788 *Inorg. Chem.* **1996,** *35,* 788−790

Metal Hydroperoxides as Oxygen Atom Transfer Reagents

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Received September 8, 1995

Introduction

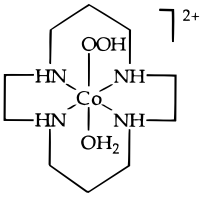
Transition-metal hydroperoxo complexes, LMO_2H, (L = ligand system) are gaining increasing recognition as reactive intermediates in the reduction of O_2 by transition metal complexes in chemical[1−6] and biological systems.[7−9] As a result, several preparative routes to the more stable MO_2H complexes have been developed,[9,13−17] and the number of known MO_2H compounds has increased greatly in recent years. Several studies of the reactivity of such complexes have appeared,[2,9,13,17−19] but surprisingly little is known about the kinetics and mechanisms of such reactions.

An evaluation of the reactivities of LMO_2H and H_2O_2 toward common substrates would provide a useful and meaningful measure of the activation of H_2O_2 by metal complexes. To this goal, we have previously studied several oxidations by $(H_2O)_5CrO_2H^{2+}$, $(H_2O)([14]aneN_4)CoO_2H^{2+}$, and $(H_2O)(Me_6[14]aneN_4)CoO_2H^{2+}$.[13,18,20] The rate constants for one-electron oxidations of transitions metal complexes were found to be comparable for LMO_2H and H_2O_2, with H_2O_2 being somewhat more reactive. On the other hand, the two-electron (oxygen atom transfer) reactions of the same three LMO_2H complexes were significantly faster than the corresponding reactions of H_2O_2. The two types of reactions are exemplified by eqs 1 and 2.

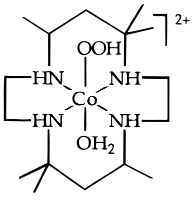
$$(H_2O)_5CrO_2H^{2+} + Fe(H_2O)_6{}^{2+} \rightarrow (H_2O)_5CrO^{2+} + (H_2O)_5FeOH^{2+} + H_2O \quad (1)$$

$$(H_2O)_5CrO_2H^{2+} + PPh_3 \rightarrow (H_2O)_5CrOH^{2+} + Ph_3PO \quad (2)$$

This intriguing reactivity pattern has led us to conduct a full kinetic study of the oxidation of iodide by the same three metal hydroperoxides. The results are the subject of this report.



$L^1CoO_2H^{2+}$



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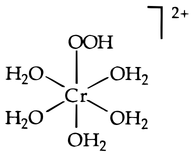

CrO_2H^{2+}

Experimental Section

The complex ions $(H_2O)_5CrO_2H^{2+}$, $(H_2O)([14]aneN_4)CoO_2H^{2+}$ and $(H_2O)(Me_6$-$[14]aneN_4)CoO_2H^{2+}$ (hereafter CrO_2H^{2+}, $L^1CoO_2H^{2+}$, and $L^2CoO_2H^{2+}$, respectively) were prepared as previously described.[13,18] Stock solutions of sodium iodide were prepared in water and kept under argon to prevent aerial oxidation.

The kinetics of oxidation of iodide by the metal hydroperoxides were studied spectrophotometrically by monitoring the growth of I_3^- at 352 nm ($\epsilon = 2.6 \times 10^4$ M^{-1} cm^{-1}). The reaction was initiated by injecting a small volume of iodide into a spectrophotometric cell containing the appropriate metal hydroperoxide (~0.1 mM) and all the other ingredients. Iodide was used in a large excess (>30-fold) over the hydroperoxides, so that the ratio $[I_3^-]/[I_2]$, eq 3,[21] remained practically

$$I_2 + I^- \leftrightarrows I_3^- \qquad K = 830\ M^{-1} \quad (3)$$

unchanged in the course of each run. In most of the experiments, the ionic strength was held constant at 0.075 M ($NaI + HClO_4 + NaClO_4$). In the reaction between I^- and $L^2CoO_2H^{2+}$ at high concentrations of H^+, ≤ 1M, the ionic strength was kept at 1.0 M.

