Kinetics and Mechanisms of the Redox Reactions of the Hydroperoxochromium(III) Ion

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The reactions of the hydroperoxochromium(III) ion, $(H_2O)_5CrO_2H^{2+}$ (CrO_2H^{2+}), with Fe^{2+}, VO^{2+}, V^{2+}, Cu^+, Ti^{3+}, $Co([14]aneN_4)^{2+}$, $Co(Me_6[14]aneN_4)^{2+}$, $Co(tim)^{2+}$, and $[Ru(NH_3)_6]^{2+}$ have been studied in acidic aqueous solution. The reactions are accompanied by large negative entropies of activation, −110 J mol^{-1} K^{-1} for Fe^{2+} and −85 J mol^{-1} K^{-1} for Ti^{3+}. All the reactions studied follow an isokinetic relationship in that $\Delta H^{\ddagger}$ is a linear function of $\Delta S^{\ddagger}$. The same is true for the analogous reactions of H_2O_2. It is proposed that the reactions of CrO_2H^{2+} take place by an inner-sphere, Fenton-type process yielding pentaaquaoxochromium(IV), $(H_2O)_5CrO^{2+}$ (CrO^{2+}), as an intermediate. The reactivity of CrO_2H^{2+} as an oxygen transfer reagent is about 20 times greater than that of H_2O_2. For example, the reactions with $(en)_2CoSCH_2CH_2NH_2^{2+}$ to yield $(en)_2CoS(O)CH_2CH_2NH_2^{2+}$ have rate constants 20.5 ± 0.4 M^{-1} s^{-1} (CrO_2H^{2+}) and 1.36 M^{-1} s^{-1} (H_2O_2), both in 0.1 M $HClO_4$ at 25°C. The chromyl ion, CrO^{2+}, oxidizes CrO_2H^{2+} to CrO_2^{2+} with a rate constant of (1.34 ± 0.06) × 10^3 M^{-1} s^{-1} in 0.10 M $HClO_4$ in H_2O and 266 ± 10 $M^{-1}s^{-1}$ in D_2O.

Introduction

The activation of molecular oxygen by aquachromium(II) ion, Cr^{2+}, yields several chromium-containing species, corresponding to different reduction stages of molecular oxygen.[1] One of these species is the hydroperoxochromium(III) ion,[1b,c] $(H_2O)_5CrO_2H^{2+}$ (henceforth CrO_2H^{2+}), an analogue of H_2O_2. Although metal hydroperoxides have been proposed as intermediates in many metal-catalyzed oxidation reactions of organic substrates by H_2O_2, very little is known about their reactivity.[2] To compare the redox properties of hydrogen peroxide[2,3] with that of a metal hydroperoxide, we have studied the reduction of CrO_2H^{2+} by ferrous ion.[4] The reaction takes place by inner-sphere electron transfer and yields a chromyl intermediate. We have now extended our study to a number of transition metal complexes in order to establish the role of the reduction potentials and substitutional lability on the rates of electron transfer.

In the absence of data on similar systems it is impossible to predict the effect of the Cr(III) center on the reactivity of the peroxide. CrO_2H^{2+} can formally be regarded as a result of the substitution of one Lewis acid (a proton) in H_2O_2 by another (Cr^{3+}). This might lead one to expect a higher reactivity for CrO_2H^{2+} owing to the inductive effect of the trivalent metal center. However, the electronegativity of H^+ is in fact greater than that of Cr^{3+},[5] which would imply that H_2O_2 is a better oxidant than CrO_2H^{2+}. Admittedly, one has to exercise caution in using the gas-phase parameters, such as electronegativity, to predict the solution behavior of chemical species. Probably the best solution parameter to consider in the present case is the pK_a value of the species of interest. The pK_a for CrO_2H^{2+}/CrO_2^+ is unfortunately not known, but if we assume that the effect of Cr(III) will be qualitatively the same at a higher level of protonation, then the values for $H_3O_2^+$ (pK_a −1.7)[6] and $Cr(H_2O_2)^{3+}$ (pK_a 1–3)[1c] provide a good reference point. The much larger pK_a of $Cr(H_2O_2)^{3+}$ shows that Cr^{3+} has a smaller inductive effect than H^+ and leads to the same conclusion as the gas-phase data, i.e. that H_2O_2 should be a stronger oxidant than CrO_2H^{2+}.

