

Acid-Catalyzed Oxidation of Iodide Ions by Superoxo Complexes of Rhodium and Chromium

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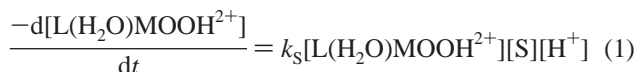
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Superoxometal complexes $L(H_2O)MOO^{2+}$ ($L = (H_2O)_4, (NH_3)_4,$ or N_4 -macrocycle; $M = Cr^{III}, Rh^{III}$) react with iodide ions according to the stoichiometry $L(H_2O)MOO^{2+} + 3I^- + 3H^+ \rightarrow L(H_2O)MOH^{2+} + 1.5I_2 + H_2O$. The rate law is $-d[L(H_2O)MOO^{2+}]/dt = k [L(H_2O)MOO^{2+}][I^-][H^+]$, where $k = 93.7 M^{-2} s^{-1}$ for $Cr_{aq}OO^{2+}$, 402 for $([14]aneN_4)(H_2O)-CrOO^{2+}$, and 888 for $(NH_3)_4(H_2O)RhOO^{2+}$ in acidic aqueous solutions at 25 °C and 0.50 M ionic strength. The $Cr_{aq}OO^{2+}/I^-$ reaction exhibits an inverse solvent kinetic isotope effect, $k_{H_2O}/k_{D_2O} = 0.5$. In the proposed mechanism, the protonation of the superoxo complex precedes the reaction with iodide. The related $Cr_{aq}OOH^{2+}/I^-$ reaction has $k_{H_2O}/k_{D_2O} = 0.6$. The oxidation of $(NH_3)_5Rupy^{2+}$ by $Cr_{aq}OO^{2+}$ exhibits an $[H^+]$ -dependent pathway, rate = $(7.0 \times 10^4 + 1.78 \times 10^5[H^+])[Ru(NH_3)_5py^{2+}][Cr_{aq}OO^{2+}]$. Diiodine radical anions, $I_2^{\bullet-}$, reduce $Cr_{aq}OO^{2+}$ with a rate constant $k = 1.7 \times 10^9 M^{-1} s^{-1}$.

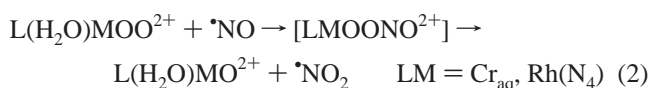
Introduction

The acid-catalyzed oxidation of halides, phosphines, and sulfides by hydroperoxo metal complexes in aqueous solutions^{1–5} takes place by oxygen atom transfer, as demonstrated in several examples by isotopic labeling.^{2,4} Unlike the parent hydrogen peroxide, which exhibits both acid-independent and acid-catalyzed pathways in the reactions with these substrates,^{1,6,7} most of the metal hydroperoxides react exclusively through the acid-catalyzed path, eq 1, where L represents the equatorial ligand(s) ($L = (H_2O)_4, (NH_3)_4,$ or N_4 -macrocycle), S is the substrate, and M is the metal ion ($Cr^{III}, Rh^{III},$ or Co^{III}). The same is true for the anionic complex $(CN)_5CoOOH^{3-}$.⁵

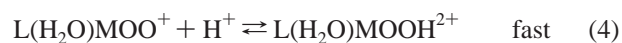
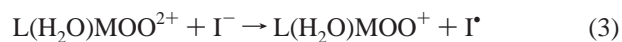


We have now turned to the reactions of the corresponding superoxometal complexes, $L(H_2O)MOO^{2+}$, with one of these

substrates, iodide ions. The guiding question was one of mechanism. There are no convincing examples of O atom transfer in the chemistry of superoxometal ions except in the reactions with $\bullet NO$, where radical coupling precedes the O–O bond cleavage,^{8,9} eq 2.



Direct O atom transfer to iodide, a nonradical species, would thus be unprecedented. Electron transfer, however, would initially generate iodine atoms in a thermodynamically unfavorable reaction, eq 3. Surely, rapid follow-up steps, eqs 4 and 5, could drive the reaction to completion, but the uphill thermodynamics of the first step should make the overall reaction rather slow.



Another option begins with a complex or $L(H_2O)MOO^{2+}/I^-$ ion pair followed by a rate-determining attack by the second iodide to produce $I_2^{\bullet-}$, a species less energetic than

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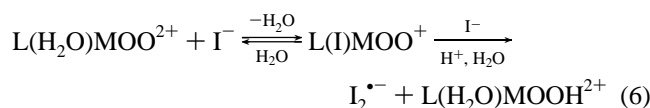
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I[•]. Such a mechanism, eq 6, adopted, for example, by the reaction between Fe³⁺ and I⁻,^{10,11} would exhibit a second-order dependence on iodide concentration.



