr(VI), Mo(VI), W(VI), Re(VII), etc.

Transition metal hydroperoxides LMOOH (L = ligand system) are also often involved as intermediates in the process of activation of dioxygen by transition metal complexes in chemical and biological systems. The detailed mechanisms by which LMOOH is formed may involve one-

electron reduction of superoxo precursors or a direct interaction of H₂O₂ with the metal complex. The –OOH group is coordinated in an end-on fashion to the metal, which is typically present in some intermediate oxidation state,⁶ i.e., Rh(III), Fe(III), Co(III), Cr(III), etc., although high oxidation state hydroperoxides are also known, e.g., Pt(IV).⁷ In some instances, an acid-induced peroxo–hydroperoxo transformation, accompanied by changes in reactivity, has been observed.^{8–11}

A number of studies of oxygen atom transfer from peroxometal complexes have been published. Much less has been done with the hydroperoxides, which are the less readily available of the two. Previously,^{12–14} we have shown that

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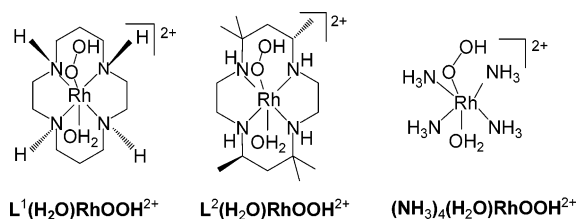
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some chromium and cobalt hydroperoxides, namely $(\text{H}_2\text{O})_5\text{CrOOH}^{2+}$, $([\text{14}] \text{aneN}_4)(\text{H}_2\text{O})\text{CoOOH}^{2+}$, and *meso*- $(\text{Me}_6[\text{14}] \text{aneN}_4)(\text{H}_2\text{O})\text{CoOOH}^{2+}$, react by oxygen atom transfer significantly faster than H_2O_2 does, but the reactivity in one-electron, Fenton-type processes was comparable for LMOOH and H_2O_2 .

We have now extended our studies of hydroperoxo chemistry to three rhodium complexes of the general formula *trans*- $\text{L}(\text{H}_2\text{O})\text{RhOOH}^{2+}$ $\{\text{L} = [\text{14}] \text{aneN}_4 (\text{L}^1), \text{meso-Me}_6[\text{14}] \text{aneN}_4 (\text{L}^2), \text{ and } (\text{NH}_3)_4\}$. These complexes are more stable than their chromium and cobalt analogues and permit a much greater variation of reaction conditions in kinetic and mechanistic studies. We were especially interested in establishing whether the acid catalysis, observed in our previous studies with chromium and cobalt complexes, was perhaps a general feature of O-atom transfer from the hydroperoxides. The substrates chosen, bromide and iodide ions, have been identified previously as good oxygen atom acceptors.

The structures of the complexes used in this work are shown here.



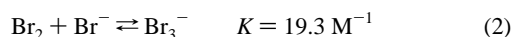
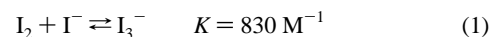
Experimental Section

Samples of $[\text{L}^1(\text{H}_2\text{O})\text{RhH}](\text{ClO}_4)_2$ and $[\text{L}^2(\text{H}_2\text{O})\text{RhH}](\text{CF}_3\text{SO}_3)_2$ were available from our previous work,^{15,16} and $[(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhH}](\text{SO}_4)_2$ was prepared according to a literature procedure. The purity of the hydrides was confirmed by UV spectroscopy, which will detect even minute amounts of the decomposition products, all of which absorb light much more intensely than the hydrides do at $\lambda < 250 \text{ nm}$.¹⁶ Perchloric acid, sodium perchlorate, bromine (all Fisher), sodium iodide, and sodium bromide (both Baker) were reagent grade or better and were used as received. Stock solutions (0.020–0.50 M) of iodide and bromide ions were prepared by dissolving weighed samples of the salts in air-free deionized water.