Any reaction of CrO_2H^{2+} by a Fenton-type mechanism would lead to the formation of CrO^{2+}, the Cr(III) analogue of the HO· radical, eq 1, as shown previously for the reaction with Fe^{2+}.[4]

$$CrO_2H^{2+} + M \rightarrow CrO^{2+} + MOH \qquad (1a)$$

$$H_2O_2 + M \rightarrow HO^{\bullet} + MOH \qquad (1b)$$

The present study of the *reduction* of CrO_2H^{2+} by transition metal reductants was undertaken to find out how general is the formation of CrO^{2+} and whether an inner-sphere path is necessary for the electron transfer to take place. We also studied the reaction of CrO_2H^{2+} by CrO^{2+}, whereby CrO_2H^{2+} is *oxidized* to CrO_2^{2+}.

Experimental Section

Reagents. Stock solutions of VO^{2+} were prepared by ion exchanging vanadyl sulfate on a column of Dowex 50W-X4 cation exchange resin. The complex was eluted with 1.93 M $HClO_4$. The concentration of VO^{2+} was determined spectrophotometrically ($\epsilon_{760\,nm}$ = 17.5 M^{-1} cm^{-1}).[7] Solutions of V^{2+} were prepared by the anaerobic reduction of VO^{2+} over zinc amalgam. The solution of $TiCl_3$[8,9] in 1.5 M HCl was standardized spectrophotometrically ($\epsilon_{500\,nm}$ = 3.9 M^{-1} cm^{-1}). The solution of Cu^+ was prepared by Cr^{2+} reduction of Cu^{2+}.[10] The complexes $Co([14]aneN_4)(H_2O)_2^{2+}$ (L^1Co^{2+}) and $Co(Me_6[14]aneN_4)(H_2O)_2^{2+}$ (L^2Co^{2+})

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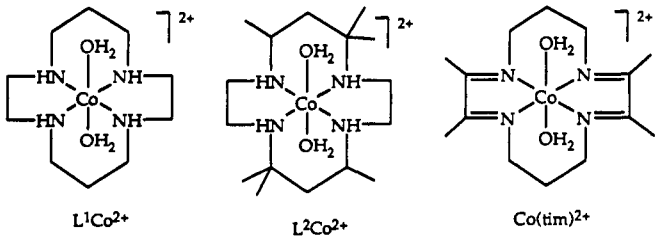
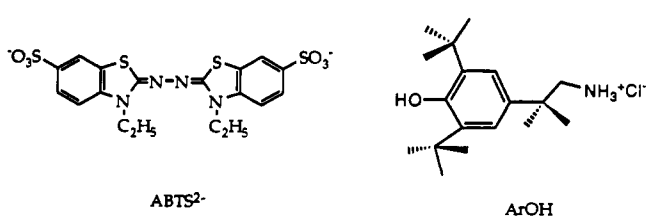


were prepared by literature procedures,[11a] as was $Co(tim)(H_2O)_2^{2+}$ ($Co(tim)^{2+}$).[11b] The hydroperoxochromium(III) ion, CrO_2H^{2+}, was prepared by addition of 1 equiv of $Ru(NH_3)_6^{2+}$ to a solution of CrO_2^{2+} (0.05–0.3 mM) under Ar. This solution was stored at 0 °C and used within 30 min.

Kinetics. All the kinetic experiments were carried out at 25.0 ± 0.2 °C. Reactions with half-lives of >10 s were conducted by use of a Cary 219 or Shimadzu UV-3101PC spectrophotometer equipped with an internal timer and a thermostated cell-holder. For the reactions with L^1Co^{2+} and Cu^+, a Durrum stopped-flow instrument was used. Many of the measurements were performed at a constant $[H^+]$ of 0.10 M. For the reactions carried out at different proton concentrations, the ionic strength was maintained with $LiClO_4$. In most of the experiments the kinetics were monitored directly at a wavelength giving the best absorbance change. In the reaction with VO^{2+} the absorbance changes were inconveniently small. This necessitated the use of the kinetic probes ArOH ([2-methyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]ammonium chloride) or $ABTS^{2-}$ (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate)). The absorbance (D)-time data were fitted to the equation $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ by use of the programs Spectracalc or GraFit.



The activation parameters for the reactions with CrO_2H^{2+} and the reactions with H_2O_2 were calculated from the Eyring equation. The kinetic measurements were usually conducted in the temperature range 5.0–40.0 °C.

