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Oxygen Activation with Transition-Metal Complexes in Aqueous Solution

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Coordination to transition-metal complexes changes both the thermodynamics and kinetics of oxygen reduction. Some of the intermediates (superoxo, hydroperoxo, and oxo species) are close analogues of organic oxygen-centered radicals and peroxides ($ROO^•$, ROOH, and $RO^•$). Metal-based intermediates are typically less reactive, but more persistent, than organic radicals, which makes the two types of intermediates similarly effective in their reactions with various substrates. The self-exchange rate constant for hydrogen-atom transfer for the couples $Cr_{aq}OO^{2+}/Cr_{aq}OOH^{2+}$ and $L^1(H_2O)RhOO^{2+}/L^1(H_2O)RhOOH^{2+}$ was estimated to be $10^{1\pm1}$ M^{-1} s^{-1}. The use of this value in the simplified Marcus equation for the $Cr_{aq}O^{2+}/Cr_{aq}OOH^{2+}$ cross reaction provided an upper limit $k_{CrO,CrOH} \leq 10^{(-2\pm1)}$ M^{-1} s^{-1} for $Cr_{aq}O^{2+}/Cr_{aq}OH^{2+}$ self-exchange. Even though superoxo complexes react very slowly in bimolecular self-reactions, extremely fast cross reactions with organic counterparts, i.e., acylperoxyl radicals, have been observed. Many of the intermediates generated by the interaction of O_2 with reduced metal complexes can also be accessed by alternative routes, both thermal and photochemical.

Introduction

Molecular oxygen is a powerful but kinetically sluggish oxidant. Two-electron oxidations of closed-shell organic substrates lack a convenient mechanism and are further thwarted by the triplet electronic structure of ground-state O_2. One-electron oxidations suffer from the poor thermodynamics of the initial step, as explained below.

The four-electron-reduction potential for the O_2/H_2O couple, 1.27 V in strongly acidic solutions, is an average of the four individual one-electron potentials shown in Figure 1a. The least facile first step ($E^0 = 0.12$ V) generates $HOO^•$, a powerful oxidant ($E^0 = 1.44$ V). Of the two remaining intermediates, one is a moderate (H_2O_2) and the other an extremely potent ($HO^•$) one-electron oxidant.

The small $O_2/O_2^{•-}(HOO^•)$ reduction potential is one of the reasons for the slow kinetics in one-electron oxidations, which do not suffer from spin restrictions. Another factor, which is essential in outer-sphere reactions, is the modest self-exchange rate constant (450 M^{-1} s^{-1}) for the $O_2/O_2^{•-}$ couple.[5]

Various approaches have been explored to overcome these kinetic barriers, to activate molecular oxygen for oxidations, and, ultimately, to replace the expensive, unsafe, corrosive, and waste-generating oxidants with the "greenest" and most economical of them all. Our focus, and that of several other groups, has been on the use of transition-metal complexes as activating agents. This area of our work is the topic of the present article. Unless stated otherwise, the kinetic data are quoted at 25 °C.

The emphasis of our research is on the reactivity of mononuclear superoxo, hydroperoxo, and oxo transition-metal complexes in aqueous solutions. There are clear connections and similarities but also some differences in the chemistry and oxidation states of "activated oxygen" in this work and those carried out by other groups in nonaqueous solutions with mononuclear and higher-nuclearity complexes. An especially active area focuses on both heme and nonheme complexes of iron,[6−10] copper,[11−15] and other metals[16−21] as models for

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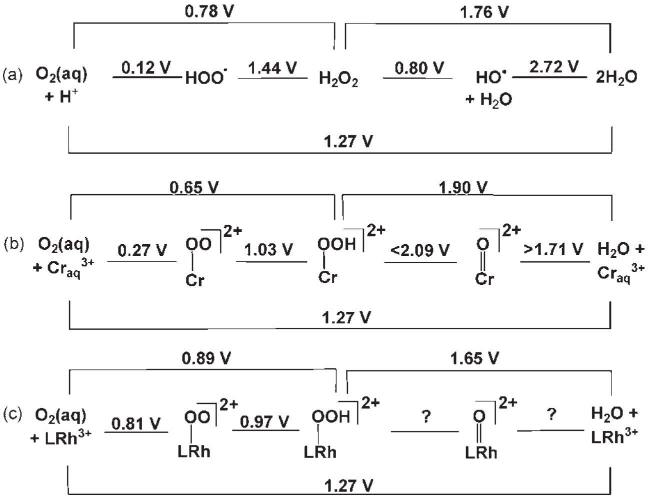

Figure 1. Reduction potentials for free and coordinated oxygen. Data are from refs 1−4. L = *meso*-Me_6-cyclam.

metalloenzymes as well as the enzymes themselves.[22] The greater complexity of the ligands (porphyrins, corroles, and bridging and end-on carboxylates) and the presence of more than one metal center in the molecule naturally lead to a larger number and types of intermediates, which can now include mixed-metal oxidation states,[23] bridging and end-on superoxide[24,25]/peroxide[26−29] groups, or isomeric dioxo versus μ-peroxo forms.[30−33] Despite the complexity of the structure and chemistry, the reactivity of such complex molecules can be sometimes reproduced with much simpler models in aqueous solution. As an example, macrocyclic hydroperoxochromium complexes $L(H_2O)CrOOH^{2+}$ (L = cyclam and *meso*-Me_6-cyclam) undergo a rapid intramolecular transformation to oxochromium(V) species, $L(O)Cr^{V}(OH)^{2+}$,[34−36] in close analogy with the chemistry at the iron center of cytochrome P450. More examples of this type of chemistry have been reported recently.[3738]

A unique aspect of aqueous transition-metal chemistry that cannot be duplicated in other solvents is the ability to manipulate chemical forms and the reactivity of various species, such as activated oxygen, by a simple change in the pH. Having a degree of control over the lifetime of an intermediate facilitates spectroscopic and kinetic studies and expands the range of methods and techniques that can be used in mechanistic work.

The high polarity and hydrogen-bonding ability of water also greatly impact the chemistry, but these features are not limited to water and can be exploited, at least to some extent, with other solvents as well. The beneficial effects of water on the oxygenation of carboxylate-bridged nonheme diiron complexes have been noted and attributed to a reversible shift of bridging carboxylates to chelating terminal positions.[39] Water-induced structural changes in these complexes are similar to those taking place in dioxygen-activating metalloenzymes.[40] The enhancement of the oxidizing ability of a binuclear $Fe^{III}Fe^{IV}$ complex of tris(2-pyridylmethyl)amine by the addition of water[41] was explained by the coordination of water to iron(III) and conversion of the bis(μ-oxo) structure to a ring-opened form with a terminal oxo group on iron(IV).

Thermodynamics

Activation by transition-metal complexes involves the coordination and partial reduction of O_2. The combination of the two processes changes the thermodynamics of the individual steps, as shown in Figure 1, and makes O_2 kinetically more reactive. The thermodynamics of the overall metal-assisted process are, of course, the same as that for the metal-free reduction of O_2 to H_2O, i.e., 1.27 V at pH 0.

Even though some of the values in Figure 1b are only estimates or limits, it is clear that the coordination of O_2 to Cr_{aq}^{3+} affects each of the four steps. The first electron is now removed more easily (E^0 = 0.27 V), but the superoxochromium complex $Cr_{aq}OO^{2+}$ (E^0 = 1.03 V) is a significantly weaker oxidant than $HOO^{•}$ (1.44 V). The hydroperoxochromium complex $Cr_{aq}OOH^{2+}$, on the other hand, has $E^0 \leq$ 2.09 V, about 1 V greater than that of H_2O_2 (0.80 V). Finally, despite its large reduction potential ($E^0 \geq 1.71$ V), $Cr^{IV}{}_{aq}O^{2+}$ is not nearly as oxidizing as $HO^{•}$ (2.72 V). The estimate for $Cr_{aq}OOH^{2+}$ is based on that for $Cr^{IV}{}_{aq}O^{2+}$, which was, in turn, derived from experimental observations with various reductants that could (or could not) be oxidized.