Slightly acidic stock solutions of $\text{L}(\text{H}_2\text{O})\text{RhOOH}^{2+}$ complexes were prepared from the parent hydride and O_2 as previously described.¹⁸ Concentrations of $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ were determined from the absorbance at 241 nm ($\epsilon = 4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁹ and those of L^1 and L^2 analogues by titration with $(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2^{2+}$, $\Delta\epsilon_{365} = 6200 \text{ M}^{-1} \text{ cm}^{-1}$. Solutions of $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ were prepared by quantitative reduction of the superoxo complex by $\text{Ru}(\text{NH}_3)_6^{2+}$, as described previously.¹³ Saturated ($\sim 0.1 \text{ M}$) solutions of bromine were prepared in 0.10 M HClO_4 . The concentration of bromine was determined, after dilution, from the absorbance at 452 nm ($\epsilon = 103 \text{ M}^{-1} \text{ cm}^{-1}$), an isosbestic point for $\text{Br}_2/\text{Br}_3^-$. Deionized

water was further purified by passage through a Millipore Milli-Q water purification system.

The kinetics of oxidation of iodide were studied by monitoring the growth of I_3^- at 351 nm ($\epsilon = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The $\text{L}(\text{H}_2\text{O})\text{RhOOH}^{2+}/\text{Br}^-$ reaction was monitored at either 240 nm (loss of hydroperoxide) or 266 nm (growth of Br_3^-). The halides were used in large excess (≥ 30 -fold) over the hydroperoxides to keep the ratios $[\text{X}_3^-]/[\text{X}_2]$ ($\text{X} = \text{Br}, \text{I}$),^{20,21} eqs 1–2, essentially constant during the course of each kinetic run.



The spectral and most of the kinetics measurements were carried out with a conventional UV–vis Shimadzu 3101 PC spectrophotometer. All kinetics measurements were performed at $25 \pm 0.2 \text{ }^\circ\text{C}$ in acidic aqueous solutions at a constant ionic strength maintained with sodium perchlorate. Kinetic analyses were performed by use of KaleidaGraph 3.09 PC software.

Most of the kinetics of the reaction between HOBr/Br_2 and $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ were studied by use of an Applied Photo-physics DX-17MV stopped-flow apparatus. In these experiments, solutions containing the desired amounts of Br_2 and NaBr at 2.0 M ionic strength (maintained with HClO_4 and NaClO_4) were mixed with solutions of $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ at 0.010 M ionic strength, and the disappearance of the hydroperoxide was monitored at 238 nm. The large difference in the electrolyte concentrations in the two solutions caused no visible distortions of the kinetic traces, which responded cleanly to the changes in concentrations of all the reagents. Moreover, the measured rate constants agreed well with those determined by conventional spectrophotometry at much lower concentrations of Br_2/HOBr . The stopped-flow measurements were performed in the following concentration ranges: $1.0 > [\text{H}^+] > 0.050 \text{ M}$, $6.0 > [\text{Br}^-] > 1.0 \text{ mM}$, $6.0 > [\text{Br}_2] > 0.50 \text{ mM}$. Under these conditions, the oxidation of bromide by hydroperoxide is too slow to contribute measurably to the loss of the hydroperoxide. The average concentrations of bromide ions and bromine, used in all the rate constant calculations, were obtained by correcting initial concentrations for the effects of the equilibrium in reaction 2, and for the amounts of Br^- and Br_2 consumed or generated in reactions 5 and 10. The values used were those calculated at the midpoint of each kinetic trace.

Concentrations of dissolved oxygen were measured with a YSI model 5300 biological oxygen monitor electrode in a closed system.