The stoichiometry of the reaction with Fe^{2+} was determined from the absorbance changes at 240 nm.[4] For the reaction of CrO_2H^{2+} with $Co(tim)^{2+}$ the measurement was done at 545 nm (ϵ = 3450 M^{-1} cm^{-1};[12] $\Delta Co(tim)^{2+}/\Delta CrO_2H^{2+}$ = 2.0 ± 0.1). For the reactions with L^1Co^{2+} (L^1 = [14]aneN$_4$), the measurements were done at 270 nm (ϵ = 8300 M^{-1} cm^{-1} for L^1Co^{3+}, 120 M^{-1} cm^{-1} for L^1Co^{2+}, and 1800 M^{-1} cm^{-1} for CrO_2H^{2+}; $\Delta[L^1Co^{2+}]/\Delta[CrO_2H^{2+}]$ = 2.3 ± 0.1) and for L^2Co^{2+} (L^2 = Me_6[14]aneN$_4$) at 300 nm (ϵ = 5500 M^{-1} cm^{-1} for L^2Co^{3+}, 110 M^{-1} cm^{-1} for L^2Co^{2+}, and 440 M^{-1} cm^{-1} for CrO_2H^{2+}; $\Delta[L^2Co^{2+}]/\Delta[CrO_2H^{2+}]$ = 2.1 ± 0.1). The calculations of the molar absorption coefficients at 270 and 300 nm for the cobalt macrocycles utilized concentrations that were determined from the reported spectral data in the visible region.[13]

Results

Self-Decomposition. The decomposition of CrO_2H^{2+} is slow ($t_{1/2}$ ~ 15 min at room temperature) compared to any of the reactions studied in this work. The products of decomposition in 0.42 M H^+ are Cr^{3+}, H_2O_2, and O_2. The presence of H_2O_2 in the decomposed solution was determined kinetically. After a sample of CrO_2H^{2+} decomposed, an excess of NaI was added to the solution ($[CrO_2H^{2+}]_0$ = 0.25 mM, $[I^-]$ = 0.014 M, and $[H^+]$ = 0.41 M) and the formation of I_3^- monitored spectrophotometrically at 350 nm. The reaction took place with k = 1.06 × 10^{-3} s^{-1} and yielded 0.057 mM I_3^-. Under identical conditions the reaction of I^- with authentic H_2O_2 gave k = 1.04 × 10^{-3} s^{-1}. Molecular oxygen was observed in the form of bubbles on the inner surface of the spectrophotometric cell, particularly when the initial concentration of CrO_2H^{2+} exceeded 0.1 mM. A quantity of 0.050 mM (1.6 mg/L) oxygen was detected by use of an oxygen sensitive electrode for a solution that initially contained 0.21 mM CrO_2H^{2+}. The same solution also yielded 0.051 mM H_2O_2. O_2 does not oxidize I^- rapidly enough under these conditions to interfere with the analysis.

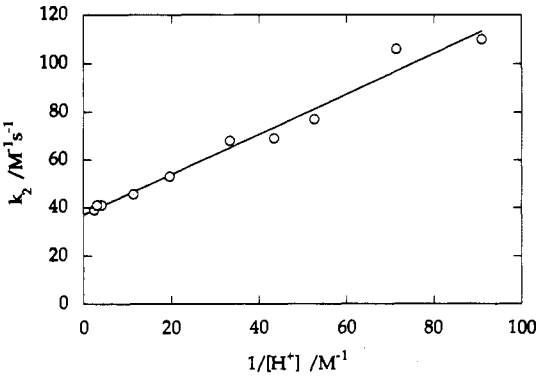


Figure 1. Dependence of k_2 on $[H^+]$ for the reaction of CrO_2H^{2+} with Fe^{2+} at μ = 0.41 M and 25 °C. Each point was calculated from the pseudo-first-order plot which contained at least three different $[Fe^{2+}]$. The concentrations of Fe^{2+} were in large excess over $[CrO_2H^{2+}]$ = 0.05 mM.

Table I. Kinetic and Stoichiometric Data for the Reaction of CrO_2H^{2+} with Fe^{2+} at 25.0 ± 0.2 °C

$[H^+]$ (M)	$\Delta[Fe^{2+}]/\Delta[CrO_2H^{2+}]$	k_2 (M^{-1} s^{-1})	$[H^+]$ (M)	$\Delta[Fe^{2+}]/\Delta[CrO_2H^{2+}]$	k_2 (M^{-1} s^{-1})
0.41	2.2	39 ± 1	0.030		68 ± 1
0.32	2.0	41 ± 1	0.023		69 ± 2
0.24	2.3	41 ± 1	0.019		77 ± 2
0.088	2.1	45.6 ± 0.6	0.014		106 ± 6
0.051	2.0	53 ± 2	0.011		110 ± 4