The results of a detailed kinetic and mechanistic study of the oxidation of iodide with three L(H₂O)MOO²⁺ complexes are presented herein.

Experimental Section

The superoxometal complexes L(H₂O)MOO²⁺ were prepared as described previously.^{8,9,12} Their concentrations were determined spectrophotometrically^{2,8,9} immediately before the reaction with iodide. Except in a few experiments that utilized an argon or dioxygen atmosphere, most kinetic solutions contained 0.4 mM O₂, the “natural” concentration that resulted from mixing the O₂-saturated stock solutions of L(H₂O)MOO²⁺, air-saturated solutions of dilute HClO₄ and NaClO₄, and argon-saturated solutions of iodide. The results were unaffected by the variations in the concentration of O₂.

Stock solutions of iodide (0.10 M) were prepared by dissolving KI (certified A.C.S., Fisher) or NaI (99.999%, Aldrich) in H₂O. The iodide content was determined spectrophotometrically ($\lambda_{\text{max}} = 226 \text{ nm}$, $\epsilon = 1.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) after diluting to appropriate concentration levels. Stock solutions were deaerated with a stream of argon and kept in the dark.

Kinetics of the L(H₂O)MOO²⁺/I⁻ reactions were determined at the 350- or 290-nm maximum in the absorption spectrum of I₃⁻ by using a UV-vis Shimadzu 3101 PC spectrophotometer. The kinetic study of the I₂^{•-}/Cr_{aq}OO²⁺ reaction utilized an LKS 50 Applied Photophysics laser flash photolysis instrument.¹³ The radicals were generated from I₂/I₃⁻ in the presence of excess Cr_{aq}OO²⁺ by a 355-nm flash from a Nd:YAG laser. The reaction was monitored at 380 nm, where I₂^{•-} exhibits a maximum, $\epsilon = 9.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁴ All of the experiments utilized 0.6 mM I⁻, 0.030 mM I₂, and 0.10 M HClO₄. For the oxidation of Ru(NH₃)₅py²⁺ by the superoxometal complexes, we used an Olis RSM 1000 stopped-flow spectrophotometer.

The ionic strength was maintained in some experiments at the 0.50 M level with NaClO₄ + HClO₄. Laboratory-distilled water was purified further by passage through a Millipore Milli-Q water purification system. All of the kinetic experiments were performed at 25.0 ± 0.2 °C.

Results

Cr_{aq}OO²⁺/I⁻ Reaction. In the presence of a large excess of iodide, the build-up of I₂/I₃⁻ followed exponential kinetics in most of the experiments (see below) and yielded identical rate constants at 350 and 290 nm. The reaction is first order in iodide as shown by the linear plot of k_{obs} against [I⁻] (Figure S1, Supporting Information). At constant acid

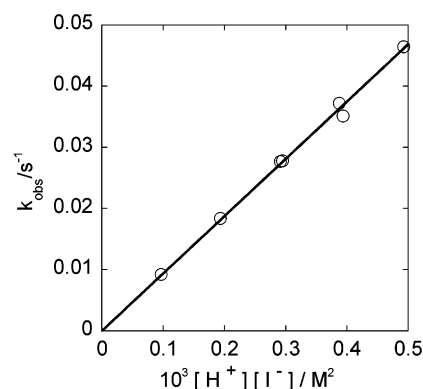
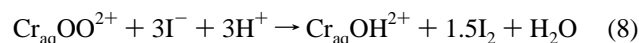


Figure 1. Plot of k_{obs} vs the product [I⁻] × [H⁺] for the reaction of Cr_{aq}-OO²⁺ (0.010–0.035 mM) with iodide ions in 0.10 M HClO₄.

concentration, 0.10 M H⁺, the measured rate constant was $9.44 \pm 0.22 \text{ M}^{-1} \text{ s}^{-1}$.

The reaction is first order in [H⁺]. Figure 1 shows a plot of k_{obs} against the product [H⁺] × [I⁻] at 0.50 M ionic strength. The line has a zero intercept and a slope $k_{\text{Cr}} = 93.7 \pm 1.0 \text{ M}^{-2} \text{ s}^{-1}$.

