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Article

Hydrogen-Atom Transfer from Transition Metal Hydroperoxides, Hydrogen Peroxide, and Alkyl Hydroperoxides to Superoxo and Oxo Metal Complexes

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Superoxochromium(III) complexes $L(H_2O)CrOO^{2+}$ ($L = (H_2O)_4$ and 1,4,8,11-tetraazacyclotetradecane) oxidize hydroperoxo complexes of rhodium and cobalt in an apparent hydrogen-atom transfer process, i.e., $L(H_2O)CrOO^{2+} + L(H_2O)RhOOH^{2+} \rightarrow L(H_2O)CrOOH^{2+} + L(H_2O)RhOO^{2+}$. All of the measured rate constants fall in a narrow range, 17–135 M^{-1} s^{-1}. These values are about 2.5–3.0 times smaller in D_2O, where the hydroperoxo hydrogen is replaced by deuterium, and coordinated molecules of water by D_2O. The failure of the back reaction to take place in the available concentration range places the O–H bond dissociation energy in $RhOO{-}H^{2+}$ at $\leq$320 kJ/mol. The rates of oxidation of $L(H_2O)RhOOH^{2+}$ by $Cr_{aq}OO^{2+}$ are comparable to those for the oxidation of the corresponding hydrides despite the great difference ($\geq$80 kJ/mol) in the driving force for the two types of reactions. A chromyl ion, $Cr^{IV}{}_{aq}O^{2+}$, oxidizes $L(H_2O)RhOOH^{2+}$ and the cobalt analogs to the corresponding superoxo complexes. The rate constants are $\sim$$10^2$-fold larger than those for the oxidation by $Cr_{aq}OO^{2+}$. The oxidation of *tert*-BuOOH by $Cr^{IV}{}_{aq}O^{2+}$ has $k = 160$ M^{-1} s^{-1} and exhibits an isotope effect $k_{BuOOH}/k_{BuOOD} = 12$. Hydrogen atom transfer from H_2O_2 to $Cr_{aq}OO^{2+}$ is slow, $k \approx 10^{-3}$ M^{-1} s^{-1}.

Introduction

Coordination and stepwise reduction of molecular oxygen at metal centers in biological, industrial, and laboratory oxidations generates a number of intermediates. Mononuclear superoxo and peroxo (including hydroperoxo) species are formed in the early stages of oxygen activation and serve either as active oxidants or precursors to more reactive species. In the DuPont K/A oil process for the oxidation of cyclohexane, for example, a peroxocobalt(III) species is one of the key intermediates. This species is responsible for the decomposition of $C_6H_{11}OOH$ into alkoxyl and peroxyl radicals that sustain the reaction.[1,2]

Examples in the bioinorganic domain include the (formally) superoxo iron(III) hemes that are generated at the individual reaction centers of the biological oxygen carriers in oxygen-rich environments,[3,4] the (P)FeOOH and $(P^{\bullet+})$-$Fe^{IV} = O$ forms (P = porphyrin) of reactive intermediates in cytochrome P450-mediated oxidations,[5−7] and hydroperoxo and oxo species involved in the mechanism of action of the antitumor antibiotic bleomycin.[8,9] For many of these and other enzymatic oxidation reactions, the assignments regarding specific reactivity of various intermediates are not definitive. In chemically simpler, nonenzymatic systems, the mechanistic assignments are somewhat more straightforward. Superoxo, hydroperoxo, and high-valent oxo complexes of various transition metals have been generated and characterized both chemically and spectroscopically.[10−18] Such work with well-defined species provides solid mechanistic infor-

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mation about the reaction or specific intermediates under study. It also provides means to address the feasibility of similar chemistry in complex biological or industrial catalytic reactions, where various pathways or species may be obscured by the spectral and/or chemical complexity of the overall system.

A great majority of mechanistic work with transition metal-activated oxygen has focused on oxidations of organic substrates.[13,14,18,19] That work, combined with mechanistic organic chemistry of hydrocarbon autoxidation, has produced valuable information about the reactivity of organic intermediates, such as carbon or oxygen radicals, toward various substrates. Much less is known, however, about the interactions between metal-based and organic intermediates and even less about the reactions of different inorganic intermediates with each other[20] or the role that such chemistry may play in real-life catalytic systems.

Our recent work on the reaction between a superoxochromium(III) ion and acylperoxyl radicals is, to our knowledge, the first example of a kinetic and mechanistic study of this type of chemistry between organic and metal-based intermediates.[21,22] The reaction is rapid and generates products that suggest an initial Russell-type interaction[21] and involvement of Cr(V), which finally disproportionates to yield the observed stable oxidation states of the metal, Cr_{aq}^{3+} and $HCrO_4^-$. The reaction in eq 1, as well as hydrogen-atom transfer (HAT) from various substrates to oxo and superoxo metal complexes that we reported earlier,[23] parallel the chemistry of the organic counterparts, i.e., alkoxyl ($RO^•$) and alkylperoxyl ($ROO^•$) radicals.[24-27] Inorganic intermediates are typically less reactive, but their persistence provides more time for the reactions to take place.

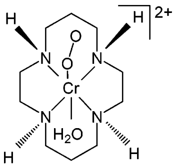
$$Cr_{aq}OO^{2+} + {}^{•}OOC(O)R \rightarrow\rightarrow \{Cr(III) + Cr(VI)\} + \{CO_2 + R_{-H} + RCOOH\} \quad (1)$$

We have now turned to the reactions between inorganic intermediates generated in the process of oxygen activation. Such reactions may take place in catalytic systems utilizing more than one type of metal catalyst or in biological systems where a number of metal ions and complexes are routinely present. Most importantly, however, this study was undertaken to get an insight into this unexplored area of mechanistic chemistry of oxygen activation. We were particularly interested in identifying the types of reactions taking place between various intermediates, in examining the kinetics of such reactions, and, where possible, extracting thermodynamic information which is especially scarce in this field. In the present paper we focus on the reactions in eqs 2 and 3, where M is a transition metal ion (Cr, Rh or Co), and L = $(H_2O)_4$, $(NH_3)_4$, L^1 (1,4,8,11-tetraazacyclotetradecane), or L^2 (*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). We also examined the reactivity of chromium superoxo and oxo complexes toward H_2O_2 and *tert*-BuOOH.