At 0.10 M H^+, the UV–vis spectra of the decomposed solutions exhibited maxima at 261 and 338 nm, consistent with the presence of $HCrO_4^-$ among the products. The formation of I_3^- by addition of excess I^- (0.0152 M) to this solution took place with an observed-rate constant of 3.35 × 10^{-3} s^{-1}. Under the same conditions, the observed-rate constants of 2.3 × 10^{-3} s^{-1} and 5.22 × 10^{-4} s^{-1} were obtained for the reactions of $HCrO_4^-$ and H_2O_2 with I^-, respectively. The kinetic result is qualitatively consistent with both $HCrO_4^-$ and H_2O_2 being present in the decomposed solution. A detailed analysis of the product distribution will be given in the Discussion.

Reactions with Metal Reductants. Iron(II) reduces CrO_2H^{2+} according to the stoichiometry of eq 2 with a second order rate

$$CrO_2H^{2+} + 2Fe^{2+} + 3H^+ \rightarrow Cr^{3+} + 2Fe^{3+} + 2H_2O \qquad (2)$$

constant of 48 M^{-1} s^{-1}.[4] The stoichiometry is independent of $[H^+]$ in the range examined, Table I. However, the rate constant increases with a decrease in $[H^+]$ below 0.1 M. A plot of the second order rate constant against $1/[H^+]$ is linear, Figure 1. The line drawn corresponds to the equation k_2/M^{-1} s^{-1} = 37 + 0.84$[H^+]^{-1}$.

Vanadium(II). The reaction of CrO_2H^{2+} with V^{2+} was monitored at 270 nm. The CrO_2H^{2+} was produced in situ from CrO_2^{2+} and V^{2+}, eq 3. The rate constant for this reaction,[1b] 2

$$CrO_2^{2+} + V^{2+} + H^+ \rightarrow CrO_2H^{2+} + V^{3+} \qquad (3)$$

$$CrO_2H^{2+} + V^{2+} \rightarrow \text{products} \qquad (4)$$

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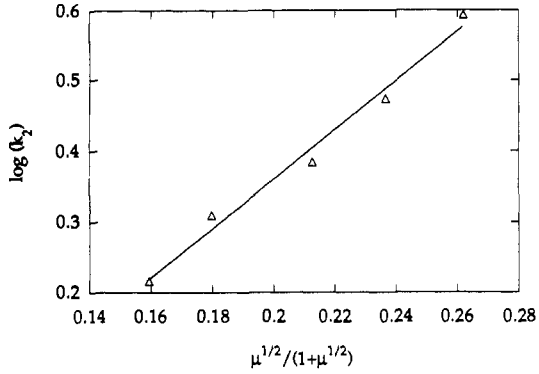

Figure 2. Ionic strength dependence of the second-order rate constant for the reaction of CrO_2H^{2+} with V^{2+} at 25 °C. The ionic strength was varied from 0.0165 M to 0.126 M and maintained by perchloric acid only. The slope of the line is 3.5 ± 0.3.

Table II. Bimolecular Rate Constants for the Reaction of CrO_2H^{2+} with Ti^{3+} at μ = 0.44 M and 25 °C

$[H^+]$ (M)	$[Cl^-]$ (M)	k_{298} (M^{-1} s^{-1})	$[H^+]$ (M)	$[Cl^-]$ (M)	k_{298} (M^{-1} s^{-1})
0.10	0.44	116 ± 1	0.032	0.028	28 ● 1
0.10	0.25	38 ± 2	0.44	0.028	26.7 ● 0.8
0.10	0.028	28.4 ± 0.8			

× 10^5 M^{-1} s^{-1}, is sufficiently large to ensure that the formation of CrO_2H^{2+} is "instantaneous" on the time scale of the subsequent reaction of interest, eq 4. Reaction 4 obeys mixed second-order kinetics with k_4 = 3.6 ± 0.2, 4.2 ± 0.3, and 4.5 ± 0.4 M^{-1} s^{-1} at μ = 0.78 M and $[H^+]$ = 0.78, 0.050, and 0.034 M, respectively. The value of k_4 decreased with decreasing ionic strength. A slope of 3.5 was obtained from the plot of $\log(k_2)$ against $\mu^{1/2}/(1 + \mu^{1/2})$, Figure 2. This is acceptably close to the theoretical value of 4.07, calculated from the Bronsted–Debye–Huckel equation as a product of the ionic charges (4+) and the constant $2A$ of electroionic theory (A = 0.509).