The availability of all four individual reduction potentials for Cr_{aq}^{3+}-mediated oxidation with O_2 appears to be the only such example in the literature,[1,2] even though two of the values are only limits. Partial data are available,[3,42] and shown in Figure 1c, for the $L^2Rh(H_2O)_2^{3+}$-mediated reaction (see Chart 1). The potential for the first step, E^0 = 0.81 V, is much greater than that for the uncoordinated oxygen, illustrating the enormity of the effect that metals can have on the thermodynamics of oxygen reduction.

The scarcity of thermodynamic data for metal−oxygen intermediates is not surprising, given the difficulties associated with measurements on species that are typically

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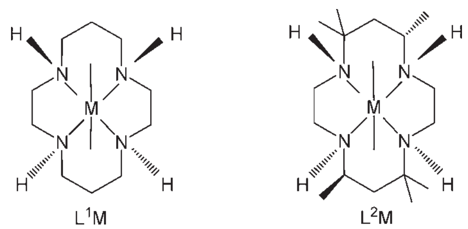
Chart 1. Structures of Some Complexes Used in This Work (M = Rh, Cr, Co)[a]



[a] Axial positions are occupied by H_2O/OH^- and/or activated oxygen (−OO, −OOH).

short-lived and present at low concentrations in complex mixtures with other intermediates and reagents. Even when feasible, spectroscopic and electrochemical measurements generate data that are often difficult to unravel. To obtain the critically important thermodynamic information for metal-activated oxygen, new methods and adaptations of the existing ones are needed.

One approach that has proven useful in our work is based on kinetics. If a convenient and specific reaction is found for a given intermediate, then the kinetic and thermodynamic parameters can be determined without interference from other species. As an example, the acidity constant of coordinated water in $(H_2O)L^2RhOOH^{2+}$ was determined[42] from the pH dependence of the reaction with I^-, shown in Figure 2. Other species present in reaction solutions, $(H_2O)_2L^2Rh^{3+}$ and possibly some H_2O_2, did not interfere because neither reacts with iodide on the time scale of the $(H_2O)L^2RhOOH^{2+}/I^-$ reaction.

The source of the first-order dependence on $[H^+]$ in a strongly acidic region ($0 \leq pH \leq 4$) in Figure 2 is believed to be the protonation of the hydroperoxide to generate small amounts of highly reactive $(H_2O)L^2Rh(H_2O_2)^{3+}$. Only a small fraction of the complex exists in this form even at the highest concentrations of H^+ used, which accounts for the observed linearity of the function over this entire pH range. At pH ≥ 4, the parent aqua−hydroperoxo form $(H_2O)L^2RhOOH^{2+}$ is the reactive species. Its concentration decreases as the pH approaches and finally exceeds the acidity constant of coordinated water, resulting in the observed pH−rate profile. This chemistry is shown in eqs 1−3 and leads to the rate law in eq 4. The solid line in Figure 2 is a fit to eq 4, yielding $K_a = 1.17 \times 10^{-7}$ M ($pK_a = 6.9$), $k_H = 525\ M^{-2}\ s^{-1}$, and $k_{H_2O} = 0.131\ M^{-1}\ s^{-1}$.

$$L^2(H_2O)RhOOH^{2+} \leftrightarrows L^2(HO)RhOOH^{+} + H^{+} \quad K_a \quad (1)$$

$$L^2(H_2O)RhOOH^{2+} + I^- + H^+ \longrightarrow \text{products} \quad k_H \quad (2)$$

$$L^2(H_2O)RhOOH^{2+} + I^- \longrightarrow \text{products} \quad k_{H_2O} \quad (3)$$

$$k_{obs} = \left(k_H[H^+] + \frac{k_{H_2O}[H^+]}{K_a + [H^+]}\right)[I^-] \quad (4)$$

Other types of equilibrium constants, such as those for O_2 binding/dissociation, are often determined from the kinetics of forward and reverse reactions. The dissociation of O_2 from $L^2(H_2O)RhOO^{2+}$, eq 5, was recently studied in the presence of several scavengers for $L^2(H_2O)Rh^{2+}$ and yielded a consistent value for $k_d = 2.18 \times 10^{-4}\ s^{-1}$.[3] The combination with the previously determined rate constant for O_2 binding to $L^2Rh(H_2O)^{2+}$ in laser-flash photolysis experiments, $k_O = 8.2 \times 10^7\ M^{-1}\ s^{-1}$,[43] yielded the equilibrium constant for O_2 binding, $K_O = k_O/k_d = 3.7 \times 10^{11}\ M^{-1}$.

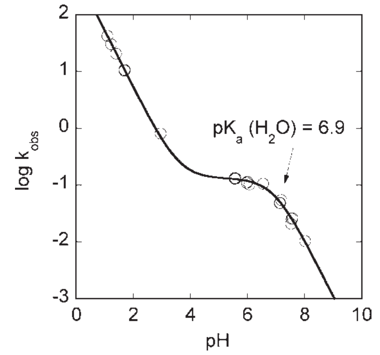
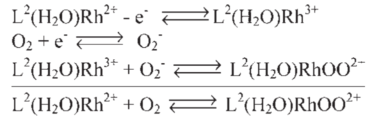


Figure 2. Determination of the pK_a of coordinated water in $(H_2O)L^2RhOOH^{2+}$ from the kinetics of iodide oxidation.

Scheme 1



$$\begin{aligned}
&L^2(H_2O)Rh^{2+} - e^- \rightleftharpoons L^2(H_2O)Rh^{3+}\\
&O_2 + e^- \rightleftharpoons O_2^-\\
&L^2(H_2O)Rh^{3+} + O_2^- \rightleftharpoons L^2(H_2O)RhOO^{2-}\\
\hline
&L^2(H_2O)Rh^{2+} + O_2 \rightleftharpoons L^2(H_2O)RhOO^{2+}
\end{aligned}$$

$$L^2(H_2O)Rh^{2+} + O_2 \underset{k_d}{\overset{k_O}{\rightleftharpoons}} L^2(H_2O)RhOO^{2+} \quad k_O \quad (5)$$

This value of K_O is 10^9-fold greater than that for the analogous cobalt complex, $L^2Co(H_2O)OO^{2+}$, for which $K_O = 300\ M^{-1}$, $k_O = 5.0 \times 10^6\ M^{-1}\ s^{-1}$, and $k_d = 1.66 \times 10^4\ s^{-1}$. The much stronger O_2 binding to rhodium can be rationalized by the much lower reduction potential for the $L^2Rh(H_2O)_2^{3+/2+}$ couple (0.13 V) than for cobalt (0.49[44] or 0.59 V[45]). The reaction in eq 5 involves both the binding/release of oxygen and a degree of electron transfer, which should be related to the reduction potential. The overall reaction can be (conceptually) broken into contributions from electron transfer and coordination, as in Scheme 1. Assuming that the two metal complexes differ only in their reduction potentials and depending on the choice of E^0 for cobalt, the binding constant K_O for the rhodium complex can be calculated to be greater than that for cobalt by a factor of 10^6 or 10^8, close to the observed factor of 10^9, making the difference in the reduction potentials a major source of the enhanced O_2 binding to $L^2(H_2O)Rh^{2+}$.