The yield of [I₂ + I₃⁻] was calculated from the final absorbance at 350 nm, using $K_{\text{I}} = 830 \text{ M}^{-1}$ (eq 7)¹⁵ and $\epsilon(\text{I}_3^-) = 26\,000 \text{ M}^{-1} \text{ cm}^{-1}$. These data, combined with the initial concentration of Cr_{aq}OO²⁺, yielded the stoichiometric ratio $R = [\text{I}_2 + \text{I}_3^-]_{\infty} / [\text{Cr}_{\text{aq}}\text{OO}^{2+}]_0 = 1.47 \pm 0.05$, consistent with the reaction in eq 8 followed by rapid I₂/I₃⁻ equilibration of eq 7. This stoichiometry defines the rate constant k_{Cr} as in eq 9.



$$\frac{-d[\text{Cr}_{\text{aq}}\text{OO}^{2+}]}{dt} = 0.667 \frac{d[\text{I}_2]}{dt} = k_{\text{Cr}}[\text{Cr}_{\text{aq}}\text{OO}^{2+}][\text{I}^-][\text{H}^+] \quad (9)$$

On occasion, the kinetic traces would come to an unusual, abrupt stop, especially at high iodide concentrations ($\geq 2 \text{ mM}$), as shown in Figure 2a. Such behavior would persist for several stock solutions of Cr_{aq}OO²⁺, but eventually the system would return to normal and yield traces such as that shown in Figure 2b.

Prior to the break, the traces were strictly exponential. The fit to first-order kinetics with floating Abs_∞ yielded the same rate constant as that obtained from well-behaved traces that exhibited no break. The stoichiometry calculated from the final measured absorbance remained the same as that in eq 8. Clearly, the stoichiometry calculated from the fitted Abs_∞ was greater than $R = 1.5$. In the worst case, the deviation was about 10%, but more typically it was within 1–5%.

We looked for the potential role of several species that are known or suspected to be present in our solutions, but most had no effect; that is, they neither improved the “broken” traces nor introduced a break for solutions that gave well-behaved kinetics. In solutions containing O₂, the following additives at concentrations up to 1 mM were without

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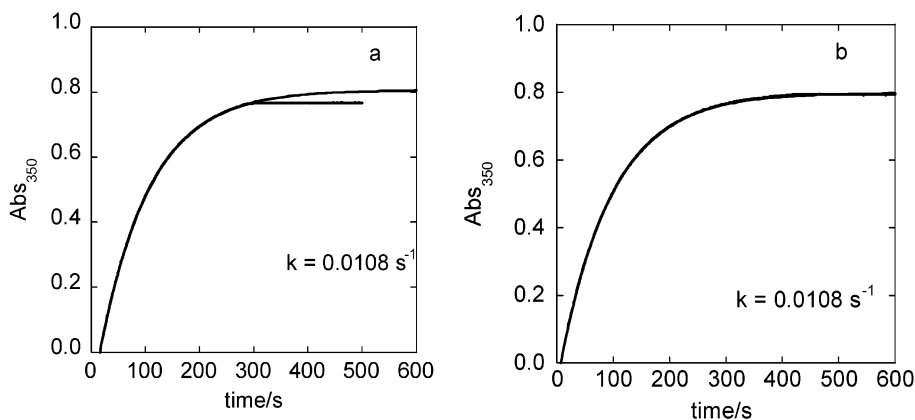


Figure 2. Kinetic plots and fits to the first-order rate equation for the reaction of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ with iodide ions obtained for different stock solutions under identical conditions: $[\text{I}^-] = 1.0 \text{ mM}$, $[\text{H}^+] = 0.10 \text{ M}$, $[\text{O}_2] = 0.4 \text{ mM}$, and $[\text{CH}_3\text{OH}] = 0.01 \text{ M}$; $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]_0 = 0.021 \text{ mM}$ (a) and 0.020 mM (b).

effect: Cl^- , $\text{Fe}_{\text{aq}}^{3+}$ (both potential impurities in solutions containing transition metals and perchlorate ions), $\text{Mn}_{\text{aq}}^{2+}$ (scavenger for $\text{Cr}_{\text{aq}}\text{O}^{2+}$), $\text{Cu}_{\text{aq}}^{2+}$ (scavenger for superoxide), $\text{Zn}_{\text{aq}}^{2+}$ (formed during Zn/Hg reduction of $\text{Cr}_{\text{aq}}^{3+}$), and CH_2O (produced from $\text{Cr}_{\text{aq}}\text{O}^{2+}$ and methanol during the preparation of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$). Also, the behavior of the system was unchanged when methanol was replaced with ethanol as a scavenger for $\text{Cr}_{\text{aq}}\text{O}^{2+}$ in the preparation of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$.