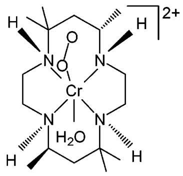
$$L(H_2O)MOO^{2+} + L(H_2O)M'OOH^{2+} \rightarrow L(H_2O)MOOH^{2+} + L(H_2O)M'OO^{2+} \quad (2)$$

$$L(H_2O)M^{IV}O^{2+} + L(H_2O)M'OOH^{2+} + H^+ \rightarrow L(H_2O)_2M^{3+} + L(H_2O)M'OO^{2+} \quad (3)$$

The reactions studied here are formally analogous to those taking place between the organic species, e.g., $ROO^•/ROOH$ vs $Cr_{aq}OO^{2+}/Cr_{aq}OOH^{2+}$, but predicting the outcome of the all-metal reactions on the basis of the known $ROO^•/ROOH$ chemistry is by no means straightforward. Electronic properties, charge distribution, spin density on the terminal oxygens, and (less importantly) overall charges differ greatly for $ROO^•$ and $L(H_2O)OO^{2+}$. This study allows a direct comparison between purely organic and purely inorganic species and their chemistry in oxygen activation.



$L^1(H_2O)CrOO^{2+}$



$L^2(H_2O)CrOO^{2+}$

Experimental Section

Aqueous solutions of the superoxo, hydroperoxo, and aqua metal complexes were prepared by our previously published procedures.[21,28] Solutions of $Cr_{aq}OO^{2+}$ typically contained 50−100 mM CH_3OH which stabilizes the superoxo complex by removing traces of highly reactive $Cr^{IV}O^{2+}$.[11,21] UV−vis spectral and kinetic measurements utilized a Shimadzu 3101 PC spectrophotometer at a constant temperature of 25 ± 0.2 °C. For faster reactions, an

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OLIS RSM-1000 stopped-flow spectrophotometer was used. Water was used as solvent throughout.

The kinetics of reaction 2 were studied by the method of initial rates. The concentration of each species was varied to the maximum extent possible. In the $Cr_{aq}OO^{2+}$/$LRh(H_2O)OOH^{2+}$ reactions, $[Cr_{aq}OO^{2+}] = (7-160) \times 10^{-6}$ M, $[(NH_3)_4(H_2O)RhOOH^{2+}] = (1.4-14) \times 10^{-5}$ M, $[L^1(H_2O)RhOOH^{2+}] = (1.4-18) \times 10^{-5}$ M, $[L^2(H_2O)RhOOH^{2+}] = (1.2-16) \times 10^{-5}$ M, and $[H^+] = 0.02-0.04$ M. The narrow available $[H^+]$ range was determined by the effect of H^+ on the limited lifetimes of the two reactants. Hydroperoxorhodium complexes are more stable at low H^+ (<0.01 M), but the superoxochromium species require 0.1 M H^+ for maximum stability. Our standard medium, 0.02 M H^+, was chosen as a compromise where both species exhibit reasonably long lifetimes (minutes to hours, depending on concentrations).

The overall stoichiometry of the $Cr_{aq}OO^{2+}$/$L(H_2O)RhOOH^{2+}$ reactions was calculated from the absorbance changes at 270 nm, where the molar absorptivities for the reactants and products are: 3.0×10^3 ($Cr_{aq}OO^{2+}$), 1.6×10^3 ($L(H_2O)RhOOH^{2+}$), 1.5×10^3 ($Cr_{aq}OOH^{2+}$), and $(9.2-9.5) \times 10^3$ M^{-1} cm^{-1} for $L(H_2O)RhOO^{2+}$ (L = $(NH_3)_4$, L^1, L^2). For a 1:1 $[Cr_{aq}OO^{2+}]$/ $L(H_2O)RhOOH^{2+}$ stoichiometry, the average calculated $\Delta\epsilon$ is $6.2 (\pm 0.2) \times 10^3$ M^{-1} cm^{-1} for all three rhodium complexes. A more realistic standard deviation for $\Delta\epsilon$ is probably around 10%, which also places a 10% error on the kinetic data obtained from initial rates. For that reason, we report the kinetic data to only two significant figures.

The $L^2(H_2O)CoOOH^{2+}$/$Cr_{aq}OO^{2+}$ and $(NH_3)_4(D_2O)RhOOD^{2+}$/$Cr_{aq}O^{2+}$ reactions were studied under pseudo-first-order conditions using one of the reagents in large excess. The reactions were monitored for at least three half-lives, and the rate constants were obtained from the fits to the exponential rate equation, eq 4, where Abs_t, Abs_∞, and Abs_0 represent absorbance at indicated times. Some of the kinetic data for the $L^2(H_2O)CoOOH^{2+}$/$Cr_{aq}OO^{2+}$ reaction were collected under second-order conditions and fitted to eq 5, where $[A]_0$ and $[B]_0$ are the initial concentrations of the limiting and excess reagents, respectively, $\Delta_0 = a[B]_0 - b[A]_0$, and a and b are the stoichiometric factors.

$$Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)\exp(-k_{obs}t) \qquad (4)$$

$$Abs_t = \frac{Abs_\infty + \left\{Abs_0\left(1 - \frac{[A]_0}{[B]_0}\right) - Abs_\infty\right\}e^{-k\Delta_0 t}}{1 - \frac{[A]_0}{[B]_0}e^{-k\Delta_0 t}} \qquad (5)$$

Oxygen evolution was measured with a YSI model 5300 biological oxygen monitor at 25 ± 1 °C. In-house-distilled water was further purified by a passage through a Barnstead EASYpure III system. The program Chemical Kinetics Simulator was used to simulate kinetic traces.

Results

$Cr_{aq}OO^{2+}$/$L(H_2O)RhOOH^{2+}$ Reaction (L = $(NH_3)_4$, L^1, L^2). An intense absorption band at ~270 nm, characteristic of the superoxorhodium complexes, developed upon mixing of $Cr_{aq}OO^{2+}$ with $(NH_3)_4(H_2O)RhOOH^{2+}$ or with the macrocyclic analogues $L(H_2O)RhOOH^{2+}$ (L = L^1, L^2). Spectral data are shown in Figures S1−S2 in the Supporting Information. The observed absorbance change was consistent with the reaction in eq 6. The stoichiometry, $\Delta[Cr_{aq}OO^{2+}]/\Delta[L(H_2O)RhOOH^{2+}] = 1:1$ was calculated from the molar absorptivity change, $\Delta\epsilon_{270} = 6.2 (\pm 0.3) \times 10^3$ M^{-1} cm^{-1} for the reactions with all three rhodium complexes.