Thermodynamic data, obtained by a combination of approaches for various forms of $L^2(H_2O)Rh$-activated oxygen, are summarized in Figure 3. An interesting feature is the virtual pH independence of the reduction potential for the superoxo/hydroperoxo couple, $E^0 = 0.97$ V for $L^2(H_2O)RhOO^{2+}/L^2(H_2O)RhOOH^{2+}$ and 0.96 V for $L^2(HO)RhOO^{+}/L^2(HO)RhOOH^{+}$. This is the result of the acidity constants of

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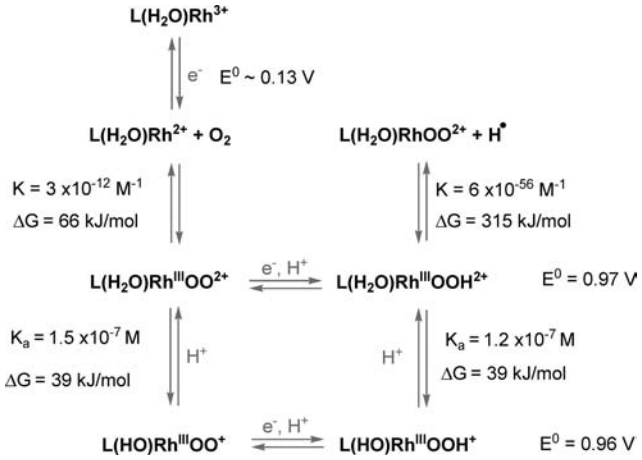

Figure 3. Thermodynamic data for oxygen activation by $L^2(H_2O)$-Rh^{2+}. Sources: refs 3, 42, and 46.

coordinated H_2O being almost identical for the superoxo and hydroperoxo complexes, 1.5×10^{-7} M and 1.2×10^{-7} M, so that they cancel each other in the square scheme of Figure 3.

Another point of interest is the actual value of the reduction potential for the superoxo complex, 0.97 V, which is almost 0.5 V smaller than the corresponding value for $HOO^•$ and alkylperoxyl radicals, $ROO^•$ ($E^0 = 1.47$ V).[47] Despite this difference in potentials, the reactivity of superoxometal complexes toward various substrates (see later) is not much lower than that of $ROO^•$.

Reactivity of Organic versus Metal-Based Intermediates

Bearing in mind that the ultimate goal of oxygen activation is the metal-catalyzed oxidation of (typically) organic substrates and that in such reactions both metal-based and substrate-derived intermediates will be generated, it is essential to explore the reactivity of both toward potential substrates. As shown later, it may also be critical to understand the reactivity of the two kinds of intermediates toward each other.

Formally, monometallic metal superoxo (LMOO, where L = ligand system and M = metal), hydroperoxo (LMOOH), and oxo (LMO) complexes are the respective analogues of alkylperoxyl radicals ($ROO^•$), alkyl hydroperoxides (ROOH), and alkoxyl radicals ($RO^•$). An abundance of kinetic and mechanistic data exists for the organic series.[48,49] Also, a number of studies have been carried out with metal complexes, but it has rarely been possible to examine different types of intermediates in the same metal−ligand system. Such a lack of systematic data is a serious impediment to the rational design of catalytic oxidation reactions.

The most complete series where systematic work has been possible is based on aquachromium ions, where intermediates containing oxygen in three different oxidation states (superoxo, hydroperoxo, and oxo)[1,50,51] are known, i.e., $Cr^{III}_{aq}OO^{2+}$, $Cr^{III}_{aq}OOH^{2+}$, and $Cr^{IV}_{aq}O^{2+}$. Also, several persistent superoxo and hydroperoxo compounds of aminorhodium(III) ions are available.[3,42,51]

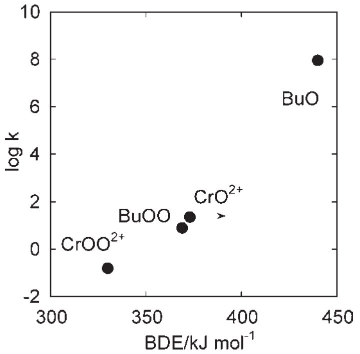

Figure 4. Plot of log *k* against the energy of the O−H bond formed upon hydrogen-atom abstraction from $(CH_3)_3CHO$ by $Cr_{aq}OO^{2+}$, $Cr_{aq}O^{2+}$, *tert*-$BuOO^•$, and *tert*-$BuO^•$. The BDE value for $Cr_{aq}O^{2+}$ is a lower limit. Data are from ref 52.

Hydrogen-Atom Transfer. One of the typical reactions of alkylperoxyl and alkoxyl radicals is hydrogen-atom transfer (HAT). This reaction type was also established in several cases for metal superoxo and oxo complexes. Typically, alkoxyl radicals and metal oxo complexes were found to be more reactive than the respective $ROO^•$ and LMOO compounds. For hydrogen-atom abstraction from one compound, pivaldehyde, kinetic data are available for all four types of intermediates considered here, i.e., *tert*-$BuO^•$, *tert*-$BuOO^•$, $Cr_{aq}O^{2+}$, and $Cr_{aq}OO^{2+}$.[52] As shown in Figure 4, a qualitative correlation exists between the kinetic data and the strength of the O−H bond formed. The latter is a good measure of the thermodynamics for the overall process in eq 6, for which ΔH = BDE(C−H) − BDE(XO−H) and $XO^• = RO^•, ROO^•, Cr_{aq}OO^{2+}$, and $Cr_{aq}O^{2+}$, and the hydrogen-atom donor, in this case pivaldehyde, is constant throughout the series.

$$(CH_3)_3CHO + XO^• \longrightarrow (CH_3)_3C^•O + XO{-}H \qquad (6)$$

Of the four oxidants in Figure 4, *tert*-$BuO^•$ is by far the most reactive. The rate constant exceeds that for $Cr_{aq}O^{2+}$ by a factor of 10^6. Similarly, *tert*-$BuOO^•$ reacts faster than $Cr_{aq}OO^{2+}$ does, although by a smaller factor. Despite the greater reactivity of the organic species, the metal-derived intermediates would be quite competitive in a scheme where both kinds are produced in the presence of an aldehyde. This is so because the more reactive organic intermediates are also shorter-lived. Alkoxyl radicals, such as *tert*-$BuO^•$, decay by β-elimination on microsecond time scales (eq 7), while the chromium counterpart $Cr_{aq}O^{2+}$ has a lifetime of about 1 min in acidic aqueous solutions at room temperature.

$$(CH_3)_3CO^• \longrightarrow CH_3{}^• + (CH_3)_2CO \qquad (7)$$

$ROO^•$ radicals decay in bimolecular self-reactions. The bulky *tert*-$BuOO^•$ reacts quite slowly ($k = 1 \times 10^4\ M^{-1}\ s^{-1}$),[53] but it would still disappear in several minutes at an initial concentration of 1 μM. The chromium analogue, $Cr_{aq}OO^{2+}$, persists for several hours. Thus, the

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

oxidant	reductant	$k//M^{-1}\ s^{-1}$	KIE[b]
$Cr_{aq}OO^{2+}$	$(NH_3)_4(H_2O)RhOOH^{2+}$	46	2.9
	$(NH_3)_4(D_2O)RhOOD^{2+}$	16	
	$L^1(H_2O)RhOOH^{2+}$	23	
	$L^2(H_2O)RhOOH^{2+}$	17	
	$L^2(H_2O)CoOOH^{2+}$	135	~3
	H_2O_2	$\sim 10^{-3}$	
$L^1(H_2O)CrOO^{2+}$	$(NH_3)_4(H_2O)RhOOH^{2+}$	19	
	$L^1(H_2O)RhOOH^{2+}$	36	
	$L^2(H_2O)RhOOH^{2+}$	< 2	

[a] Data are from ref 54. In acidic aqueous solutions at 25 °C. [b] KIE = k_{H_2O}/k_{D_2O}.