All of the spectral and kinetic data were collected by use of a Shimadzu 3101 PC spectrophotometer equipped with a thermostated cell compartment.

Results

All three hydroperoxides reacted with I^- according to the stoichiometry of eq 4. In the presence of a large excess of I^- and H^+, the absorbance increase at 352 nm was exponential, and the pseudo-first-order rate constants were evaluated from the expression $D_t = D_\infty + (D_0 - D_\infty)e^{-k_{obs}t}$ (D = absorbance). The measured rate constants k_{obs} are directly proportional to $[I^-]$ and $[H^+]$, eqs 5 and 6.

$$MO_2H^{2+} + 3I^- + 3H^+ \rightarrow I_3^- + M^{3+} + 2H_2O \quad (4)$$

$$-d[MO_2H^{2+}]/dt = d[I_3^-]/dt = k_{obs}[MO_2H^{2+}] \quad (5)$$

$$k_{obs} = k_H[I^-][H^+] \quad (6)$$

Figure 1 shows the plots of $k_{obs}/[I^-]$ against $[H^+]$ for the reactions of the three metal hydroperoxides with I^-. As expected from eq 6, the plots are linear with zero intercepts. The slopes yielded the third-order rate constants in Table 1. Also listed in Table 1 are the data for other 2-electron reactions of LMO_2H^{2+} [18] and H_2O_2.[22,23] In some instances the kinetic data were obtained at only one acid concentration, and the third-order rate constants are not available. To facilitate the comparison between different reactions, the pseudo-second-order

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Table 1. Summary of the Rate Constants (M^{-2} s^{-1})[a,b] for the 2-Electron Reactions of Transition Metal Hydroperoxides[c] and H_2O_2 in Aqueous Solution at 25 °C

MO_2H	I^-	Br^-	PPh_3[d]	$CoSR^{2+}$[e]	ref
CrO_2H^{2+}	988 ± 16 (98)	(0.063)	(75)	20.5	this work, 18, 20
$L^1CoO_2H^{2+}$	100 ± 1.8 (10)		($\ll$1)	52 (5.0)	this work, 13
$L^2CoO_2H^{2+}$	72.3 ± 2.1 (7.23)				this work
	59.2 ± 0.8[f] (5.9)				
H_2O_2	0.173 (0.029)[g]	2.3×10^{-4} (2.3×10^{-5})[h]	(3.0)	1.8 (1.36)[i]	13, 22, 23

[a] Rate = k[substrate][hydroperoxide][H^+]. [b] Numbers in parentheses are pseudo-second-order rate constants at [H^+] = 0.1 M. [c] Ionic strength = 0.075 M, [I^-] = 2−7 mM, [H^+] = 0.02−0.07 M. [d] In 50% MeCN, [H^+] = μ = 0.1 M. [e] The complex is $(en)_2Co(SCH_2CH_2NH_2)^{2+}$. [f] [$H^+$] = 0.05−1.0 M, μ = 1.0 M. [g] An additional, [H^+]-independent term has $k_0 = 0.0115$ M^{-1} s^{-1}. [h] [H^+]-independent term has $k_0 = 3.8 \times 10^{-7}$ M^{-1} s^{-1}. [i] [H^+]-independent term has $k_0 = 1.18$ M^{-1} s^{-1}.

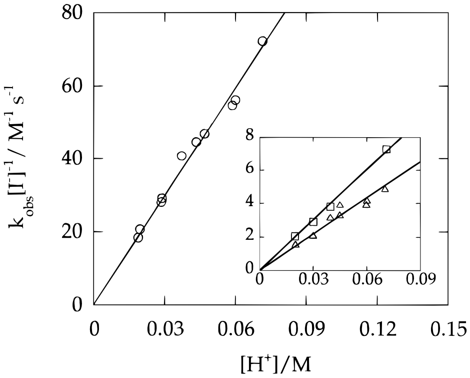
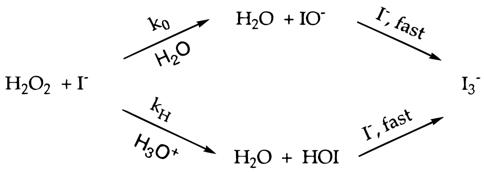