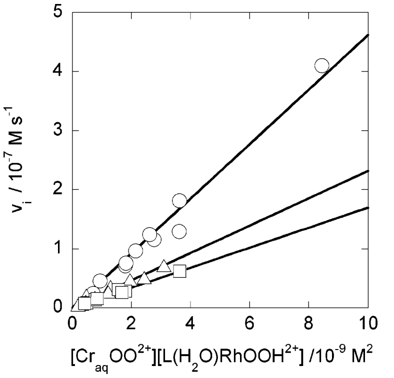

Figure 1. Dependence of the initial rates of oxidation of $L(H_2O)RhOOH^{2+}$ with $Cr_{aq}OO^{2+}$ on the concentration product $[Cr_{aq}OO^{2+}] \times [L(H_2O)RhOOH^{2+}]$, where L = $(NH_3)_4$ (circles), L^1 (triangles), and L^2 (squares). Conditions: $[Cr_{aq}OO^{2+}] = (7-160) \times 10^{-6}$ M, $[Rh(H_2O)(NH_3)_4OOH^{2+}] = (1.4-14) \times 10^{-5}$ M, $[L^1(H_2O)RhOOH^{2+}] = (1.4-18) \times 10^{-5}$ M, and $[L^2(H_2O)RhOOH^{2+}] = (1.2-16) \times 10^{-5}$ M, $[H^+] = \mu = 0.02$ M.

$$Cr_{aq}OO^{2+} + L(H_2O)RhOOH^{2+} \rightarrow Cr_{aq}OOH^{2+} + L(H_2O)RhOO^{2+} \quad L = (NH_3)_4, L^1, L^2 \qquad (6)$$

The kinetics were expected to follow a mixed second-order rate law, but the absorbance−time traces at 270 nm were more complicated and exhibited either some tailing in the later stages of the reaction or an apparent exponential behavior under non-pseudo-first-order conditions. In all of the cases, the deviations from the expected kinetics could be explained and simulated by the known slow decomposition of the reactants, both $Cr_{aq}OO^{2+}$ [11,12] and $L(H_2O)RhOOH^{2+}$,[29] and/or products, including $Cr_{aq}OOH^{2+}$,[28] at longer times. Even though such decay reactions are slow on the time scale of reaction 6, the effect on the absorbance change becomes measurable late in the reaction. For that reason, we turned to the initial rates for all the kinetic determinations for reaction 6.

Plots of the initial rates, v_i, against the product of the initial reactant concentrations, $[L(H_2O)CrOO^{2+}]_i \times [L(H_2O)RhOOH^{2+}]_i$, are linear throughout the range of concentrations used, as shown in Figure 1 for the reactions of $Cr_{aq}OO^{2+}$ and in Figure S3 for those of $L^1(H_2O)CrOO^{2+}$. This result establishes first-order dependence on the concentration product, as well as on each individual species, eq 7. Also, the plots of log(v_i) vs log($[Cr_{aq}OO^{2+}] \times [L(H_2O)RhOOH^{2+}]$), shown in Figure S4, are linear with slopes (i.e., reaction orders) of 1.08 (L = $(NH_3)_4$), 0.97 (L^1), and 0.99 (L^2), confirming the rate law in eq 7. Analogous plots for the reactions of $L^1(H_2O)CrOO^{2+}$, Figure S5, confirmed the same form of the rate law for this complex as well.

$$v_i = k[L(H_2O)CrOO^{2+}][L(H_2O)RhOOH^{2+}] \qquad (7)$$

The rate constants k_6, obtained as slopes of the lines in Figure 1, have the following values: 46 ± 2 (L = $(NH_3)_4$), 23 ± 1 (L^1), and 17 ± 1 M^{-1} s^{-1} (L^2) in 0.020 M $HClO_4$.

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Table 1. Summary of Kinetic Data for the Reactions of Superoxo and Oxo Complexes of Chromium with Hydroperoxides[a]

oxidant	reductant	$k//M^{-1}\ s^{-1}$	kie[b]
$Cr_{aq}OO^{2+}$	$(NH_3)_4(H_2O)RhOOH^{2+}$	46 ± 2[c]	2.9
	$(NH_3)_4(D_2O)RhOOD^{2+}$	16 ± 2	
	$L^1(H_2O)RhOOH^{2+}$	23 ± 1	
	$L^2(H_2O)RhOOH^{2+}$	17 ± 1[c]	
	$L^2(H_2O)CoOOH^{2+}$	135 ± 10	~3
	H_2O_2	$\sim 10^{-3}$	
$L^1(H_2O)CrOO^{2+}$	$(NH_3)_4(H_2O)RhOOH^{2+}$	19 ± 1	
	$L^1(H_2O)RhOOH^{2+}$	36 ± 2	
	$L^2(H_2O)RhOOH^{2+}$	<2	
$Cr_{aq}O^{2+}$	$(NH_3)_4(H_2O)RhOOH^{2+}$	$>10^4$	>5
	$(NH_3)_4(D_2O)RhOOD^{2+}$	$(2.00 \pm 0.20) \times 10^3$	
	$Cr_{aq}OOH^{2+}$[d]	$(1.30 \pm 0.10) \times 10^3$	5.0
	H_2O_2[e]	$(1.90 \pm 0.10) \times 10^2$	3.6
	tert-BuOOH	$(1.60 \pm 0.37) \times 10^2$	12
	tert-BuOOD	13.5 ± 1.8	

[a] Acidic aqueous solutions, 25 °C. [b] kie = k_{H_2O}/k_{D_2O}. [c] Reverse reaction has $k < 1\ M^{-1}\ s^{-1}$. [d] Reference 30. [e] Reference 31.