Results

Reactions with Iodide. In the presence of large concentrations of I^- , the reaction with $\text{L}(\text{H}_2\text{O})\text{RhOOH}^{2+}$ obeyed pseudo-first-order kinetics. The observed pseudo-first-order rate constants were first order in $[\text{H}^+]$, first order in $[\text{I}^-]$, and independent of the initial concentrations of hydroperoxide, eq 3. These kinetic dependences are illustrated for $\text{L}^2(\text{H}_2\text{O})\text{RhOOH}^{2+}$ in the linear plots of $k_{\text{obs}}/[\text{H}^+]$ versus $[\text{I}^-]$ and $k_{\text{obs}}/[\text{I}^-]$ versus $[\text{H}^+]$ in Figure 1. The values of k_1 obtained for the three hydroperoxides are $(8.80 \pm 0.06) \times 10^3 \text{ [L} = (\text{NH}_3)_4]$, $536 \pm 7 \text{ (L}^1)$, and $530 \pm 11 \text{ (L}^2) \text{ M}^{-2} \text{ s}^{-1}$.

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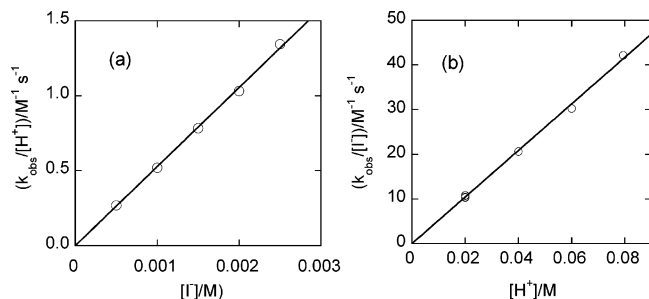
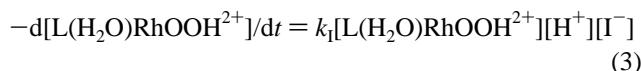
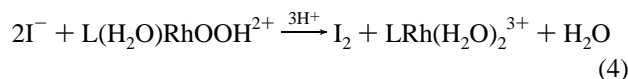


Figure 1. Plots of $k_{\text{obs}}/[H^+]$ vs $[I^-]$ (a) and $k_{\text{obs}}/[I^-]$ vs $[H^+]$ (b) for the oxidation of iodide by $1.3 \times 10^{-5} M L_2(H_2O)RhOOH^{2+}$.

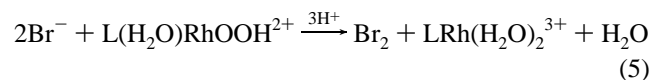


The absorbance increase at 350 nm, combined with the I_2/I_3^- equilibrium of eq 1, yielded the stoichiometric ratio $[I_2]_{\infty}/[L(H_2O)RhOOH^{2+}]_0 = 1.0$, eq 4. Variable amounts of additional iodide are consumed in the rapid follow-up equilibrium of eq 1 which also serves as a reaction indicator.

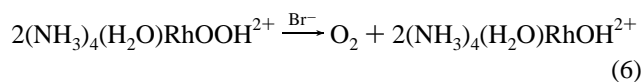


Reactions with Bromide. At high concentrations of bromide (0.010–0.100 M) and acid (0.50–1.0 M), the reaction produced Br_2 (Figure 2a).

Assuming a 1:1 $[Br_2]_{\infty}/[L(H_2O)RhOOH^{2+}]_0$ stoichiometry, eq 5, the yield of Br_2/Br_3^- under the conditions in Figure 2a was 55%, and it reached 100% in an experiment having 1.0 M H^+ and 0.10 M Br^- .

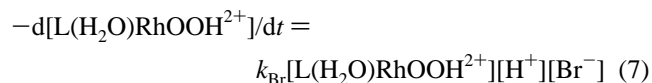


As the concentrations of bromide and acid decreased, the yield of Br_2/Br_3^- and the associated absorbance change at 267 nm ($\epsilon = 3.85 \times 10^4 M^{-1} cm^{-1}$) decreased much more than had been predicted solely on the basis of the Br_2/Br_3^- equilibrium of eq 2. At the limit ($[H^+] \leq 0.1 M$ and $[Br^-] \leq 0.01 M$), no Br_2/Br_3^- was produced. Under these conditions, the reaction was accompanied by an absorbance decrease associated with the disappearance of the hydroperoxide, Figure 2b. Molecular oxygen was generated under these conditions, eq 6. The role of bromide has changed from that of a reductant at high acid and bromide concentrations (eq 5) to that of a catalyst for the disproportionation of coordinated hydroperoxide at the opposite end of the concentration limits (eq 6).