Figure 1. Plot of k_{obs}/[I^-] against [H^+] for the reaction of I^- with $(H_2O)_5CrO_2H^{2+}$ (circles), $(H_2O)([14]aneN_4)CoO_2H^{2+}$ (squares) and $(H_2O)(Me_6[14]aneN_4)CoO_2H^{2+}$ (triangles). Axis labels for the inset are the same as for the main figure. Conditions: T = 25.0 ± 0.2 °C, [I^-] = 2−7 mM, and [LMO_2H] = 0.03−0.1 mM.

rate constants at 0.1 M H^+ are given in parentheses for all the reactions in Table 1.

Discussion

The oxidation of I^- by H_2O_2, eq 7, takes place according to the rate law of eq 8, where k_0 = 0.0115 M^{-1} s^{-1} and k_H = 0.173 M^{-2} s^{-1}.[22]

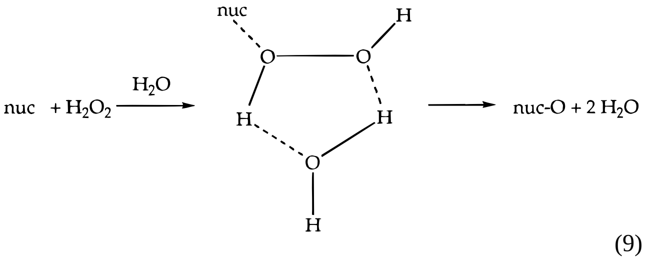


(7)

$$-d[H_2O_2]/dt = (k_0 + k_H[H^+])[H_2O_2][I^-] \tag{8}$$

Metal hydroperoxides react exclusively by the [H^+]-catalyzed path, eqs 5 and 6, and the values of k_H are significantly greater than that for H_2O_2, Table 1.

A cyclic transition state, such as that shown below, was proposed for [H^+]-independent reactions of H_2O_2 and RO_2H (R = alkyl) with nucleophiles in protic solvents.[24−26] The involvement of protic molecules in the transition state results in the hydrogen shift necessary for the utilization of the low-energy path with H_2O as leaving group.



(9)

The protonation of H_2O_2 to give $H_3O_2^+$, and the rapid reaction of $H_3O_2^+$ with I^- are the two major steps in the accepted mechanism for the acid catalyzed path, so that k_H= k_{11}/K_{10}.

$$H_3O_2^+ \leftrightarrows H_2O_2 + H^+ \tag{10}$$

$$H_3O_2^+ + I^- \rightarrow HOI + H_2O \tag{11}$$

It is reasonable to expect that the reactions of LMO_2H take place by similar mechanisms. The difference in reactivity is probably the result of the positive charge on the metal hydroperoxides. It was shown recently[25b] that methyl hydroperoxides bearing a positively charged substituent are potent O-donors. The calculations suggest that the through-space Coulombic effects are more efficient than the through-bond inductive effects in activating alkyl hydroperoxides.[25b] If the reactions of LMO_2H complexes proceed through a transition state similar to that in eq 9, then the metal cation plays a dual role. It facilitates the approach of I^- and promotes charge separation in the heterolytic process. The observation[9b] that a neutral hydroperoxoiron complex becomes a potent oxidant upon protonation supports this proposal.

The weakening of the O−O bond of coordinated H_2O_2[9a,26] may also lower the barrier for O-atom transfer, although the fact that one-electron, Fenton-type reactions of LMO_2H are not significantly faster than the corresponding reactions of H_2O_2 indicates that the reduced strength of O−O bond plays only a modest role in the kinetics.

On the basis of the arguments presented so far, it is difficult to understand why the metals affect the k_H path so much more than the k_0 path. The latter is a major component in the reaction of H_2O_2 but has not been observed in the reactions of LMO_2H. The difference in the overall charge in the transition state (2+ in the k_H path, 1+ in the k_0 path) cannot account for these observations.