Adding up to 7.0 mM Mn^{2+} or increasing the methanol concentration from the typical 0.1 to >1 M had no effect on the initial rates. These results strongly argue against the involvement $Cr^{IV}{}_{aq}O^{2+}$ which reacts readily with both of the added reagents, eq 8−9. The CH_3OH/O_2 combination converts $Cr^{IV}{}_{aq}O^{2+}$ to $Cr_{aq}OO^{2+}$, which would make the reaction catalytic in $Cr_{aq}OO^{2+}$. $Mn_{aq}{}^{2+}$ replaces $Cr^{IV}{}_{aq}O^{2+}$ with the (typically) much less reactive $Mn_{aq}{}^{3+}$, which would slow down the reaction if $Cr^{IV}{}_{aq}O^{2+}$ were an important intermediate en route to products.

$$Cr^{IV}{}_{aq}O^{2+} \xrightarrow{CH_3OH} Cr_{aq}{}^{2+} \xrightarrow{O_2,fast} Cr_{aq}OO^{2+} \tag{8}$$

$$Cr^{IV}{}_{aq}O^{2+} + Mn_{aq}{}^{2+} (+2H^+) \rightarrow Cr_{aq}{}^{3+} + Mn_{aq}{}^{3+} \tag{9}$$

Measurements with an oxygen electrode confirmed that no O_2 was evolved in the reaction between $Cr_{aq}OO^{2+}$ and $Rh(H_2O)(NH_3)_4OOH^{2+}$, except for the small amounts generated by the slow decomposition of the reactants over long times. The sluggish electrode response required that these measurements be made at times greater than 45 s after the reaction was initialized, i.e., somewhat later than the spectrophotometric measurements of initial rates (usually covering the first 60 s for a reaction taking ≥15 min for completion). There is, however, no reason to believe that the chemistry in the first minute differs from that taking place in the next several minutes. All the kinetics data are summarized in Table 1.

An experiment was carried out in D_2O, which converts $Rh(H_2O)(NH_3)_4OOH^{2+}$ to $Rh(D_2O)(NH_3)_4OOD^{2+}$. We have shown earlier that the replacement of coordinated and solvent H_2O by D_2O had no effect on the rate constants for hydrogen-atom abstraction by $Cr_{aq}OO^{2+}$ from the rhodium hydrides $L(H_2O)RhH^{2+}$.[28] We assume that the same is true in the reaction with the hydroperoxides, so that any observed effect of D_2O would have to come from the hydroperoxo hydrogen. The reaction of 5.8×10^{-5} M $Rh(D_2O)(NH_3)_4OOD^{2+}$ and 2.9×10^{-5} M $Cr_{aq}OO^{2+}$ in D_2O (99% D) yielded $k_6 = 16\ M^{-1}\ s^{-1}$, i.e., kie = k_H/k_D = 2.9.

Attempts were made to study the reverse of reaction 6, but even at the highest available concentrations of $Cr_{aq}OOH^{2+}$ (0.1 mM) and $L(H_2O)RhOO^{2+}$ (0.2 mM) (L = $(NH_3)_4$ and L^2), no reaction was observed during the lifetime of the hydroperoxochromium complex, which slowly ($t_{1/2} \approx 15$ min) decomposed to $Cr_{aq}{}^{3+}$ and $HCrO_4{}^-$. These data allow us to place a conservative limit on the rate constant for the reverse of reaction 6, $k_{-6} < 1\ M^{-1}\ s^{-1}$ for both rhodium complexes examined. The combination with the forward rate constants listed in Table 1 places the lower limit on the equilibrium constants $K_6 = k_6/k_{-6} > 45$ for the reaction with $(NH_3)_4(H_2O)RhOOH^{2+}$, and $K_6 > 17$ for $L^2(H_2O)RhOOH^{2+}$.

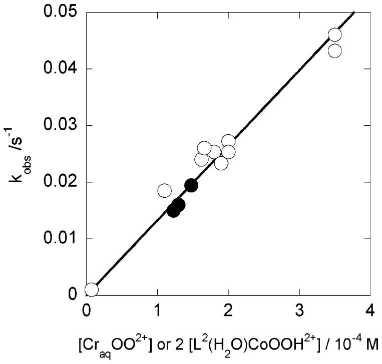

Figure 2. Plot of k_{obs} vs excess reagent, $[Cr_{aq}OO^{2+}]$ (filled circles) or $2[L^2(H_2O)CoOOH^{2+}]$ (open circles), for the oxidation of $L^2(H_2O)CoOOH^{2+}$ with $Cr_{aq}OO^{2+}$. $[HClO_4]$ = 0.05 M.

$Cr_{aq}OO^{2+}/L^2(H_2O)CoOOH^{2+}$ Reaction. The oxidation of this cobalt complex was faster than the oxidation of the hydroperoxorhodium analogues, which made the background decomposition of all the components insignificant on the time scale of the reaction, and allowed full kinetic analysis of the kinetic traces under both pseudo-first-order and second-order conditions.

The absorbance changes at 295 nm established a 2:1 $Cr_{aq}OO^{2+}/L^2(H_2O)CoOOH^{2+}$ stoichiometry. With either reagent present in large excess, the kinetic traces were exponential and yielded pseudo-first-order rate constants, k_{obs}. A plot of k_{obs} against the concentration of excess reagent adjusted for the stoichiometric factor, i.e., $[Cr_{aq}OO^{2+}]$ or $2[L^2(H_2O)CoOOH^{2+}]$, is linear, Figure 2, and yields $k_{10} = 135 \pm 10\ M^{-1}\ s^{-1}$ in 0.050 M $HClO_4$. The reaction was significantly slower in D_2O (by at least a factor of 2−3), but the precise rate constants and kie were not determined because the secondary background reactions once again interfered on these longer time scales.

$$2Cr_{aq}OO^{2+} + L^2(H_2O)CoOOH^{2+} (+H^+ + H_2O) \rightarrow 2Cr_{aq}OOH^{2+} + L^2Co(H_2O)_2{}^{3+} + O_2 \tag{10}$$

The data obtained with comparable concentrations of the two reagents (0.06−0.10 mM) were fitted to the second-order rate equation and yielded $k_{10} = 145 \pm 15\ M^{-1}\ s^{-1}$, in good agreement with the value obtained in Figure 2.