The break in kinetic traces could be eliminated or at least made much less prominent if the reactions were carried out in the presence of large amounts of methanol (2 M) or 2-PrOH (1 M). Small amounts of chromate ($\leq 20 \mu\text{M}$) removed the breaks while keeping the rate constant and the stoichiometry unchanged. Copper(II) ions had the same effect, but only if the kinetic solutions were deaerated by purging with argon prior to the reaction.

Superoxide ions appear to be responsible for the observed behavior, although neither the chemistry leading to $\text{HO}_2^*/\text{O}_2^{\bullet-}$, nor the reason why $\text{HO}_2^*/\text{O}_2^{\bullet-}$ itself would cause the observed distortion of the kinetic traces, is obvious.

Perhaps the most convincing evidence for the involvement of the superoxide is the effect of $\text{Cu}_{\text{aq}}^{2+}$, a powerful catalyst for the dismutation of superoxide under air-free conditions where the two oxidation states, $\text{Cu}_{\text{aq}}^{2+}$ and Cu_{aq}^+ , alternately oxidize and reduce $\text{HO}_2^*/\text{O}_2^{\bullet-}$.¹⁶ The situation is different in O_2 -containing solutions, where Cu_{aq}^+ generates both free and bound superoxide in the reaction with O_2 .¹⁷ Consistent with this picture, $\text{Cu}_{\text{aq}}^{2+}$ had no effect on the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}^-$ reaction in air-saturated solutions but did clean up the kinetics in the absence of O_2 .

Similarly, chromate reduces superoxide ions rapidly, which may be the source of its effect on the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}^-$ reaction. The alcohols, however, are not expected to react with $\text{HO}_2^*/\text{O}_2^{\bullet-}$ under the conditions of our work but may be involved at some stage preceding the formation of superoxide-generating intermediates in the $\text{Cr}_{\text{aq}}^{2+}/\text{O}_2$ reaction. As noted earlier,¹ this chemistry is complex, and the rates of oxygen bubbling or $\text{Cr}_{\text{aq}}^{2+}$ addition may change the proportion of various intermediates before they are converted to $\text{Cr}_{\text{aq}}\text{OO}^{2+}$,

Table 1. Summary of Kinetic Data for Acid-Catalyzed Reactions of $\text{L}(\text{H}_2\text{O})\text{MOO}^{2+}$ and $\text{L}(\text{H}_2\text{O})\text{MOOH}^{2+}$ with Iodide Ions in Acidic Aqueous Solutions at 25 °C

complex	$k/\text{M}^{-2} \text{ s}^{-1}$	source
$\text{Cr}_{\text{aq}}\text{OO}^{2+}$	93.7	this work
$\text{Cr}_{\text{aq}}\text{OO}^{2+}$	185 ^a	this work
$\text{L}^1(\text{H}_2\text{O})\text{CrOO}^{2+}$ ^b	402	this work
$(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}$	888	this work
$\text{Cr}_{\text{aq}}\text{OOH}^{2+}$	988, 1120	ref 3, this work
$\text{Cr}_{\text{aq}}\text{OOH}^{2+}$	1840 ^a	this work
$\text{L}^2(\text{H}_2\text{O})\text{RhOOH}^{2+}$ ^c	530	ref 2
$\text{L}^1(\text{H}_2\text{O})\text{RhOOH}^{2+}$ ^b	536	ref 2
$(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$	8800	ref 2

^a In D_2O , from data at 0.10 M DClO_4 . ^b $\text{L}^1 = [\text{14}] \text{aneN}_4$. ^c $\text{L}^2 = \text{Me}_6\text{[14]aneN}_4$.

$\text{Cr}_{\text{aq}}^{3+}$, and traces of HCrO_4^- . Because the unusual traces were observed only occasionally and gave the same kinetics as the fully exponential ones, they cannot be attributed to the main $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}^-$ reaction and will be ignored in further discussion. Moreover, the reactions of two other superoxo-metal complexes, $\text{L}^1(\text{H}_2\text{O})\text{CrOO}^{2+}$ ($\text{L}^1 = [\text{14}] \text{aneN}_4$) and $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}$, which always yielded clean exponential traces (see below) exhibited in their reactions with iodide ions kinetic dependencies similar to those of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. This finding strengthens our confidence in the results obtained with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, despite an occasional unusual trace in this reaction.