Table 2. Summary of the Thermodynamic Data for Some Superoxo and Hydroperoxo Complexes[a]

$L(H_2O)M$	E/V[b]	BDFE[c]	$pK_{a,MOO}$[d]	$pK_{a,MOOH}$[e]
$L^2(H_2O)Rh^{2+}$	0.97	315	6.6	6.9
$L^1(H_2O)Co^{2+}$	1.01[f]	318		~8
$(H_2O)_5Cr^{2+}$	1.03	320		
$L^2(H_2O)Co^{2+}$	1.05	322	6.42	
$L^1(H_2O)Cr^{2+}$			4.9	5.6
$L^2(H_2O)Cr^{2+}$				5.9
H[g]	1.44	360	4.8[h]	11.7[i]

[a] Data are from ref 42. [b] Reduction potential in V vs NHE for $L(H_2O)MOO^{2+}/L(H_2O)MOOH^{2+}$ couples at 1.0 M H^+. [c] Bond dissociation free energies in kJ/mol at 298 K for MOO−H bonds. [d] pK_a of coordinated H_2O in superoxo complexes. [e] pK_a of coordinated H_2O in hydroperoxo complexes. [f] In 0.5 M $HClO_4$. [g] The couple is $HO_2^{\bullet}/H_2O_2$. [h] pK_a of $HO_2^{\bullet}$. [i] pK_a of H_2O_2.

Table 3. Kinetic Data for HAT to $Cr_{aq}O^{2+}$ Ions[a]

hydrogen-atom donor	$k/M^{-1}\ s^{-1}$	KIE[bb]	k_{CrO}/k_{CrOO}
$L^1(H_2O)Rh{-}H^{2+}$	$\sim 10^4$		~80
$L^2(H_2O)Rh{-}H^{2+}$	1.1×10^3		47
$(NH_3)_4(H_2O)RhOO{-}H^{2+}$	$> 10^4$	> 5	220
$(NH_3)_4(D_2O)RhOO{-}D^{2+}$	2.00×10^3		125
$Cr_{aq}OO{-}H^{2+}$ [d]	1.30×10^3	5.0	
ArO−H	194		156
$(CH_3)_3CC(O){-}H$	23		144

[a] Data are from refs 52, 54, and 59. [b] KIE = k_{H_2O}/k_{D_2O}.

combination of reactivity and lifetimes of metal-based and organic intermediates makes them comparable in their ability to react with substrates, at least for the examples presented here. There appear to be no other instances where kinetic data are available for analogous organic and inorganic intermediates that would allow such a comparison.

To get a better understanding of the intrinsic reactivity of superoxo complexes in HAT and to estimate the HAT self-exchange rate constants for superoxo/hydroperoxo complexes, we examined the reactions of $Cr_{aq}OO^{2+}$ with several hydroperoxorhodium complexes, as in eq 8, where N_4 = $(NH_3)_4$, L^1, and L^2. Under the reaction conditions chosen (a slight excess of $Cr_{aq}OO^{2+}$), the reaction reached completion, as expected from the somewhat greater reduction potential for the $Cr_{aq}OO^{2+}/Cr_{aq}OOH^{2+}$ couple (1.03 V) than for rhodium (i.e., 0.97 V for $L^2(H_2O)RhOO^{2+}/L^2(H_2O)RhOOH^{2+}$). A summary of the rate constants is given in Table 1, along with the data for a macrocyclic superoxo chromium complex $L^1(H_2O)CrOO^{2+}$.

$$Cr_{aq}OO^{2+} + (N_4)(H_2O)RhOOH^{2+} \longrightarrow Cr_{aq}OOH^{2+} + (N_4)(H_2O)RhOO^{2+} \qquad (8)$$

The reaction products and the observed kinetic isotope effect k_{RhOOH}/k_{RhOOD} ~3 for the reactions of $Cr_{aq}OO^{2+}$ with the cobalt and rhodium complexes support the proposed HAT mechanism. The change of solvent from H_2O to D_2O that was required in these experiments should not contribute measurably to the observed KIE based on our previous work that showed no solvent effect in hydrogen-atom abstraction from rhodium hydrides by these same superoxometal complexes in H_2O and D_2O.[43]

With the exception of a slow reaction between $L^1(H_2O)CrOO^{2+}$ and the sterically encumbered $L^2(H_2O)RhOOH^{2+}$, $k < 2\ M^{-1}\ s^1$, the range of the rate constants for the reactions of both superoxochromium complexes with the hydroperoxides of rhodium and cobalt is strikingly narrow, $17 \le k \le 135\ M^{-1}\ s^{-1}$. The fact that the spread in the reduction potentials for these and related $LMOO^{2+}/LMOOH^{2+}$ couples is only about 0.08 V (Table 2) suggests that the HAT self-exchange rate constants are also close to each other, ca. $10^{1\pm1}\ M^{-1}\ s^{-1}$.

Another important comparison is that between free H_2O_2 and a coordinated hydroperoxide. As shown in Table 1, H_2O_2 reacts with $Cr_{aq}OO^{2+}$ ($k \sim 10^{-3}\ M^{-1}\ s^{-1}$) much more slowly than $LMOOH^{2+}$ complexes do. This result is simply a demonstration of peroxide activation by the metal and reflects the more favorable thermodynamics for the hydroperoxo complexes. The $Cr^{III}{}_{aq}$-OO−H and $L^2(H_2O)Rh^{III}$OO−H bonds are weaker than the HOO−H bond by 39 and 44 kJ/mol, respectively.[42,46]

Several rate constants for the oxidation of $LMOOH^{2+}$ complexes with an aquachromyl(IV) ion, $Cr^{IV}{}_{aq}O^{2+}$ (eq 9), have also been determined. The yields of superoxo products were quantitative, and the kinetics again exhibited moderate KIEs, supporting the HAT mechanism for $Cr^{IV}{}_{aq}O^{2+}$ as well. The data are listed in Table 3, along with the rate constants for HAT from several other substrates from our earlier work. In every case, $Cr^{IV}{}_{aq}O^{2+}$ reacts somewhat faster (about 10^2-fold) than $Cr_{aq}OO^{2+}$ does.

$$Cr^{IV}{}_{aq}O^{2+} + (N_4)(H_2O)RhOOH^{2+} \longrightarrow Cr^{III}{}_{aq}OH^{2+} + (N_4)(H_2O)RhOO^{2+} \qquad (9)$$

In the past, we had rationalized such data by the ≥43 kJ/mol thermodynamic advantage of $Cr^{IV}O^{2+}$ over $Cr_{aq}OO^{2+}$[52] and the assumption that $Cr^{IV}O^{2+}$ and $Cr_{aq}OO^{2+}$ have similar self-exchange rate constants for HAT.

The application of the simplified Marcus equation to the reactions of $Cr^{IV}O^{2+}$ and $Cr_{aq}OO^{2+}$ with a common hydrogen-atom donor, such as $(N_4)(H_2O)RhOOH^{2+}$ in reactions (8) and (9), leads to the expression in eq 10, where $k_{RhOO,RhOOH}$, $k_{CrO,CrOH}$, and $k_{CrOO,CrOOH}$ stand for HAT self-exchange rate constants for $(N_4)(H_2O)RhOO^{2+}$, $Cr_{aq}{}^{IV}O^{2+}$, and $Cr_{aq}OO^{2+}$, respectively, and $K_{CrO,CrOOH}$ is the equilibrium constant for the cross reaction between $\mathrm{Cr_{aq}}^{IV}\mathrm{O}^{2+}$ and $\mathrm{Cr_{aq}OOH^{2+}}$ (eq 11).