The kinetics were determined at 240 nm, the wavelength of maximum absorbance for $(NH_3)_4(H_2O)RhOOH^{2+}$. The data adhered strictly to the mixed third-order rate law of eq 7 and yielded $k = 4.70 M^{-2} s^{-1}$ at 0.10 M ionic strength,

$0.02 \leq [H^+] \leq 0.10 M$, and $1.5 \leq [Br^-] \leq 10 mM$. As will be shown later, the rate constant $k = 2k_{Br}$ under these conditions.



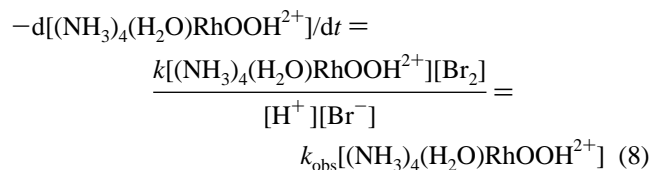
At 1.0 M ionic strength and constant 10 mM Br^- , the plot of k_{obs} against $[H^+]$, Figure 3, is linear at low acidities and yields a third-order rate constant (slope/0.010) of $3.60 M^{-2} s^{-1}$. The slope decreases with $[H^+]$, and the third-order rate constant approaches the value of $1.8 M^{-2} s^{-1}$ at the highest acid concentrations used (0.80 M). In the presence of a large excess of bromide (10 mM), the first-order plots were linear over the whole range of acid concentrations used, $0.040 \leq [H^+] \leq 0.80 M$.

The change in products but not in the rate law (except for the kinetic factor of 2) under two sets of conditions suggests a common mechanism followed by a rapid step in which the product (Br_2) reacts with the limiting reagent, $(NH_3)_4(H_2O)RhOOH^{2+}$, at low $[H^+]$ and $[Br^-]$. This idea was examined in a direct experimental study, as will be described herein.

Reaction of $(NH_3)_4(H_2O)RhOOH^{2+}$ with Br_2/Br^- Mixtures. Upon mixing of $(NH_3)_4(H_2O)RhOOH^{2+}$ (0.10 mM) with Br_2 (2.11 mM) and Br^- (3.03 mM) in 1.0 M $HClO_4$, the $(NH_3)_4(H_2O)RhOOH^{2+}$ disappeared with a half-life of less than 1 s. In the absence of Br_2 , the $(NH_3)_4(H_2O)RhOOH^{2+}/Br^-$ reaction under the same conditions would have a half-life of over 2 min. Clearly, $(NH_3)_4(H_2O)RhOOH^{2+}$ reacts rapidly with Br_2 .

The reaction generates O_2 quantitatively, as shown in an experiment having 0.49 mM $(NH_3)_4(H_2O)RhOOH^{2+}$, 0.90 mM Br_2 , and 0.076 M H^+ . The concentration of produced oxygen was 0.48 mM.

The kinetics were studied over a wide range of concentrations, but always under the conditions where the competing reaction of $(NH_3)_4(H_2O)RhOOH^{2+}$ with bromide contributed less than 5% to the overall rate of disappearance of the hydroperoxide. Both conventional and stopped-flow spectrophotometries were used in these experiments. The loss of $(NH_3)_4(H_2O)RhOOH^{2+}$ obeyed the rate law of eq 8, as illustrated by the linear plot of $k_{\text{obs}}/[Br_2]$ against the reciprocal of the product $[H^+][Br^-]$ in Figure 4. The slope of the line gives $k = 1.78 \pm 0.02 M s^{-1}$.