Deuterium Isotope Effect. Two sets of experiments, one in H_2O and one in D_2O (95–96% D content), were carried out for the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}^-$ reaction. At 0.10 M $\text{H}(\text{D})\text{ClO}_4$, the rate constants were $9.35 \text{ M}^{-1} \text{ s}^{-1}$ (H_2O) and 18.5 (D_2O), yielding an inverse solvent kinetic isotope effect, $k_{\text{H}}/k_{\text{D}} = 0.5$. Similar experiments with the hydroperoxo complex, $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$, in 0.10 M $\text{H}(\text{D})\text{ClO}_4$ yielded $k_{\text{H}} = 112$ and $k_{\text{D}} = 184 \text{ M}^{-1} \text{ s}^{-1}$, and thus $k_{\text{H}}/k_{\text{D}} = 0.6$. The k_{H} value agrees well with the one calculated from our earlier data, $98.8 \text{ M}^{-1} \text{ s}^{-1}$.³ All of the kinetic data are summarized in Table 1.

$\text{L}^1(\text{H}_2\text{O})\text{CrOO}^{2+}/\text{I}^-$ Reaction. The reaction stoichiometry is $[\text{I}_2 + \text{I}_3^-]_{\infty}/[\text{L}^1(\text{H}_2\text{O})\text{CrOO}^{2+}]_0 = 1.42 \pm 0.05$, consistent with the chemistry analogous to that shown for $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in eqs 8 and 9. In the presence of a large excess of iodide and H^+ , the kinetic traces were exponential and yielded values of k_{obs} that were linearly dependent on the concentration of

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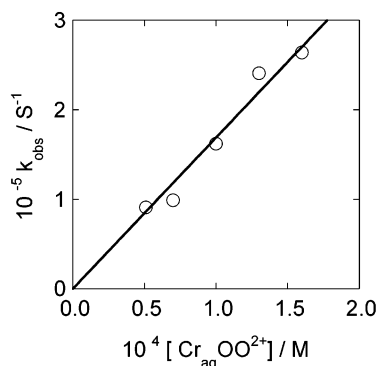
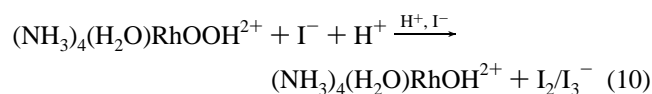


Figure 3. Plot of k_{obs} vs $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ for the reaction of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ with $\text{I}_2^{\bullet-}$. Conditions: $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]_0 = 0.05\text{--}0.16$ mM, $[\text{I}^-] = 0.6$ mM, $[\text{I}_2] = 0.03$ mM, and $[\text{H}^+] = 0.10$ M.

iodide and H^+ , Supporting Information, Figures S2 and S3. At 0.50 M ionic strength, the third-order rate constant k_{LCr} , defined in the same way as k_{Cr} in eq 9, is 402 ± 7 $\text{M}^{-2} \text{s}^{-1}$.

$(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}/\text{I}^-$ Reaction. Solutions of $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}$, prepared photochemically from $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhH}^{2+}$ in oxygen-saturated solutions,¹² contained large amounts of $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$ as a natural impurity. Because both species react with iodide, the kinetic traces were biexponential. The data analysis by consecutive kinetic treatment yielded two sets of rate constants. The faster of the two agreed with the independently known rate constant for the $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}/\text{I}^-$ reaction, 8.80×10^3 $\text{M}^{-2} \text{s}^{-1}$, eq 10, although the precision of the data was low. The reason is the choice of concentrations in the present work, where we sought to optimize conditions for the slower $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}/\text{I}^-$ reaction so that a large portion (up to 80%) of the hydroperoxo stage was completed during the manual mixing of the reagents. To obtain precise rate constants for the $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}/\text{I}^-$ reaction, we fixed the rate constant for the faster stage in the calculations at its known value.



The $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOO}^{2+}/\text{I}^-$ reaction exhibited a first-order dependence on $[\text{H}^+]$ and $[\text{I}^-]$, as shown in Supporting Information, Figure S4. The value of the third-order rate constant is $k_{\text{Rh}} = 888 \pm 15$ $\text{M}^{-2} \text{s}^{-1}$.

$\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}_2^{\bullet-}$ Reaction. There is a reasonable possibility (see Discussion section) that the $\text{L}(\text{H}_2\text{O})\text{MOO}^{2+}/\text{I}^-$ reactions generate I^{\bullet} and $\text{I}_2^{\bullet-}$, which might dimerize or react with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. To determine the likelihood of the latter reaction under the conditions of the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}^-$ reaction, we determined the kinetics of the $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{I}_2^{\bullet-}$ reaction by laser flash photolysis.