$$\frac{k_9}{k_8} = \frac{k_{\mathrm{CrO}}}{k_{\mathrm{CrOO}}} = \frac{(k_{\mathrm{Rh,\,Rh}} k_{\mathrm{CrO,\,CrOH}} K_{\mathrm{CrO,\,Rh}})^{0.5}}{(k_{\mathrm{Rh,\,Rh}} k_{\mathrm{CrOO,\,CrOOH}} K_{\mathrm{CrOOH,\,Rh}})^{0.5}} = \left(\frac{k_{\mathrm{CrO,\,CrOH}}}{k_{\mathrm{CrOO,\,CrOOH}}} K_{\mathrm{CrO,\,CrOOH}}\right)^{0.5} \tag{10}$$

$$\mathrm{Cr_{aq}}^{IV}\mathrm{O}^{2+} + \mathrm{Cr_{aq}OOH^{2+}} \leftrightarrows \mathrm{Cr}^{III}{}_{aq}\mathrm{OH}^{2+} + \mathrm{Cr}^{III}{}_{aq}\mathrm{OO}^{2+} \quad \Delta G^\circ \geq 43\ \mathrm{kJ/mol} \tag{11}$$

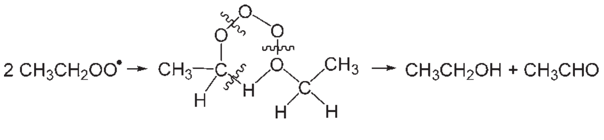
Because the self-exchange and thermodynamics data for the common reagent (Rh) in eq 10 cancel out, the ratio of the rate constants for HAT reactions of $\mathrm{Cr_{aq}}^{IV}\mathrm{O}^{2+}$ and $\mathrm{Cr_{aq}OO^{2+}}$ with any reagent is determined only by the data for $\mathrm{Cr_{aq}}^{IV}\mathrm{O}^{2+}$ and $\mathrm{Cr_{aq}OO^{2+}}$. If one assumes that $k_{\mathrm{CrO,CrOH}} \approx k_{\mathrm{CrOO,CrOOH}}$, then the calculated ratio $k_{\mathrm{CrO}}/k_{\mathrm{CrOO}}$ for HAT reactions with substrates is $\geq 6 \times 10^3$, somewhat greater than the experimental value of $\sim 10^2$. A better fit would require $k_{\mathrm{CrO,CrOH}} < k_{\mathrm{CrOO,CrOOH}}$. Using our estimate of $10^{1\pm1}$ $\mathrm{M^{-1}\ s^{-1}}$ for $k_{\mathrm{CrOO,CrOOH}}$ (see above), we can now also obtain a limiting value for $k_{\mathrm{CrO,CrOH}}$ from the kinetics of the $\mathrm{Cr}^{IV}{}_{aq}\mathrm{O}^{2+}/\mathrm{Cr_{aq}OOH^{2+}}$ reaction (eq 11 and Table 3). The value calculated from the Marcus equation for cross reactions, again without correction for work terms, is $10^{\leq(-2\pm1)}$ $\mathrm{M^{-1}\ s^{-1}}$, i.e., some 3 orders of magnitude smaller than $k_{\mathrm{CrOO,CrOOH}}$ for the superoxo complex.

It thus appears that $k_{\mathrm{CrOO,CrOOH}} = 10^{1\pm1}$ $\mathrm{M^{-1}\ s^{-1}}$ is a reasonable estimate for a HAT self-exchange rate constant for the superoxo/hydroperoxo couples in Table 1. To the best of our knowledge, this is the first such estimate reported for any metal. Despite the large uncertainty, this parameter will be undoubtedly helpful in bringing about a better understanding and semiquantitative treatment of the HAT reactions of other substrates and other metal−oxygen species. Interestingly, the value for $k_{\mathrm{CrOO,CrOOH}}$ obtained here is similar to that for the *tert*-BuOO$^\bullet$/*sec*-BuOOH reaction, $k_{\mathrm{self}} = 500$ in isopentane[55] and probably somewhat smaller in water owing to hydrogen bonding.[56]

Data for metal oxo/hydroxo exchange are somewhat more readily available. The limiting rate constant derived in this work for $\mathrm{Cr}^{IV}{}_{aq}\mathrm{O}^{2+}/\mathrm{Cr}^{III}{}_{aq}\mathrm{OH}^{2+}$ is close to one of the smallest reported to date, namely, 6.5×10^{-3} $\mathrm{M^{-1}\ s^{-1}}$ for $\mathrm{V^V(O)_2(R_2bpy)^+/V^{IV}O(OH)(R_2bpy)^+}$ (R = *tert*-Bu and Me).[57] The slow reaction of the vanadium couple reflects the large change in the V−O bond length, which, in turn, can be attributed to great changes in the π bonding upon HAT.[57] Structural data are not available for the chromium complexes in this work, but arguments similar to those used in the vanadium reaction seem applicable, provided that our assignment of the $\mathrm{Cr^{IV}O}$ structure is correct and that one complete π bond is lost as $\mathrm{Cr^{IV}O}$ accepts a hydrogen atom to generate $\mathrm{Cr^{III}OH}$.

The corresponding parameter for the *tert*-BuO$^\bullet$/*tert*-BuOH couple is $k_{\mathrm{BuO,BuOH}} \approx 3 \times 10^4$ $\mathrm{M^{-1}\ s^{-1}}$.[58] Thus, both thermodynamics and self-exchange kinetics favor *tert*-BuO$^\bullet$ over $\mathrm{Cr_{aq}O^{2+}}$ and probably over other $\mathrm{M^{IV}O}$ complexes.

Bimolecular Self-Reactions. Another appropriate comparison between metal-based and organic intermediates is their reactivity in bimolecular self-reactions. Alkylperoxyl radicals ROO$^\bullet$ generate a tetraoxo intermediate that eliminates $\mathrm{O_2}$ and rearranges by intramolecular HAT to generate an alcohol and aldehyde or ketone, as shown in eq 12 for ethyl radicals. This pathway, known as the Russell mechanism,[60,61] is available only to radicals that have an α-hydrogen atom.



(12)

When this is not the case (i.e., for R = *tert*-alkyl, acyl, or haloalkyl), free alkoxyl radicals are generated, as in eq 13 (for R = *tert*-butyl).

$$2(\mathrm{CH_3})_3\mathrm{COO}^\bullet \longrightarrow (\mathrm{CH_3})_3\mathrm{COOOOC(CH_3)_3} \longrightarrow \mathrm{O_2} + 2(\mathrm{CH_3})_3\mathrm{CO}^\bullet \tag{13}$$

While most of the parent alkyl radicals react in self-reactions at close to diffusion-controlled rates, alkylperoxyl radicals are greatly sensitive to steric factors, so that the rate constants for $\mathrm{CH_3OO^\bullet}$ and $\mathrm{(CH_3)_3COO^\bullet}$ differ by more than 5 orders of magnitude.[49]

Superoxometal complexes, on the other hand, react very slowly, or not at all, in bimolecular self-reactions. A minor second-order component ($k \sim 6$ $\mathrm{M^{-1}\ s^{-1}}$)[62] has been observed in the decay of $\mathrm{Cr_{aq}OO^{2+}}$, but the exact nature of this reaction is not clear. Most importantly, this path is too slow to contribute significantly to the overall decomposition rate in the accessible range of $\mathrm{Cr_{aq}OO^{2+}}$ concentrations.