All the results, including the 2:1 stoichiometry, are consistent with the mechanism in eqs 11−14. The product of the initial 1:1 reaction is a superoxocobalt complex which readily dissociates O_2, $k_{12} = 2 \times 10^4\ s^{-1}$, $K_{12} = 4 \times 10^{-3}$

M.[32] The $\mathrm{L^2Co(H_2O)_2^{2+}}$ generated in reaction 12 reacts rapidly with the second equivalent of $\mathrm{Cr_{aq}OO^{2+}}$, eq 13.

$$\mathrm{Cr_{aq}OO^{2+} + L^2(H_2O)CoOOH^{2+} \rightarrow Cr_{aq}OOH^{2+} + L^2(H_2O)CoOO^{2+}} \quad (11)$$

$$\mathrm{L^2(H_2O)CoOO^{2+} + H_2O \rightleftarrows L^2Co(H_2O)_2^{2+} + O_2} \quad (12)$$

$$\mathrm{L^2Co(H_2O)_2^{2+} + Cr_{aq}OO^{2+}\ (+H^+) \rightarrow L^2Co(H_2O)_2^{3+} + Cr_{aq}OOH^{2+}} \quad \text{fast} \quad (13)$$

$\mathrm{Cr_{aq}OO^{2+}/H_2O_2}$ Reaction. The rate of disappearance of $\mathrm{Cr_{aq}OO^{2+}}$ increased only slightly when $\leq$0.10 M $\mathrm{H_2O_2}$ was added to the solutions of this complex. At 0.10 M $\mathrm{H_2O_2}$, the rate was approximately twice as large as the spontaneous decomposition rate. Under the assumption that the reaction obeys mixed second-order kinetics, we estimate $k_{\mathrm{H_2O_2}} \approx 10^{-3}$ $\mathrm{M^{-1}\ s^{-1}}$.

$\mathrm{L^1(H_2O)CrOO^{2+}/L(H_2O)RhOOH^{2+}}$ Reaction (L = $\mathrm{(NH_3)_4}$, $\mathrm{L^1}$, $\mathrm{L^2}$). The reactions with this macrocyclic superoxochromium complex, eq 14, also proceeded to completion and yielded a rate constant $k_{14} = 19 \pm 1\ \mathrm{M^{-1}\ s^{-1}}$ for $\mathrm{(NH_3)_4(H_2O)RhOOH^{2+}}$ and 36 ± 2 for $\mathrm{L^1(H_2O)RhOOH^{2+}}$. No reaction was observed for the sterically more encumbered $\mathrm{L^2(H_2O)RhOOH^{2+}}$, $k < 2\ \mathrm{M^{-1}\ s^{-1}}$. The reverse of reaction 14 could not be studied because the chromium hydroperoxo product undergoes rapid irreversible conversion to Cr(V), followed by decomposition.[33]

$$\mathrm{L^1(H_2O)CrOO^{2+} + L(H_2O)RhOOH^{2+} \rightarrow L^1(H_2O)CrOOH^{2+} + L(H_2O)RhOO^{2+}} \quad (14)$$

$\mathrm{Cr^{IV}_{aq}O^{2+}/Rh(NH_3)_4(D_2O)OOD^{2+}}$ Reaction. The reaction of 10 μM $\mathrm{Cr^{IV}_{aq}O^{2+}}$ with 18 μM $\mathrm{(NH_3)_4(H_2O)RhOOH^{2+}}$ was complete in less than 5 s in conventional spectrophotometric experiments, placing a limit on the rate constant at $>10^4$ $\mathrm{M^{-1}\ s^{-1}}$. Stopped-flow measurements were not feasible in $\mathrm{H_2O}$ where $\mathrm{Cr^{IV}_{aq}O^{2+}}$ decays in about 1 min in 0.10 M $\mathrm{HClO_4}$, i.e., in the amount of time required to load the solutions into the instrument. In $\mathrm{D_2O}$, the reaction was slower and measurable by conventional spectrophotometry. Experiments were conducted with the nonabsorbing $\mathrm{Cr^{IV}_{aq}O^{2+}}$ in excess over $\mathrm{(NH_3)_4(D_2O)RhOOD^{2+}}$. The superoxorhodium complex was produced quantitatively in accordance with eq 15.

$$\mathrm{Cr^{IV}_{aq}O^{2+} + (NH_3)_4(D_2O)RhOOD^{2+}\ (+D^+) \rightarrow Cr_{aq}^{3+} + (NH_3)_4(D_2O)RhOO^{2+} + D_2O} \quad (15)$$

Under pseudo-first-order conditions, kinetic traces were exponential and yielded the rate constants k_{obs} that are plotted against the average concentration of $\mathrm{Cr^{IV}_{aq}O^{2+}}$ in Figure 3.

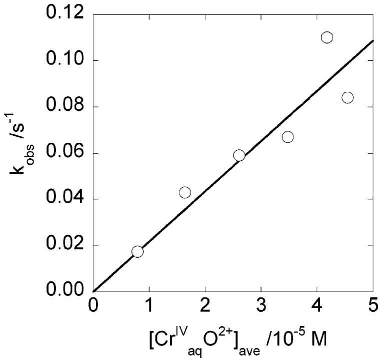

Figure 3. Plot of k_{obs} against the average concentration of $\mathrm{Cr_{aq}O^{2+}}$ for the reaction with $\mathrm{(NH_3)_4(D_2O)RhOOD^{2+}}$ (3.5−10 μM) in $\mathrm{D_2O}$ at $[\mathrm{D^+}] = \mu = 0.10$ M.

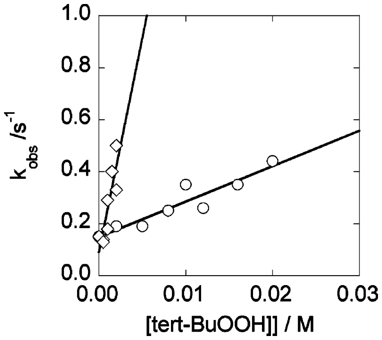

Figure 4. Plot of k_{obs} against the concentration of *tert*-BuOOH for the reaction with $\mathrm{Cr^{IV}_{aq}O^{2+}}$ (30−50 μM) in the presence of 3.0 mM $\mathrm{CH_3OH}$ in 0.10 M $\mathrm{HClO_4}$ in $\mathrm{H_2O}$ (diamonds) and $\mathrm{D_2O}$ (circles).

From the slope, we obtained $k_{15} = (2.2 \pm 0.2) \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ for the $\mathrm{Cr_{aq}O^{2+}}$/ $[\mathrm{(NH_3)_4(D_2O)RhOOD^{2+}}]$ reaction. The combination with the estimated lower limit in $\mathrm{H_2O}$ yields a kie >5.