We propose that the disproportionate enhancement of the k_H path upon substitution of one H^+ in H_2O_2 by LM^{3+} derives from the greater concentration of the protonated intermediate in the LMO_2H reaction, eqs 12−14, as explained below.

$$LM(H_2O_2)^{3+} \leftrightarrows LMO_2H^{2+} + H^+ \quad K_a \tag{12}$$

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$$LM(H_2O_2)^{3+} + I^- \rightarrow HOI + LMOH^{2+} \text{ (or } IO^- + LM(H_2O)^{3+}) \quad (13)$$

$$k_{obs} = k_{13}[H^+]/(K_a + [H^+]) \quad (14)$$

The values of the acid dissociation constants K_a for the metal hydroperoxides in this work are not known. On the basis of the pK_a's of free H_2O and H_2O_2 and of H_2O coordinated to Cr^{3+}, it has been proposed that the pK_a of $Cr(H_2O_2)^{3+}$ should lie in the range 1−3.[27] This proposal was supported by the fact that the reported pK_a of $Fe(H_2O_2)^{3+}$ is 1.2.[28,29]

However, the kinetics of I^- oxidation by all three hydroperoxides are linearly dependent on $[H^+]$ in the range 0.02−0.07 M, indicating that $K_a \gg [H^+]$ under these conditions. The same result was obtained even when the range of acid concentrations was extended to 1 M in the reaction with L^1-CoO_2H^{2+}. These results indicate that the acidity of coordinated hydrogen peroxide in the three $LM(H_2O_2)^{3+}$ complexes, pK_a $\ll 0$, is much greater than predicted previously. Still, we expect that the acidity of $H_3O_2^+$ (p$K_{10} < -7.7$)[30] is greater still, such that $([M(H_2O_2)^{3+}]/[MO_2H^{2+}]) > ([H_3O_2^+]/[H_2O_2])$ at the same pH. Thus the inequality $k_{13}/K_a \gg k_{11}/K_{10}$ holds mainly because of the differences in the pK_a's, i.e. $K_a < K_{10}$.

One-electron, Fenton-type reactions of LMO_2H, eq 1, do not require catalysis by H^+, because the products are formed in their hydrolytically stable (CrO^{2+}) or readily accessible ($FeOH^{2+}$) forms. Thermodynamically, the reaction of CrO_2H^{2+} with Fe^{2+} is much more favorable than the reaction of H_2O_2 with Fe^{2+}.[31] For both H_2O_2 and LMO_2H the coordination of the peroxide to Fe^{2+} is required,[18,20] and the similarity of the rate constants for the two reactions may result from two opposing effects, the driving force for the overall reaction and the concentration of the intermediates produced in the first step. Charge considerations and steric effects will make the activation energy for the formation of the precursor complex $Cr(O_2H)Fe^{4+}$ almost certainly greater than that for the formation of $Fe(H_2O_2)^{2+}$, eqs 15 and 16.

$$Fe^{2+} + CrO_2H^{2+} \leftrightarrows Cr(O_2H)Fe^{4+} \rightarrow CrO^{2+} + FeOH^{2+} \quad (15)$$

$$Fe^{2+} + H_2O_2 \leftrightarrows Fe(H_2O_2)^{2+} \rightarrow HO^{\bullet} + FeOH^{2+} \quad (16)$$

The lower concentration of $Cr(O_2H)Fe^{4+}$ would cancel, in part, the greater thermodynamic driving force (and probably the larger rate constant) for the conversion of $Cr(O_2H)Fe^{4+}$ to products.

Conclusions

The acid-catalyzed nucleophilic (2-electron) reactions of LMO_2H^{2+} with I^- are much faster than the corresponding reaction of H_2O_2 because the concentrations of the active forms, $LM(H_2O_2)^{2+}$ and $H_3O_2^+$, differ considerably at the same pH. The reactivities of H_2O_2 and LMO_2H^{2+} in Fenton-type (1-electron) reactions are comparable. This may be the result of the opposing effects of the driving force for the overall reactions and the concentrations of the precursor complexes $Fe(H_2O_2)^{2+}$ and $LM(O_2H)Fe^{4+}$.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-9007283). Some of the experiments were conducted with the use of the facilities of the Ames Laboratory.

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