One might expect that the reactions between LMOO complexes and ROO$^\bullet$ radicals will take place with rate constants that are between those for the self-reactions of individual couples. It was therefore surprising to find that the reaction between $\mathrm{Cr_{aq}OO^{2+}}$ ($k_{\mathrm{self}} \leq 6$ $\mathrm{M^{-1}\ s^{-1}}$) and $\mathrm{(CH_3)_3C(O)OO^\bullet}$ ($k_{\mathrm{self}} \approx 10^8$ $\mathrm{M^{-1}\ s^{-1}}$)[63] takes place with a rate constant 1.5×10^8 $\mathrm{M^{-1}\ s^{-1}}$, as determined in laser-flash photolysis experiments.[64,65]

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Two sets of products are generated, $\{Cr_{aq}^{3+} +$ isobutene $+ CO_2\}$ and $\{(CH_3)_3C(O)OH + HCrO_4^- + Cr_{aq}^{3+}\}$, consistent with the involvement of an intermediate that decays in two parallel reactions, as shown in Figure 5.[66]

An initial bimolecular head-to-head collision of the two O_2-containing species and the elimination of 1 equiv of O_2 was proposed[66] in analogy with the self-reactions of $ROO^{\bullet}$ radicals.[67,68] This hypothesis was recently confirmed in oxygen-labeling experiments.[65] Owing to the long lifetime of $Cr_{aq}OO^{2+}$ (several hours at room temperature in O_2-saturated solutions), it was possible to prepare an ^{18}O-labeled complex first, replace all of the dissolved $^{18}O_2$ with $^{16}O_2$, generate ^{16}O-labeled pivaloylperoxyl radicals as in eqs 14 and 15, and analyze the gaseous products of the cross reaction (eq 16) by gas chromatography−mass spectrometry.

$$Cr_{aq}{}^{18}O^{18}O^{2+} + RCHO \longrightarrow Cr_{aq}{}^{18}O^{18}OH^{2+} + RC^{\bullet}O \quad (14)$$

$$RC^{\bullet}O + {}^{16}O^{16}O \xrightarrow{\text{fast}} RC(O){}^{16}O^{16}O^{\bullet} \quad (15)$$

$$Cr_{aq}{}^{18}O^{18}O^{2+} + RC(O){}^{16}O^{16}O^{\bullet} \longrightarrow {}^{16}O^{18}O + \text{products} \quad (16)$$

The experiment yielded the mixed-labeled species $^{16}O^{18}O$ quantitatively and provided overwhelming support for the involvement of an intermediate/transition state of the form $[Cr_{aq}{}^{18}O^{18}O\cdots{}^{16}O^{16}O(O)CR]$, as in Figure 5. The O_2-eliminated in reaction (16) by the very nature of the process must come from the middle of the tetraoxo chain and contain one oxygen atom from each reactant. The remaining products of reaction 16 are shown in Figure 5.

A fast cross reaction between persistent and transient radicals results in the so-called Ingold−Fischer persistent radical effect.[69,70] In essence, the steady-state concentrations of persistent radicals are high, which leads to efficient trapping of the transient radicals and prevents their bimolecular self-reactions. In the present case, $Cr_{aq}OO^{2+}$ plays the role of the persistent radical. By virtue of its high concentration, it traps all of $RC(O)OO^{\bullet}$ despite the large rate constant for bimolecular self-decay of $RC(O)OO^{\bullet}$. Such cross reactions between metal-based and organic radicals are bound to take place in metal-catalyzed oxidations of organic substrates by O_2 and will lead to products that are different from those expected from "standard" autoxidation reactions. Not recognizing this fact and using reaction products as evidence for or against particular intermediates or mechanisms can be misleading. Not only can metals, in general, lead to different products, but the identity of the metal may determine the nature or distribution of products.

Hydroperoxo Complexes versus H_2O_2 and ROOH. The coordinated peroxide in LMOOH complexes reacts with one-electron reductants, such as transition-metal ions, much like free H_2O_2 or ROOH would, i.e., in a modified Fenton scheme. A metal−oxo analogue of $HO^{\bullet}$ radicals is formed, as illustrated for the $Cr_{aq}OOH^{2+}/Fe_{aq}^{2+}$ reaction in eq 17. The kinetics are also quite similar to those exhibited by free peroxides. This chemistry has been reviewed.[1,50,51]

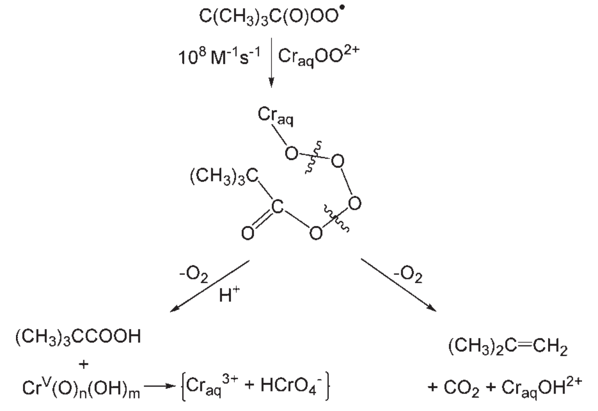

Figure 5. Proposed mechanism for the cross reaction between $Cr_{aq}OO^{2+}$ and pivaloylperoxyl radicals.

$$Cr_{aq}OOH^{2+} + Fe_{aq}^{2+} \longrightarrow Cr^{IV}{}_{aq}O^{2+} + Fe_{aq}OH^{2+} \quad (17)$$

Two-electron reactions of coordinated hydroperoxide, on the other hand, are faster than those of free H_2O_2/ROOH. Numerous examples of facile oxygen-atom transfer (OAT) from peroxo and hydroperoxo complexes are available in the literature and will not be discussed here. To a smaller or greater extent, all of the hydroperoxo complexes in our work became kinetically more competent at higher H^+ concentrations. This is attributed to the protonation of the hydroperoxo group to yield the more strongly oxidizing species,[71−73] as reviewed recently.[50,51]

Alternative Sources of Metal-Activated Oxygen

Superoxo, hydroperoxo, and oxo complexes discussed here are typically generated in sequential one- or two-electron steps of Figure 1, beginning with O_2 and employing various transition-metal complexes as electron donors. The steps outlined in Scheme 2, for example, generate various chromium intermediates, but alternative approaches are also available in some cases.

$Cr_{aq}CH_2OH^{2+}/O_2$ Reaction. This reaction is a convenient source of $Cr_{aq}OOH^{2+}$ at concentrations that can significantly exceed those obtained by the direct reduction of $Cr_{aq}OO^{2+}$.[74] This is possible because the instantaneous concentration of O_2 in solution is not limiting, even though $Cr_{aq}OO^{2+}$ is involved, as shown in Scheme 3. The initial step slowly generates Cr_{aq}^{2+}, which is quickly scavenged with O_2 to make $Cr_{aq}OO^{2+}$, followed by one-electron oxidation of the organochromium cation and the formation of $Cr_{aq}OOH^{2+}$. Because Cr_{aq}^{2+} is generated homogeneously in a slow chemical reaction, the

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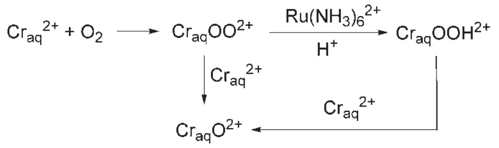
Scheme 2. Generation of Some Chromium Intermediates

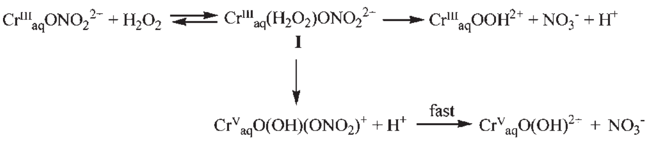


consumption of O_2 is also slow, so that it can be continuously replenished and kept close to the saturation level throughout the experiment. This allows $Cr_{aq}OOH^{2+}$ to accumulate steadily to levels exceeding the solubility of O_2. All of the steps in Scheme 3 have been confirmed independently.