Cobalt(II) Macrocycles. The reactions of CrO_2H^{2+} with L^1Co^{2+} and L^2Co^{2+} are accompanied by large absorbance increases in the 300 nm range, corresponding to the formation of Co(III) complexes. Both reactions occur with a 1:2 stoichiometry of eq 5. The reaction with $Co(tim)^{2+}$ was monitored at 545 nm, and the absorbance change was used to calculate the stoichiometry, which is also given by eq 5.

$$CrO_2H^{2+} + 2LCo^{II} + 3H^+ \rightarrow Cr^{3+} + 2LCo^{III} + 2H_2O \quad (5)$$

The kinetic data yielded k = 1520 ± 20 M^{-1} s^{-1} for L^1Co^{2+} and 24.8 ± 0.4 for L^2Co^{2+}, independent of $[H^+]$ in the range 0.020–0.10 M. $Co(tim)^{2+}$ reacts with k = 41 ± 1 M^{-1} s^{-1} at 0.10 M H^+.

Titanium(III). Stock solutions of Ti^{3+} were prepared by dissolving titanium metal in HCl,[8,9] and thus all the kinetic solutions in the CrO_2H^{2+}/Ti^{3+} system necessarily contained some chloride. The reaction was conducted in both chloride and mixed chloride/perchlorate media. In these experiments Ti^{3+} was always added last to avoid the reduction of $HClO_4$. (At 0.028 M Cl^- and 0.10 M H^+, Ti^{3+} reduces ClO_4^- with k = 0.094 M^{-1} s^{-1} at 40°C.)[9b]

The kinetics of the CrO_2H^{2+}/Ti^{3+} reaction were acid and chloride independent at low $[Cl^-]$ in the acidity range 0.03–0.44 M. At high $[Cl^-]$ (>0.1 M) the rate constant increased with increasing $[Cl^-]$, indicating that an additional pathway operates under these conditions. All the data are listed in Table II. Attempts to prepare CrO_2H^{2+} by reduction of CrO_2^{2+} by Ti^{3+} were not successful, suggesting an inner-sphere mechanism for this reaction, like that between CrO_2^{2+} and Fe^{2+}.[1b]

Vanadium(IV). The reaction of CrO_2H^{2+} with VO^{2+} takes place with an absorbance change that was too small for direct kinetic measurements in the UV–visible range. The kinetics were thus conducted in the presence of either $ABTS^{2-}$ or ArOH as a kinetic probe. In the presence of $ABTS^{2-}$ as a probe, a two-stage reaction was observed owing to the reaction of $ABTS^{2-}$ with CrO^{2+} and the further oxidation of $ABTS^{2-}$ by a reaction product, VO_2^+:

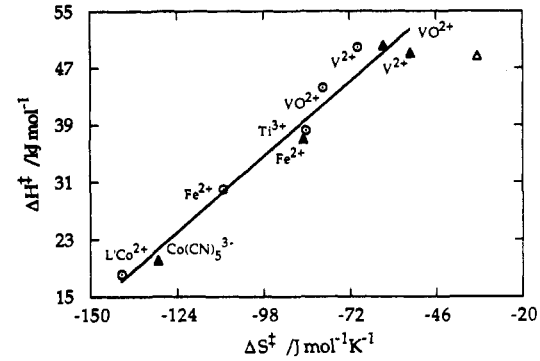

Figure 3. Plot of $\Delta H^‡$ vs $\Delta S^‡$ for the reactions of transition metal complexes with CrO_2H^{2+} (open circles) and with H_2O_2 (solid triangles). The slope defines the isokinetic temperature as 400 K. The open triangle is for the reaction of H_2O_2 with L^2Co^{2+}, which is known to adopt a different mechanism.

$$VO^{2+} + CrO_2H^{2+} \rightarrow VO_2^+ + CrO^{2+} + H^+ \quad (6)$$

$$CrO^{2+} + ABTS^{2-} \rightarrow Cr(III)\ products + ABTS^{\bullet-} \quad (7)$$

$$VO_2^+ + ABTS^{2-} + 2H^+ \rightarrow VO^{2+} + ABTS^{\bullet-} + H_2O \quad (8)$$