$\mathrm{Cr^{IV}_{aq}O^{2+}}$/*tert*-BuOOH Reaction. The absorbance differences between the reactants and products throughout the UV−visible range are too small for a direct kinetic measurements. The rate constant was determined by competition with methanol (3 mM) which reacts with $\mathrm{Cr_{aq}O^{2+}}$ in the presence of $\mathrm{O_2}$ to generate $\mathrm{Cr_{aq}OO^{2+}}$, as shown in eq 8. The formation of $\mathrm{Cr_{aq}OO^{2+}}$ was monitored at 293 nm. The observed rate constant increased, and the amount of generated $\mathrm{Cr_{aq}OO^{2+}}$ decreased with increasing concentrations of *tert*-BuOOH, in accordance with a scheme whereby $\mathrm{CH_3OH}$ and *tert*-BuOOH compete for $\mathrm{Cr_{aq}O^{2+}}$, eq 16. The slopes of the plots in Figure 4 yielded the rate constant k_{BuOOH} in the two solvents, 160 ($\mathrm{H_2O}$) and 13.5 $\mathrm{M^{-1}\ s^{-1}}$ ($\mathrm{D_2O}$).

$$-\mathrm{d}[\mathrm{Cr_{aq}O^{2+}}]/\mathrm{d}t = (k_8[\mathrm{CH_3OH}] + k_{\mathrm{BuOOH}}[\textit{tert}\text{-}\mathrm{BuOOH}])[\mathrm{Cr_{aq}O^{2+}}] \quad (16)$$

Discussion

The stoichiometry, products, kinetics, and isotope effects all point to HAT as the most likely mechanism for the superoxo/hydroperoxo reactions presented for a general case in eq 2. To the best of our knowledge, this is the first reported example of such chemistry taking place between two inorganic species. The analogous reaction in the absence of metals is the identity $\mathrm{HO_2^{\bullet}/H_2O_2}$ reaction, not observable

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Table 2. Kinetic and Thermodynamic Data for Hydrogen-Atom Transfer to $Cr_{aq}OO^{2+}$

reductant	$k_{CrOO}/M^{-1}s^{-1}$	BDE /kJ mol^{-1}	K
$(NH_3)_4(H_2O)Rh{-}H^{2+}$	135	ca. 250 (Rh−H)	10^{14}
$L^1(H_2O)Rh{-}H^{2+}$	129	ca. 250 (Rh−H)	10^{14}
$L^2(H_2O)Rh{-}H^{2+}$	24	ca. 250 (Rh−H)	10^{14}
$(NH_3)_4(H_2O)RhOO{-}H^{2+}$	45	< 321 (O−H)[a]	>45
$L^1(H_2O)RhOO{-}H^{2+}$	23	< 322 (O−H)[a]	>23
$L^2(H_2O)RhOO{-}H^{2+}$	16.9	< 323 (O−H)[a]	>17
ArOH[b]	1.24[c]	340[d]	2×10^{-2}
t-BuCHO	0.16[e]	371[f]	4×10^{-8}

[a] Calculated from the equilibrium constant and taking bde for $Cr_{aq}OO{-}H^{2+}$ = 330 kJ/mol (solution value).[28] [b] Ar = 2,6-$(t\text{-}Bu)_2$(4-$CMe_2CH_2NH_3^+$)C_6H_2. [c] Reference 35. [d] Value for 2,4,6-$(t\text{-}Bu)_3C_6H_2OH$.[36] [e] Reference 23. [f] Value for EtCHO.[36]

under normal conditions in the absence of isotopic labeling. The Haber−Weiss reaction of eq 16 involves the same reactants, but the chemistry[34] is quite different from that observed with the metal-based species in this work.

$$H_2O_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + H_2O + O_2 \qquad (16)$$

The most unexpected finding in this work is the similarity in the rate constants for hydrogen abstraction by $Cr_{aq}OO^{2+}$ from $L(H_2O)RhOOH^{2+}$and from the previously studied[28] $L(H_2O)RhH^{2+}$. The same is true for the oxidation of the same two groups of rhodium complexes by $Cr_{aq}O^{2+}$.

The difference in bond dissociation energies (bde) between $L(H_2O)RhH^{2+}$ (ca 250 kJ/mol)[28] and $Cr_{aq}OOH^{2+}$ (ca 330 kJ/mol)[28] places the equilibrium constant for reaction 17 at about 10^{14}.

$$L(H_2O)RhH^{2+} + Cr_{aq}OO^{2+} \rightarrow L(H_2O)Rh^{2+} + Cr_{aq}OOH^{2+} \qquad (17)$$

The bde for $L(H_2O)RhOO{-}H^{2+}$ is not available, but it has to be less than that for $Cr_{aq}OO{-}H^{2+}$ given that the reverse of reaction 6 was not observed, $k_{-6} < 1$ M^{-1} s^{-1}. The combination of the kinetic data for the forward and reverse reaction places the equilibrium constant K_6 at ≥(17−45) for the three hydroperoxo rhodium complexes, i.e., about 10^{12}-fold lower than K_{17} for the corresponding hydrides, as summarized in Table 2. This translates into a bde for RhOO−H of ≤321 kJ/mol. Admittedly, this figure is only an upper limit, but several observations suggest that the reduction potential of $L(H_2O)RhOO^{2+}$, as well as the bde of $L(H_2O)RhOO{-}H^{2+}$, are not dramatically smaller than those of the chromium analogues. This conclusion is based on the similar reactivity of superoxorhodium and superoxochromium complexes toward tempo[29] and other nitroxyl free radicals ($E^0 \leq 0.92$ V) and on the failure to observe the reverse reaction between the hydroperoxo complexes and oxoammonium cations. Also, none of the hydroperoxo complexes are oxidized by tempo. In other words, the O−H bde in $L(H_2O)RhOO{-}H^{2+}$ is probably close to the estimated upper limit of ≤321 kJ/mol.

In view of the enormous difference in the driving forces, the similarity in rate constants for reactions 17 and 6 are astounding. Moreover, hydrogen bonding to the solvent water should be stronger for the hydroperoxo complexes, which should inhibit reaction 6 even more.