Immediately after the flash, the absorbance at 380 nm increased, owing to the formation of $\text{I}_2^{\bullet-}$, and then decreased exponentially with $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ -dependent kinetics, eqs 11 and 12 followed by eq 7. A plot of k_{obs} against the average $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ concentration, Figure 3, yielded $k_{12} = (1.7 \pm 0.1) \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$. The reaction probably takes place by initial radical coupling, as observed earlier for other $\text{Cr}_{\text{aq}}\text{OO}^{2+}/$

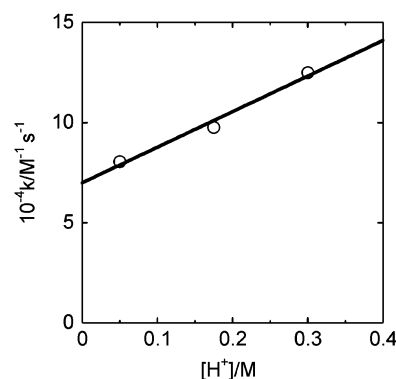
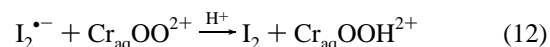


Figure 4. Plot of k_{obs} vs $[\text{H}^+]$ for the reaction between $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$.

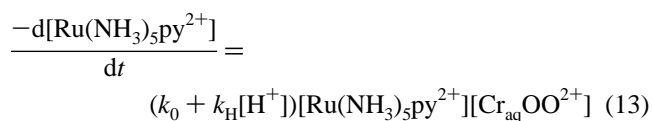
radical reactions,¹⁸ but an outer-sphere mechanism cannot be entirely ruled out. Self-exchange rate data are not reliably known for either partner¹⁹ in reaction 12, which prevents us from making a Marcus estimate for the rate constant.



In support of the chemistry in eq 12, the final absorbance at 380 nm was consistent with the formation of 1 equiv of I_2/I_3^- . Also, the absorbance of the reaction solutions grew between successive laser shots, consistent with the additional, slower formation of I_2/I_3^- from $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ and I^- . As written, reaction 12 has a driving force of 0.8 V.

$\text{L}(\text{H}_2\text{O})\text{MOO}^{2+}/\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ Reactions. The first-order dependence on $[\text{H}^+]$ in the reactions of $\text{L}(\text{H}_2\text{O})\text{MOO}^{2+}$ complexes with iodide raised questions about timing and the site of proton attack. Specifically, does a protonated form of the superoxo complex $\text{L}(\text{H}_2\text{O})\text{MOOH}^{3+}$ exist and play a kinetic role? To help provide some answers and to find out whether $[\text{H}^+]$ catalysis is a general feature of the reductions of $\text{L}(\text{H}_2\text{O})\text{MOO}^{2+}$, we examined the effects of H^+ on the reactions of two superoxometal complexes, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and $\text{L}^2(\text{H}_2\text{O})\text{RhOO}^{2+}$ ($\text{L}^2 = \text{Me}_6\text{-[14]aneN}_4$), with a typical outer-sphere reductant, $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$.

At a constant acid concentration, mixed second-order kinetics were observed for both reactions, as expected. As shown in Figure 4, the dependence on $[\text{H}^+]$ for $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ is well described by eq 13, where $k_0 = 7.0 \times 10^4$ $\text{M}^{-1} \text{s}^{-1}$ and $k_{\text{H}} = 1.78 \times 10^5$ $\text{M}^{-2} \text{s}^{-1}$ at 0.30 M ionic strength.



The observation of a pronounced acid-dependent term lends credence to our assertion that protonated superoxometal complexes are involved, especially when the reduction of $\text{L}(\text{H}_2\text{O})\text{MOO}^{2+}$ to $\text{L}(\text{H}_2\text{O})\text{MOO}^+$ is thermodynamically unfavorable; see Discussion section.

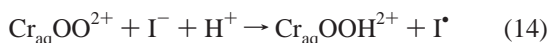
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On the other hand, the $L^2(H_2O)RhOO^{2+}/Ru(NH_3)_5py^{2+}$ reaction showed no dependence on $[H^+]$ ($k = (4.96 \pm 0.13) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at $0.050 \leq [H^+] \leq 0.30 \text{ M}$).

Discussion

One-electron oxidation of I^- by $Cr_{aq}OO^{2+}$, as in eq 14, is thermodynamically uphill by $>0.3 \text{ V}$.^{1,20,21} Potential data for the other $L(H_2O)MOO^{2+}$ complexes in this work are not available, but they are not expected to differ dramatically from those for $Cr_{aq}OO^{2+}$.