The inverse dependence on the concentrations of Br^- and H^+ strongly implicates $HOBr$ as the active oxidant, as shown in eqs 9–10. In this scenario, the composite rate constant k in eq 8 is the product $K_{HOBr} \times k_{HOBr}$. By use of $K_{HOBr} = 6.1 \times 10^{-9} M^{-2}$,²¹ one obtains $k_{HOBr} = 2.9 \times 10^8 M^{-1} s^{-1}$.

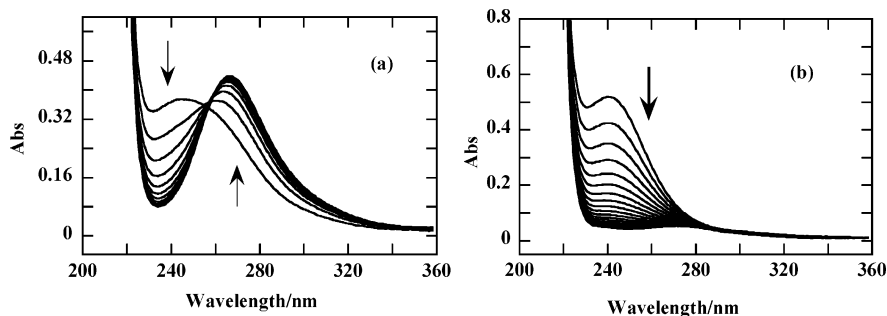


Figure 2. Spectral changes observed in the reaction between $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ (0.13 mM) and Br^- (10 mM) in 1.0 M H^+ (a) and 0.10 M H^+ (b). In part a, the formation of $\text{Br}_2/\text{Br}_3^-$ (55% yield) is observed at 267 nm. In part b, only the disappearance of $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$, $\lambda_{\text{max}} = 240$ nm, is seen.

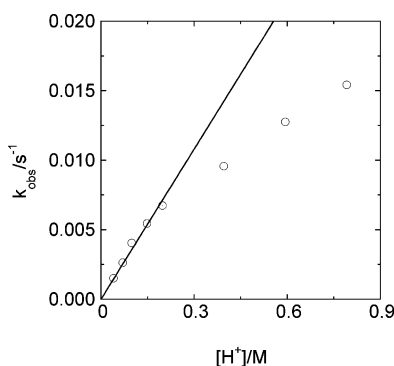


Figure 3. Plot of k_{obs} vs $[\text{H}^+]$ for the oxidation of Br^- (10 mM) with $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ (5×10^{-5} M) at 25 °C and 1.0 M ionic strength.

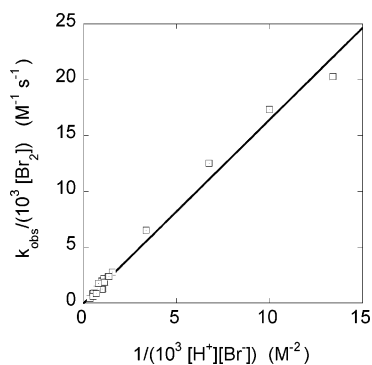
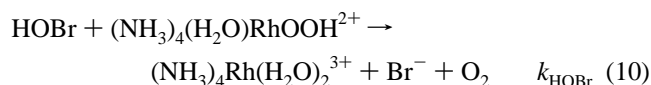
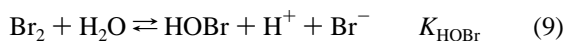


Figure 4. Plot of $k_{\text{obs}}/[\text{Br}_2]$ against $1/[\text{H}^+][\text{Br}^-]$ for the reaction between $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ and Br_2 at 1.0 M ionic strength.



Reaction of $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ with Br_2/Br^- Mixtures. Previously, we reported that the reaction between $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ and bromide produced $\text{Br}_2/\text{Br}_3^-$ in two parallel paths.¹³ The major, acid-catalyzed path, equivalent to that in eq 5, had $k = 0.52 \text{ M}^{-2} \text{ s}^{-1}$. A minor term, independent of the $[\text{H}^+]$, had $k = 0.035 \text{ M}^{-1} \text{ s}^{-1}$.