In a formal sense, the two reactions are similar, but they differ in one major aspect. In reaction 17, the rhodium−hydrogen bond is broken and the oxidation state of the metal changes from 3+ to 2+. In reaction 6, the chemistry takes place entirely at the oxygen entity while the oxidation state of the metal remains unchanged. Nonetheless, it is not clear why reaction 17 should be so much slower, but there is no question that it is the unusual one as shown by the data in Table 2. The energies of element−hydrogen bonds for the other substrates examined (pivaldehyde,[21] phenols,[35] and hydroperoxides) fall in the range 320−371 kJ/mol,[36] but the rate constants are only negligibly or moderately lower than those for rhodium hydrides (bde ≈ 250 kJ/mol). Even though the kinetics qualitatively follow thermodynamics, the most dramatic change in the bde (rhodium hydrides to hydroperoxides) results in the smallest relative change in the rate constants.

Another interesting result was obtained in the oxidation of a water-soluble substituted phenol (ArOH) and of pivaldehyde by $Cr_{aq}OO^{2+}$, although in this case it is only the magnitude of the effect, but not the direction, that appears unusual. The equilibrium constant for the pivaldehyde reaction is almost 6 orders of magnitude smaller than that for ArOH, and the identity reactions involving C−H bonds in nonaqueous solvents are typically much slower than those involving O−H bonds.[37] On the basis of these considerations, one would predict a rate constant that is 10^5−10^6-fold greater for ArOH than for pivaldehyde, but the observed factor is <10, which represents an unusually strong response to the change of the medium from nonhydroxylic solvents to strongly hydrogen-bonding water. The decrease in the rate constant for $ArOH/ArO^{\bullet}$ identity reaction upon transfer to water can be expected to be no more than a factor of 10^2,[38−42] not nearly enough to explain the observed data. Steric factors may play a role, but they are already taken into account in the identity reaction which has $k = 200$ M^{-1} s^{-1} in CCl_4 for a closely related tri-*tert*-butylphenol.[43] Further discussion of these issues will have to await experimental determination of the rate constants for H-atom exchange reactions in water for the three couples involved, $ArOH/ArO^{\bullet}$, $RCHO/RC^{\bullet}O$, and $Cr_{aq}OO^{2+}/Cr_{aq}OOH^{2+}$.

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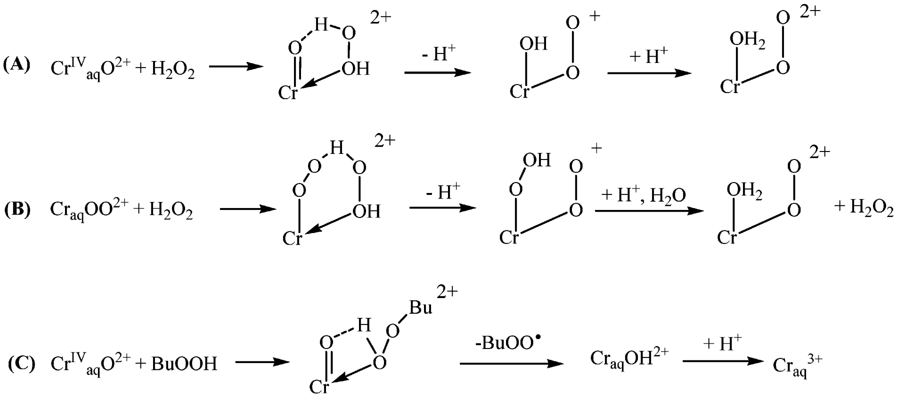

Figure 5. Hydrogen-atom transfer from coordinated hydroperoxide to $Cr_{aq}O^{2+}$ and $Cr_{aq}OO^{2+}$. There is a net chemical change in reactions (A) and (C), but the $Cr_{aq}OO^{2+}/H_2O_2$ reaction will result in site-exchange only, as in (B).

One distinguishing difference between the hydroperoxides and hydrides in their reactions with superoxometal complexes is the sensitivity to ligand steric requirements. HAT from the hydrides becomes imperceptibly slow when both partners bear macrocyclic ligands which prevent close contact between the metal acceptor and the hydride in the transition state which we picture as $[(H_2O)LRhHOOCrL(H_2O)^{4+}]^{\ddagger}$. As an example, the rate constant for hydrogen abstraction from $L^1(H_2O)RhH^{2+}$ by $Cr_{aq}OO^{2+}$ is 129 $M^{-1}\ s^{-1}$, and by $L^1(H_2O)CrOO^{2+}$, it is $<1\ M^{-1}\ s^{-1}$. In contrast, the rate constants for the reaction of $L^1(H_2O)RhOOH^{2+}$ with the same two superoxochromium reagents are 23 and 36 $M^{-1}\ s^{-1}$, the larger value being associated with the macrocyclic complex. Steric effects become a factor only when at least one of the macrocycles is the more crowded L^2, as exemplified by the slow $L^1(H_2O)CrOO^{2+}/L^2(H_2O)RhOOH^{2+}$ reaction, $k < 2\ M^{-1}\ s^{-1}$, Table 1. The diminished sensitivity to steric effects in the $L(H_2O)MOOH^{2+}/L(H_2O)M'OO^{2+}$ reactions can be attributed to the much greater separation between the metal centers (and their ligands) in the transition state for HAT, $[L(H_2O)RhOO(H)OOCr(H_2O)L^{4+}]^{\ddagger}$. In fact, in view of the four-atom separation between the metal centers, it is surprising that steric factors play a role at all. This result may point to a nonlinear transition state, as suggested by a reviewer. The moderate isotope effects are also consistent with this picture, although we can only speculate about the details of the transition-state structure at this point.

The driving force and reaction rates for oxidations by $Cr_{aq}O^{2+}$ are larger than those for $Cr_{aq}OO^{2+}$. In fact, in keeping with our earlier studies of HAT from various substrates,[11] the rate constants for the oxidation of metal hydroperoxides by $Cr_{aq}O^{2+}$ are about 10^2 times larger than those for the oxidations by $Cr_{aq}OO^{2+}$, i.e., $k_{CrO}/k_{CrOO} \approx 10^2$. Every additional example of such behavior reinforces our original interpretation,[23,28] i.e., that the factor of 10^2 is determined by the thermodynamics of the element−hydrogen bonds involved.