If the reaction adopts the one-electron path, then the unfavorable thermodynamics must be overcome in part by the rapid follow-up formation of $I_2^{\bullet-}$ and its irreversible oxidation with $Cr_{aq}OO^{2+}$, eqs 5 and 12.

The first-order dependence on $[H^+]$ clearly rules out an outer-sphere oxidation of I^- by $Cr_{aq}OO^{2+}$, for which ΔG would be greater than that for reaction 14 by an amount determined by the pK_a of the product $Cr_{aq}OOH^{2+}$. This pK_a is probably around 7–8, similar to the value estimated for a macrocyclic cobalt compound, $L^1(H_2O)CoOOH^{2+}$.²² The equilibrium constant for reaction 15 at 1 M H^+ is thus only $\sim 10^{-12} \text{ M}^{-1}$. Even if the reverse of reaction 15 proceeds at a diffusion-controlled rate, the forward path could have a rate constant of no more than $10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, 4 orders of magnitude less than that for the experimentally observed reaction.



Most likely, a rapid acid–base equilibrium generates small amounts of the reactive, protonated superoxometal complex, which oxidizes iodide in the next step, eqs 16 and 17, followed by the known chemistry of I^* , $I_2^{\bullet-}$, and $Cr_{aq}OOH^{2+}$ in eqs 5, 12, and 18.

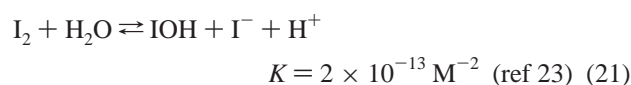
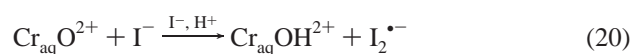
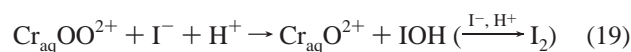


The equilibrium constant for reaction 14 taking place by any mechanism, including the sequence shown in eqs 16 and 17, is $\sim 10^{-5} \text{ M}^{-1}$. Again, setting the limit for k at $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the reverse step, the forward reaction must have $k < 10^5 \text{ M}^{-2} \text{ s}^{-1}$. The experimental value, $93.7 \text{ M}^{-2} \text{ s}^{-1}$, satisfies this requirement. Thus, the one-electron process of eq 14 or its equivalent is consistent with the data.

A good test for the chemistry in eq 14 (or eqs 16 and 17) would be the observation of either $Cr_{aq}OOH^{2+}$ or $I_2^{\bullet-}$ as an intermediate. Unfortunately, measurable amounts of $Cr_{aq}OOH^{2+}$ did not and could not accumulate even if the reaction took place as in eq 14 because this hydroperoxide reacts with

I^- faster than $Cr_{aq}OO^{2+}$ does. The same is true for the other two $L(H_2O)MOO^{2+}/L(H_2O)MOOH^{2+}$ couples. We were not able to find a specific, selective reagent for $I_2^{\bullet-}$ in the presence of the other reaction components.

As an alternative to the one-electron path of eq 14, the reaction might take place in a two-electron oxygen atom transfer step, as shown in eqs 19 and 20. From an upper limit for the $Cr_{aq}OO^{2+}/Cr_{aq}O^{2+}$ potential ($<1.5 \text{ V}$ in 1 M HClO_4)¹, reduction potentials for the couples I^*/I^- (1.33 V) and $I_2^{\bullet-}/2I^-$ (1.03 V), and equilibrium constants for reactions 5 and 21, we estimate the driving force for reaction 19 in 1.0 M HClO_4 to be $\leq 0.5 \text{ V}$. Even though this is only an upper limit, it would seem that no reasonable correction of the estimated $Cr_{aq}OO^{2+}/Cr_{aq}O^{2+}$ potential could make reaction 19 thermodynamically less favorable than reaction 14, for which $\Delta E = -0.33 \text{ V}$ at 1.0 M H^+ .



Despite the thermodynamic considerations, there is no experimental evidence for such a path. Tests for $Cr_{aq}O^{2+}$ proved to be inconclusive. Mn_{aq}^{2+} and Ce_{aq}^{3+} , both of which are rapidly oxidized by $Cr_{aq}O^{2+}$, had no effect on the reaction. This result, however, does not rule out the involvement of $Cr_{aq}O^{2+}$ because the oxidized forms of both scavengers react rapidly with I^- and would simply replace $Cr_{aq}O^{2+}$ in that role.