$Cr_{aq}ONO_2^{2+}/H_2O_2$ Reaction. The formation of hydroperoxo complexes by the simple coordination of hydrogen peroxide to a metal is clearly limited to labile metals and excludes substitutionally inert complexes such as hexaaquachromium(III) ion. Even if the substitution could be accelerated, as in complexes with cis-labilizing ligands, the yields of the peroxo/hydroperoxo product in aqueous solutions would be expected to be negligibly small, given that H_2O_2 and H_2O compete for the labile position(s), and water is a better Lewis base and is present at much higher concentrations. Despite these arguments, it was recently discovered that $Cr_{aq}OOH^{2+}$ can be generated in 50−60% yield from $Cr_{aq}ONO_2^{2+}$ or $Cr_{aq}O_2CCH_3^{2+}$ and 10−100 mM H_2O_2 in acidic water,[75] as shown in eq 18. A few percent of $Cr_{aq}OO^{2+}$ was also generated.

The reaction in eq 18 has a rate constant $k = 0.043\ M^{-1}\ s^{-1}$, independent of $[H^+]$ in the range $0.10\ M \le [H^+] \le 0.50\ M$. A mechanism proposed to account for these results is shown in eq 19.

$$Cr_{aq}ONO_2^{2+} + H_2O_2 \longrightarrow Cr_{aq}OOH^{2+} + NO_3^-(+\ Cr_{aq}OO^{2+} + Cr_{aq}^{3+}) \qquad (18)$$



(19)

The labilization of one or more positions at the metal, most likely the four cis sites,[75,76] allows H_2O_2 to coordinate and form the mixed nitrato/peroxo intermediate **I** followed by the release of nitrate. If this mechanism is correct, then it follows that the hydroperoxo group must have even stronger cis-labilizing properties than nitrate does or else the proportion of coordinated hydroperoxide could not be much greater than its proportion in solution, i.e., ≤0.2%, in stark contrast to the experimental yield of > 50%. The cis-labilizing properties of the hydroperoxide ligand are currently being tested in our laboratory.

Intermediate **I** is probably also the source of the superoxo complex. We postulate that **I** reacts in two competing reactions: substitution to generate $Cr_{aq}OOH^{2+}$ and internal electron transfer to yield Cr^V, which will disproportionate to Cr^{IV} and chromate. Both of these products are known independently to react with H_2O_2 and give $Cr_{aq}OO^{2+}$.[51] The chemistry involved here may represent a route to high-valent chromium from Cr^{III} in biological environments. It is plausible that the anionic ligands (nitrate and acetate), just like the electron-rich N_4 macrocycles,[34−36] facilitate the hydroperoxo-to-Cr^V conversion in eq 19.

Scheme 3. Mechanism of $Cr_{aq}OOH^{2+}$ Formation by Oxidation of an Organochromium Complex with O_2

$$Cr_{aq}CH_2OH^{2+} \xrightarrow{O_2} Cr_{aq}^{2+} + CH_2O + H^+ \qquad \text{slow}$$
$$Cr_{aq}^{2+} + O_2 \rightleftharpoons Cr_{aq}OO^{2+} \qquad \text{fast}$$
$$Cr_{aq}OO^{2+} + Cr_{aq}CH_2OH^{2+} \rightarrow Cr_{aq}OOH^{2+} + Cr_{aq}^{2+} + CH_2O$$

Reactions with Ozone. O_3 has proven useful both as the source of oxygen in oxo complexes and as oxidant. The great advantage of ozone is its large reduction potential,[46] which helps the kinetics. Also, the reduction of ozone generates O_2 and sometimes H_2O_2 species that are already present as natural components in solutions of activated oxygen, keeping the systems chemically as simple as possible.

One of the most convenient ways to prepare the superoxorhodium(III) complex $Rh(NH_3)_4(H_2O)OO^{2+}$ is by oxidation with ozone of a hydroperoxo precursor,[46] itself generated by O_2 insertion into the hydride (eq 20).

$$(NH_3)_4(H_2O)RhH^{2+} \xrightarrow{O_2} (NH_3)_4(H_2O)RhOOH^{2+} \xrightarrow{O_3} (NH_3)_4(H_2O)RhOO^{2+} \qquad (20)$$

The detailed mechanism of the latter reaction is currently under investigation, but it appears that slow deprotonation of the hydride is the rate-determining step.[77]

In the reaction with Fe_{aq}^{2+}, ozone acts as an oxygen-atom donor[78−80] and generates $Fe^{IV}{}_{aq}O^{2+}$ (eq 21). OAT from O_3 to other aquametal complexes can probably also be accomplished, and some of the work is currently in progress in our laboratory, but more oxidizable ligands are not expected to survive intact in the presence of this powerful oxidant.

$$Fe_{aq}^{2+} + O_3 \longrightarrow Fe_{aq}O^{2+} + O_2 \qquad (21)$$

Despite the short, 10 s lifetime, the ferryl produced in eq 21 has been characterized by a number of techniques. The combination of Mössbauer and X-ray absorption spectroscopies and density functional theory calculations[78] revealed that the compound is a rare high-spin[81] Fe^{IV} species. The overall charge was determined in conductometric experiments to be 2+, and exchange reactions with isotopically labeled oxygen established the presence of one unique oxygen in the molecule. On the basis of all of this information, the best description of the product of reaction (21) is $Fe(H_2O)_5O^{2+}$.

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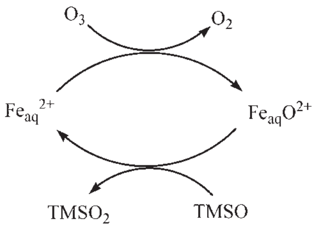
Scheme 4



Consistent with the $Fe^{IV}O$ structure, $Fe_{aq}O^{2+}$ is a powerful oxygen-atom donor. In addition, it reacts with a large number of organic and inorganic substrates by HAT, electron transfer, and hydride transfer, often by a combination of pathways and mechanisms. Alcohols, for example, react in comparable proportions in one- and two-electron processes.[79]

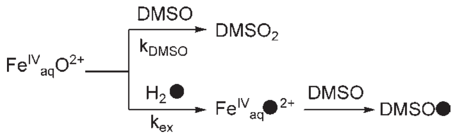
Two-electron transformations by OAT or any other mechanisms regenerate iron(II), and they are crucial in the context of catalytic oxidations with iron. The involvement of 3+ oxidation state is undesirable because the reoxidation to Fe^{IV} is much more difficult and has not been observed even with ozone. Such oxidations are, of course, possible for complexes with electron-rich ligands that stabilize high oxidation states.[82]

OAT to sulfoxides is fast ($k \sim 10^5$ M^{-1} s^{-1}), which makes the catalytic $Fe_{aq}^{2+}/O_3/R_2SO$ reaction quite efficient (Scheme 4), where TMSO = *p*-tolyl methyl sulfoxide. In the absence of Fe_{aq}^{2+}, the oxidation of 100 μM TMSO with 100 μM O_3 requires more than 5000 s and yields 90% sulfone. In the presence of 5 μM Fe_{aq}^{2+}, under otherwise identical conditions, the reaction gives 100% sulfone in several seconds.