HAT to the two superoxochromium complexes is much faster for the hydroperoxometal species in Table 1 than for H_2O_2. This result would appear consistent with the more favorable thermodynamics for the hydroperoxo complexes, i.e., with the weakening of the hydroperoxo O−H bond upon coordination to the metal. The estimated O−H bde in $Cr_{aq}OO{-}H^{2+}$ in solution is 330 kJ/mol,[28] which represents a 39 kJ/mol decrease from the value for H_2O_2 and *tert*-BuOOH.[36] The RhOO−H bond, estimated at <320 kJ/mol, is even weaker. Thus observing a much slower reaction between $Cr_{aq}OO^{2+}$ and H_2O_2, $k \approx 10^{-3}\ M^{-1}\ s^{-1}$, is not surprising.

These considerations seem to be contradicted, however, by the findings in the reactions of $Cr_{aq}O^{2+}$ with H_2O_2 and *tert*-BuOOH. Both hydroperoxides appear to react unusually fast, with rate constants (190 and 160 $M^{-1}\ s^{-1}$, respectively) only slightly smaller than that for $Cr_{aq}OOH^{2+}$ ($k = 1.3 \times 10^3\ M^{-1}\ s^{-1}$). We attribute this result to prior coordination of H_2O_2 (and *tert*-BuOOH) to $Cr_{aq}O^{2+}$, as depicted in Figure 5a. In other words, the coordination of the peroxide to $Cr_{aq}O^{2+}$ itself followed by intramolecular electron transfer is kinetically almost as beneficial as is prior coordination to another metal, such as Cr_{aq}^{3+} or $L(H_2O)Rh^{3+}$ followed by a bimolecular process of eq 3.

In contrast, the $Cr_{aq}OO^{2+}/H_2O_2$ reaction is exceptionally slow and is the first case that violates our empirical rule about the reactivity of $Cr_{aq}O^{2+}$ being $\sim 10^2$ times greater than that of $Cr_{aq}OO^{2+}$ toward the same substrate. In the H_2O_2 reaction, this ratio is about 10^5.

There are two likely explanations for this apparent discrepancy. First, the substitution of *cis*-H_2O by H_2O_2 in the d^3 $Cr^{III}{}_{aq}OO^{2+}$ is probably much slower than that in the d^2 $Cr^{IV}{}_{aq}O^{2+}$, which would slow down the $Cr_{aq}OO^{2+}$ reaction. Moreover, even if the substitution in $Cr^{III}{}_{aq}OO^{2+}$ did take place, the HAT between the hydroperoxo and superoxo groups would result only in the exchange of sites, but no net chemical reaction, as sketched in Figure 5b. Thus, the small k_{CrO}/k_{CrOO} ratio in the reactions with H_2O_2 seems to be a result of the mechanistic change; the observed rate constant for the $Cr^{IV}{}_{aq}O^{2+}$ reaction is a combination of the binding constant for H_2O_2 and intramolecular HAT, but in the case of $Cr_{aq}OO^{2+}$, the rate constant is a measure of a true bimolecular event.

The reaction of $(NH_3)_4(D_2O)RhOOD^{2+}$ with $Cr_{aq}O^{2+}$ is >5-fold slower than the reaction of the protiated analogue, $(NH_3)_4(H_2O)RhOOH^{2+}$. A similarly large kie was observed in the reaction of $Cr_{aq}O^{2+}$ with $Cr_{aq}OOH^{2+}$,[31] and a somewhat smaller value, kie = 3.6, in the reaction with H_2O_2,[30] Table 1. Of all the hydroperoxides, the largest kie is exhibited by *tert*-BuOOH which has $k_H/k_D = 12$, comparable to that for

$Cr_{aq}O^{2+}/C_6H_5OH$ reaction (kie = 14.7).[44] The $Cr_{aq}O^{2+}$/*tert*-BuOOH reaction is believed to involve the precoordination of the peroxide, similar to H_2O_2, followed by intramolecular HAT. After this point, the two reactions differ. A formal proton shift between coordinated hydroperoxyl radical and $Cr^{III}-OH$ site in the H_2O_2 reaction yields the superoxochromium product, $Cr_{aq}OO^{2+}$, as shown in Figure 5a. The alkyl hydroperoxide cannot utilize this route. Our data are consistent with the alkylperoxyl radical, *tert*-$BuOO^{\bullet}$, dissociating from the metal, which would yield the observed product, $Cr_{aq}{}^{3+}$, as shown in Figure 5c. It is not obvious why the kie for the two hydroperoxides should be so different, unless the multiple proton shifts in the H_2O_2 reaction are part of the activation process, and not just rapid steps following HAT. In such a case, the opposing kie's for various steps could result in a smaller overall kie.

The $LMOO^{2+}/LMOOH^{2+}$ reactions resemble, at least formally, those of the $ROO^{\bullet}/R'OOH$ pairs (R, R′ = alkyl). The kinetics are somewhat faster for the organic counterparts but not by a large margin. For example, the rate constants for the reactions of *tert*-butylperoxyl radicals with several hydroperoxides are around 600 M^{-1} s^{-1} in isopentane,[45,46] i.e., about 10−50 times greater than the rate constants for the metal-based species in Table 2. The data are insufficient to establish whether the organic reactions are also subject to steric effects as was observed in the present work.

Given that the electronic and steric factors are quite different for peroxyalkyl radicals and the inorganic superoxometal complexes, the similar reactivity in hydrogen abstraction *within each series* is surprising. One might have expected that the large degree of electron transfer between oxygen and the metal in $LMOO^{2+}$, which is best considered a metal-coordinated superoxide anion, would reduce the ability of these complexes to engage in HAT. It is probably a combination of two features—unpaired electron density at the terminal oxygen and electron-withdrawing effect of the metal—that provides, respectively, the mechanism and thermodynamics for hydrogen abstraction by $LMOO^{2+}$.

For reasons of complex stability, the effect of acidity on the kinetics of the reactions described in this work could be examined only in a narrow range that typically covered no more than a factor of 2 in $[H^+]$. Within these narrow limits, no effect was observed, but this does not rule out acid-catalyzed pathways at higher H^+ concentrations, as was observed in some other oxidations by hydroperoxo and superoxo complexes.[11]

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Supporting Information Available: UV−vis spectra and rate plots, Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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