$L^1(H_2O)CrOO^{2+}$ is unique among the three superoxides in this work. This ion gives rise to a hydroperoxide that undergoes an intramolecular transformation to a strongly oxidizing Cr(V) complex.²⁴ Under carefully selected experimental conditions (low concentrations of iodide and acid), the one-electron reduction of $L^1(H_2O)CrOO^{2+}$ with iodide should initiate a rapid chain reaction, provided that $L^1Cr(V)$ reacts with I^- in one-electron steps. Under such circumstances, the limiting step in the overall reaction should be the hydroperoxo-to-oxo conversion, which has $k = 0.19 \text{ s}^{-1}$.²⁵ No chain reaction was observed, suggesting that either the $L^1(H_2O)CrOO^{2+}/I^-$ reaction proceeds by a two-electron route that bypasses the hydroperoxide or, more likely, that $L^1Cr(V)$ reacts with iodide in a two-electron process that bypasses $I^*/I_2^{\bullet-}$.

The experimental data for the reactions of I^- with all three superoxides are consistent with both electron transfer and O atom transfer, as shown for $Cr_{aq}OO^{2+}$ in eqs 14 and 19, respectively. At this stage, the one-electron path appears preferable despite the less-favorable thermodynamics (available only for the aquachromium case). Our mechanistic preference is based on the similarities of the rate constants,

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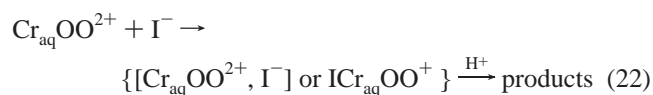
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which lie within a factor of <10 for the three superoxo complexes. Such a small spread seems reasonable for one-electron reactions yielding hydroperoxo complexes.^{24,25} Oxygen atom transfer, however, would initially produce $LM^{IV}O^{2+}$ complexes. Although the thermodynamic data are not available, we would expect reaction 19 to be more favorable for the oxophilic chromium than for the rhodium, opposite from the order of the rate constants in Table 1. Admittedly, this analysis is complicated by the observed acid catalysis. In addition to intrinsic reactivity, the differences in protonation constants will also influence the observed kinetic trends.

Regardless of whether the reaction takes place by electron or atom transfer, the involvement of H^+ helps the reaction thermodynamically and kinetically. In our proposed mechanism, the superoxo complex accepts a proton prior to the reaction with iodide, eqs 16 and 17, so that the observed rate constant is the product $K_{16}k_{17}$. A different order of events, for example, the formation of an ion pair or a complex, followed by the reaction with H^+ , eq 22, appears less likely in view of the observed solvent isotope effect.



In general, the greater strength of the O–D bonds relative to the O–H bonds causes the equilibrium protonation constants to be greater in D_2O .^{26,27} Translated to the present case, the major reason for the increased reactivity in D_2O is

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the greater value for K_{16} . The magnitude of the effect ($k_H/k_D = 0.5$) is similar to that observed in the $Cr_{aq}OOH^{2+}/I^-/H^+$ reaction ($k_H/k_D = 0.6$), for which the prior protonation mechanism is considered most likely.³ Also, the protonation constant for a macrocyclic oxoruthenium(V) complex has $k_H/k_D = 0.46 M^{-1}$.²⁸ The similarity between these values strongly supports the prior protonation mechanism for all three $L(H_2O)MOO^{2+}/I^-/H^+$ reactions in this work.

Another argument in favor of such a scheme is the observation of an acid-dependent path in the $Cr_{aq}OO^{2+}/(NH_3)_5Rupy^{2+}$ and $Cr_{aq}OO^{2+}/hydrazine$ ²⁹ reactions. In both cases, the involvement of an ion pair/complex is highly unlikely. The operation of a parallel, acid-independent path in the $Cr_{aq}OO^{2+}/(NH_3)_5Rupy^{2+}$ reaction and the lack of any acid dependence in the $L^2(H_2O)MOO^{2+}/(NH_3)_5Rupy^{2+}$ reaction are consistent with the much greater reducing power of $(NH_3)_5Rupy^{2+}$ ($E = 0.305 V$)³⁰ compared to that of I^- (1.33 V),²¹ which is clearly sufficient for the reaction to generate even the hydrolytically less stable $L(H_2O)MOO^+$ ions with the rate constants exceeding $10^4 M^{-1} s^{-1}$.

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Supporting Information Available: Kinetic plots showing acid and iodide dependence. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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