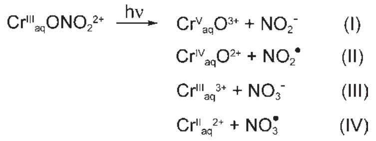
Fe_{aq}^{2+}-catalyzed oxidation of dimethyl sulfoxide (DMSO) with O_3 in $H_2{}^{18}O$ was employed to determine the rate constant for oxo oxygen exchange with solvent oxygen. Kinetic data for this type for reactive metal−oxo complexes are quite limited in the literature. A competition for $Fe^{IV}{}_{aq}O^{2+}$ between solvent water ($H_2{}^{18}O$, k_{ex}) and DMSO (k_{DMSO}) should result in the partial incorporation of an O_3-derived oxo (^{16}O) group into the product sulfone, as shown in Scheme 5. Indeed, the yield of $DMS(^{16}O)_2$ increased with the concentration of DMSO, yielding $k_{ex} = (1.4 \pm 0.1) \times 10^3$ s^{-1} upon fitting of the data to an expression for competition kinetics.[83]

Having $Fe_{aq}O^{2+}$ on hand allowed us to also address a long-standing mechanistic question regarding the nature of the intermediate generated in the Fe_{aq}^{2+}/H_2O_2 (i.e., Fenton) reaction.[84,85] The distinction between the two most likely candidates, $HO^\bullet$ radicals and $Fe_{aq}O^{2+}$, was not possible until both were known and chemically characterized. The discovery of some unique chemistry of $Fe_{aq}O^{2+}$, including OAT to sulfoxides, allowed us to definitely rule out the involvement of $Fe_{aq}O^{2+}$ in the Fenton reaction, which is known to oxidize sulfoxides to alkyl radicals and sulfinic acid. The same products are generated in oxidations of sulfoxides with $HO^\bullet$ radicals, clearly the most likely intermediate in Fenton chemistry. Importantly, Fe^{IV} intermediates are formed in the reactions of some iron complexes with H_2O_2. The straightforward elimination of such a possibility in our work pertains only to the Fe_{aq}^{2+}/H_2O_2 reaction in acidic and neutral aqueous solutions, i.e., the Fenton reaction.

Scheme 5



Scheme 6. Possible Photochemically Induced Cleavage Reactions of $Cr_{aq}ONO_2^{2+}$



Photochemical Generation of Activated Oxygen. UV photolysis of nitrato complexes, such as $Cr_{aq}ONO_2^{2+}$, may be expected to take place by homolytic or heterolytic cleavage of either Cr−O or N−O bonds, i.e., by one or more of the pathways shown in Scheme 6.

The photolysis of free nitrate produces nitrite and O_2 (eqs 22 and 23). The source of nitrite is $^\bullet NO_2$, generated either directly or via $OONO^{-}$[86,87]

$$NO_3^- \xrightarrow{hv} OONO^- + (NO + O_2^{\bullet -}) \text{ or } (NO^- + O_2) \qquad (22)$$

$$OONO^- + H^+ \leftrightarrows HOONO \longrightarrow (HO^\bullet + {}^\bullet NO_2) + (H^+ + NO_3^-) \qquad (23)$$

In the limited literature on complexed nitrate, we found that nitrato complexes of manganese(III) and iron(III) porphyrins form metal(IV) oxo species and $^\bullet NO_2$ (eq 24), as in pathway II in Scheme 6 and in formal analogy to reaction (23).[88]

$$(P)M^{III}ONO_2 \xrightarrow{hv} (P)MO + {}^\bullet NO_2 \quad (P = \text{porphyrin, } M = \text{Mn, Fe}) \qquad (24)$$

Photoredox reactions of compounds such as $Co(NH_3)_5X^{2+}$ and $Cr_{aq}X^{n+}$, on the other hand, almost inevitably lead to the *reduction* of the metal center, as in eq 25, where R = alkyl.[89] If $Cr_{aq}ONO_2^{2+}$ were to follow the pattern, it would generate a strongly oxidizing nitrate radical and strongly reducing Cr_{aq}^{2+}, with an overall charge separation of greater than 3 V. All three alternative pathways in Scheme 6 would generate lower-energy products.

$$Cr_{aq}X^{n+} \xrightarrow{hv} Cr_{aq}^{2+} + X^\bullet \; (X = O_2, {}^\bullet NO, R^\bullet) \qquad (25)$$

The mechanism of $(H_2O)_5CrONO_2^{2+}$ photolysis (λ_{exc} = 266 nm) was addressed by a combination of

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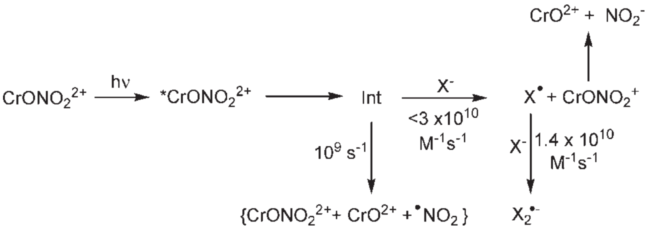
Scheme 7. Photochemical Reactions of $(H_2O)_5CrONO_2^{2+}$ (X = Cl, Br, or I)



laser-flash and steady-state photolysis in the presence of scavengers for potential intermediates.[89] The initial photochemical step generates a short-lived ($\tau \sim 1$ ns) powerful oxidant that resembles but is distinctly different from $^{\bullet}NO_3$ radicals and can oxidize bromide, chloride, and iodide ions to the respective atoms $X^{\bullet}$ at diffusion-controlled rates. In the absence of added substrates, the intermediate decays to $Cr_{aq}O^{2+}$ and $^{\bullet}NO_2$. The addition of methanol leads to $Cr_{aq}OO^{2+}$ by virtue of the chemistry in eq 26. The overall picture is shown in Scheme 7.

$$Cr_{aq}O^{2+} + CH_3OH \xrightarrow{-CH_2O} Cr_{aq}{}^{2+} \xrightarrow{O_2} Cr_{aq}OO^{2+} \quad (26)$$

In the end, the photochemical behavior of $(H_2O)_5CrONO_2^{2+}$ does not follow exclusively either of the two preferred possibilities outlined above. Instead, it involves both in succession. The initial intramolecular electron transfer resembles the "standard" photochemistry of eq 25, but the two components, $Cr_{aq}{}^{2+}$ and $^{\bullet}NO_3$, do not seem to be fully separated. This conclusion is based on the extremely rapid reactions of the intermediate with halide ions and on the failure to observe $Cr_{aq}OO^{2+}$ in O_2-saturated solutions, where the combination of concentrations and the rate constant for the $Cr_{aq}{}^{2+}/O_2$ reaction would have to outweigh kinetically every other bimolecular reaction of $Cr_{aq}{}^{2+}$. [$Cr_{aq}OO^{2+}$ was observed, and its concentration could be competitively controlled, in slow steady-state photolysis experiments in the presence of methanol when reaction (26) took over]. The intermediate, which we denote as $\{Cr_{aq}{}^{2+}, {}^{\bullet}NO_3\}$, converts rapidly to $Cr_{aq}O^{2+}$ and $^{\bullet}NO_2$, so that the final products are analogous to those obtained with porphyrin complexes and, to some extent, with nitrate itself (eqs 23 and 24).

The photochemical step itself and the follow-up chemistry of various intermediates turn out to be a source of several species of "activated" oxygen. Especially exciting is this new route to the rapid (1 ns) generation of $Cr_{aq}O^{2+}$, and, by implication, other high-valent metal−oxo species, for kinetic and mechanistic studies from thermally inert precursors.

Conclusions

The interaction of oxygen with transition-metal complexes generates a variety of reactive species with an impressive chemistry repertoire that includes electron transer, HAT, and OAT, accelerated substitution, and homolytic and heterolytic cleavage of metal−oxygen and oxygen−oxygen bonds. Some of these reactive species can also be generated by alternative methods, both thermal and photochemical. Judged by the example of $Cr_{aq}ONO_2^{2+}$, the photochemistry of nitrato complexes seems quite promising as a method for the generation of highly reactive species.

In reactions that parallel those of organic counterparts, metal-activated species appear to be less reactive but longer-lived, although the number of examples where a valid comparison can be made is quite limited. In the available cases, however, the opposing effects of reactivity and lifetimes make the two types of intermediates similarly effective in reactions with substrates.

Despite the slowness of the bimolecular self-reactions of the inorganic species, cross reactions with organic oxygen-centered radicals can be quite fast and adopt a modified Russell mechanism.[60,61] The $Cr_{aq}OO^{2+}/(CH_3)_3C(O)OO^{\bullet}$ reaction, for example, has a rate constant of $> 10^8$ M^{-1} s^{-1}. This feature opens pathways to novel intermediates and products in metal-catalyzed oxidations with O_2.

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