In view of our findings on the $\text{HOBr}/(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ reaction in this work, we have now re-examined the $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ reaction for the potential occurrence of the HOBr path. We find that it indeed operates under the properly selected conditions as will be described herein. It was missed in our earlier work where its contribution was

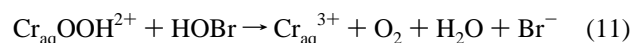
Table 1. Summary of Kinetic Data Obtained in This Work^a

LMOOH ²⁺	k_1^b	k_{Br}^b	k_{HOBr}^c	ref
$(\text{H}_2\text{O})_5\text{CrOOH}^{2+}$	988(16) ^d	0.54 ^e	9.5×10^6 ^f	14, this work
$\text{L}^1(\text{H}_2\text{O})\text{CoOOH}^{2+}$	100(2) ^d			14
$\text{L}^2(\text{H}_2\text{O})\text{CoOOH}^{2+}$	72.3(21) ^d			14
$(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$	8800(60) ^g	2.35(5) ^g	3×10^8 ^h	this work
		1.8 ^h		this work
$\text{L}^1(\text{H}_2\text{O})\text{RhOOH}^{2+}$	536(7) ^g	0.200(1) ^h		this work
$\text{L}^2(\text{H}_2\text{O})\text{RhOOH}^{2+}$	530(11) ^g	0.55(2) ^j		this work
H_2O_2	0.173 ⁱ	0.000 23 ^k	$(1.5-5.8) \times 10^4$	22-24

^a Aqueous solutions, 25 °C. Numbers in parentheses represent one standard deviation of the last significant figure. ^b k in $\text{M}^{-2} \text{ s}^{-1}$. ^c k in $\text{M}^{-1} \text{ s}^{-1}$. ^d Ionic strength (μ) = 0.075 M. ^e μ = 2.0 M. ^f μ = 0.50 M. ^g μ = 0.10 M. ^h μ = 1.0 M. ⁱ μ = 0.20 M. ^j $[\text{H}^+]$ -independent term has $k_0 = 0.0115 \text{ M}^{-1} \text{ s}^{-1}$. ^k $[\text{H}^+]$ -independent term has $k_0 = 3.8 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$.

never large, although as will be shown, it did cause some distortions at the lowest concentrations of bromide and acid.

The $\text{HOBr}/\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ reaction of eq 11 was studied at 0.50 M ionic strength in the concentration regimes carefully chosen to suppress the oxidation of bromide by $(\text{H}_2\text{O})_5\text{CrOOH}^{2+}$, as follows: $0.10 \leq [\text{H}^+] \leq 0.50$ M, $1.0 \leq [\text{Br}^-] \leq 5.0$ mM, $[\text{Br}_2] = 4.6 \times 10^{-4}$ M, and $[(\text{H}_2\text{O})_5\text{CrOOH}^{2+}] = 6 \times 10^{-5}$ M. A plot of $k_{\text{obs}}/[\text{Br}_2]$ against $K_{\text{HOBr}}/([\text{H}^+][\text{Br}^-])$ is linear (Supporting Information Figure S2), yielding $k_{\text{HOBr}} = 9.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.



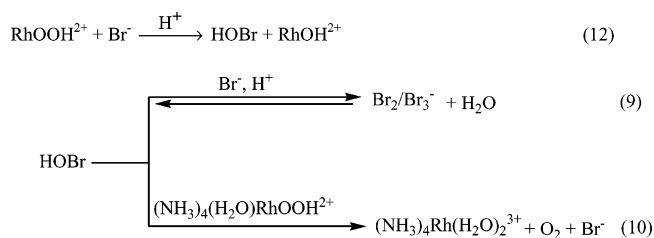
Our old data on the $\text{Cr}_{\text{aq}}\text{OOH}^{2+}/\text{Br}^-$ reaction¹³ were reanalyzed by taking into account eq 11. This analysis clearly shows that the acid-independent path is unreal, an artifact caused by the decreasing slope of k_{obs} versus $[\text{H}^+]$ at higher concentrations of H^+ , in a manner analogous to that illustrated in Figure 3 for the $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}/\text{Br}^-$ reaction. At the lowest $[\text{H}^+]$ used, 0.10 M, we estimate that the observed rate constant could be up to 40% larger than the value extrapolated from the data at high $[\text{H}^+]$. The limiting factor of 2 was never reached experimentally. After the correction for eq 11, the rate law for the $\text{Cr}_{\text{aq}}\text{OOH}^{2+}/\text{Br}^-$ reaction becomes $-\text{d}[\text{Cr}_{\text{aq}}\text{OOH}^{2+}]/\text{d}t = 0.54 [\text{Cr}_{\text{aq}}\text{OOH}^{2+}][\text{Br}^-][\text{H}^+]$. Consistent with this reinterpretation, the increase in the observed rate constant by a factor of ≤ 2 at low $[\text{H}^+]$ and $[\text{Br}^-]$ is accompanied by a decrease in the yield of $\text{Br}_2/\text{Br}_3^-$. The summary of all the kinetic data is given in Table 1.

Discussion

The reaction of iodide ions with the rhodium hydroperoxides in this work follows the pattern established previously for several other metal hydroperoxides. Unlike H_2O_2 , which exhibits both an acid-independent and an acid-catalyzed path, metal hydroperoxides react exclusively by the acid-catalyzed route. As we argued earlier,¹⁴ these kinetic differences may be explained if the protonation of the metal hydroperoxides in Table 1 is thermodynamically more favorable than the protonation of H_2O_2 .

The bromide reactions are more complex. The change from $\text{Br}_2/\text{Br}_3^-$ to O_2 as reaction products, and an increase in the rate constant by a factor of 2 as the concentrations of H^+ and Br^- decreased, are fully consistent with the mechanism in Scheme 1. Bromine, which is the initial product under all

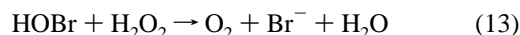
Scheme 1



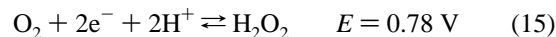
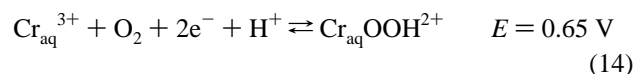
the conditions, hydrolyzes to give minute concentrations of HOBr, which was shown independently to react very rapidly with the hydroperoxides, as in eq 10. Except at the highest concentrations of acid and bromide used in this work, the steady-state concentration of HOBr, although very small ($\leq 10^{-11}$ M), was still sufficiently large to react with a portion of the hydroperoxide on the time scale of the $\text{LMOOH}^{2+}/\text{Br}^-$ reaction. Under these conditions, the final yields of $\text{Br}_2/\text{Br}_3^-$ were less than quantitative. At the low end of $[\text{H}^+]$ and $[\text{Br}^-]$, the rate of HOBr/hydroperoxide reaction was as large or larger than the rate of reaction in eq 12. As a result, 2 equiv of the hydroperoxide was lost per rate-determining step of eq 12, introducing a kinetic factor of 2.

In the intermediate range of $[\text{H}^+]$ in Figure 3, the kinetics should not be strictly first order, because the concentration of one competitor, $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$, and, with it, the competition ratio, change throughout the reaction. First-order plots were still linear, however, as often happens in such cases, because the change in rate constant during the reaction is small and gradual.

The $\text{Cr}_{\text{aq}}\text{OOH}^{2+}/\text{Br}^-$ chemistry also qualitatively follows the pattern in Scheme 1, but the rate constant for the equivalent of reaction 12 is lower than for $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$, Table 1. The same is true for the oxidation of the two hydroperoxides with HOBr in reactions 10 and 11. Still, both hydroperoxides react more rapidly by several orders of magnitude as compared to H_2O_2 , eq 13. The reported values of k_{13} lie in the range $(1.5-5.8) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.²²⁻²⁴



There are no thermodynamic data available for the hydroperoxides of rhodium, but an estimate has been made²⁵ for the redox potential for reaction 14: $E = 0.65 \text{ V}$ at pH 0. The two-electron oxidation of $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ is more favorable by 0.13 V than the oxidation of H_2O_2 in eq 15, which translates into a 25 kJ/mol advantage in terms of ΔG° , or about 2.4×10^4 in terms of equilibrium constant. The observed several hundred-fold increase in rate constant can thus be adequately explained by the thermodynamics of reactions 14 and 15.



In a neutral-to-alkaline medium, the kinetics of reaction 13 are inversely proportional to $[\text{H}^+]$.²⁶ In the proposed mechanism, eq 16, HO_2^- attacks at the bromine end of HOBr with a rate constant of $7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In acidic solutions, hydrogen peroxide is fully protonated and much less nucleophilic. As a result, the rate constant is more than 10^3 times smaller than that for reaction 16.



A similar mechanism probably operates in the reaction with metal hydroperoxides, as shown in Scheme 2. In the proposed transition state, the attack by $\text{Br}^{\delta+}$ takes place at the rhodium-bound oxygen, which is expected to be the more nucleophilic of the two peroxo oxygens.

The multiplicity of O_2 produced in the reactions of HOBr with metal hydroperoxides has not been determined. It would be interesting to learn whether singlet O_2 is produced, as is the case with H_2O_2 .²⁷

In the oxidation of both bromide and iodide, the reactivity order is $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+} > \text{Cr}_{\text{aq}}\text{OOH}^{2+}$ and $\text{L}(\text{H}_2\text{O})\text{RhOOH}^{2+} > \text{L}(\text{H}_2\text{O})\text{CoOOH}^{2+}$ ($\text{L} = \text{L}^1, \text{L}^2$). In the absence of thermodynamic data, we can only speculate that this reactivity follows the oxidizing power of the hydroperoxide.

A possibility that the reactions with Br^- and I^- take place by electron transfer, as suggested by a reviewer, is not an appealing alternative. Irrespective of the initial reaction site, electron transfer would produce highly reactive halogen atoms and metal-complex-derived intermediates (LM^{IV} or HO^\bullet). There is no experimental evidence for such species. The reactions of $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ were carried out in the presence of methanol which would scavenge HO^\bullet and at least a portion of LM^{IV} and Br^\bullet and, thus, alter the stoichiometry and complicate the kinetics. None of this was observed. Finally, the kinetic behavior of the halide reactions, including the first-order dependence on $[\text{H}^+]$, parallels that which was

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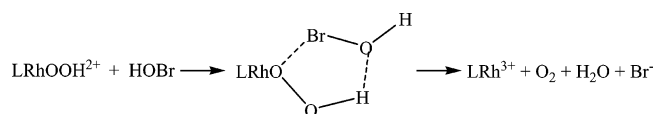
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Scheme 2



observed in the oxidation of PPh_3 . That reaction was shown by isotopic labeling to take place by O-atom transfer.²⁸

The chemistry described in this paper may be important in biological systems, as a reviewer commented. Hypohalites, hydroperoxo complexes, and halide ions are all involved in natural processes but can also be generated from therapeutic drugs. For example, the active form of an anticancer drug, bleomycin, is an iron(III) hydroperoxide, which may engage in chemistry analogous to that exhibited by the hydroper-

(28) Lemma, K.; Bakac, A. Work in progress.

oxides of chromium and rhodium. The mechanism of action and the effectiveness of the drug may be influenced by such chemistry.

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Supporting Information Available: UV-vis spectrum of tribromide ion formed in the hydroperoxorhodium/bromide reaction (Figure S1), kinetic data for hydroperoxochromium-HOBr reaction (Figure S2), and two tables of kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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