At sufficiently large concentrations of VO^{2+} (>8 mM) the two stages were separated in time. The standard treatment yielded k_6 = 8.2 ± 0.2 M^{-1} s^{-1} for the first stage and k_8 = 4.0 ± 0.2 M^{-1} s^{-1} for the second stage, both at μ = $[H^+]$ = 0.50 M and 25 °C. The reaction of CrO^{2+} with $ABTS^{2-}$ has a rate constant k_7 = 7.9 × 10^4 M^{-1} s^{-1} at $[H^+]$ = 0.10 M and 25 °C.[1d]

The addition of VO^{2+} to a solution containing ArOH and CrO_2H^{2+} leads to the formation of ArO·, as reported earlier.[4] This phenoxyl radical can be observed by its distinctive UV–vis spectrum in the region 300–450 nm. The kinetic study was done by allowing VO^{2+} (1.8–4.5 mM) to react with CrO_2H^{2+} (0.10 mM) in the presence of 2.0 mM ArOH. The absorbance increase at 400 nm, corresponding to the formation of ArO·, was used to monitor the reaction of VO^{2+} with CrO_2H^{2+}. The kinetic traces were fitted to a single exponential equation yielding the values of k_ψ. A plot of k_ψ vs $[VO^{2+}]$ gave a second-order rate constant of k = 6.0 ± 0.2 M^{-1} s^{-1} at μ = $[H^+]$ = 0.10 M and 25 °C. The dependence of the rate constant on $[H^+]$ was studied at $[CrO_2H^{2+}]$ = 0.035–0.070 mM, $[VO^{2+}]$ = 0.082–2.1 mM, and [ArOH] = 1.0 mM. At μ = 0.50 M and 25 °C the second-order rate constants were 9.5 ± 0.4 and 15.3 ± 0.3 M^{-1} s^{-1} at $[H^+]$ = 0.10 and 0.030 M. These data and those obtained from the reaction of CrO_2H^{2+} with VO^{2+} in the presence of $ABTS^{2-}$ at $[H^+]$ = 0.50 M yield a linear plot of the second-order rate constants against $1/[H^+]$ with an intercept of 7.5 M^{-1} s^{-1} and a slope of 0.23 s^{-1}.

Copper(I). The reduction of CrO_2H^{2+} by Cu^+ takes place with a rate constant k = 695 ± 20 M^{-1} s^{-1}, independent of $[H^+]$ in the range 0.010–0.50 M with constant ionic strength of 0.50 M.

Ruthenium(II). The reaction of CrO_2H^{2+} with $Ru(NH_3)_6^{2+}$ was conducted in 0.10 M CF_3SO_3H to avoid the reaction of $Ru(NH_3)_6^{2+}$ with perchlorate.[14] No reaction was observed at $[CrO_2H^{2+}]$ = 0.033 mM and $[Ru(NH_3)_6^{2+}]$ < 0.8 mM during the 15-min lifetime of CrO_2H^{2+}. Thus k << 1 M^{-1} s^{-1} for the reaction of CrO_2H^{2+} with $Ru(NH_3)_6^{2+}$.

Isokinetic Relationship. The activation parameters for the reactions of CrO_2H^{2+} with a number of metal reductants were calculated from their Eyring plots. As shown in Figure 3, $\Delta H^‡$

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Table III. Summary of the Second-Order Rate Constants and Activation Parameters for the Reactions of CrO_2H^{2+} and H_2O_2 with Metal Reductants

	CrO_2H^{2+}			H_2O_2		
reductants	k_2 (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	k_2 (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
$Fe(H_2O)_6^{2+}$	48.4	29.99 ± 0.68	−110 ± 2	58[a]	37.0 ● 1.2[a]	−86 ● 4.3[a]
$V(H_2O)_6^{2+}$	2.5	49.93 ± 0.84	−69.9 ± 2.8	17[b]	49.1 ± 3.0	−53.8 ● 10.2
$Ti(H_2O)_6^{3+}$	28	38.21 ± 0.83	−85.3 ± 2.8	920[c]		
VO^{2+}	6	44.2 ± 2.0	−80.2 ± 6.9	5.8[c]	50.2 ± 2.1	−62 ± 7
L^1Co^{2+}	1530			3970[d]		
L^2Co^{2+}	24	18.17 ± 1.26	−140.5 ± 4.4	265[d]		
$Co(tim)^{2+}$	41			142[d]		
Cu^{+}	700			4100[e]		
$Ru(NH_3)_6^{2+}$	NR			$<10^{-2}$[f]		

[a] Reference 15a. [b] Reference 3c. [c] Calculated from ref 20. [d] Reference 2c. [e] Reference 2f. [f] Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639.

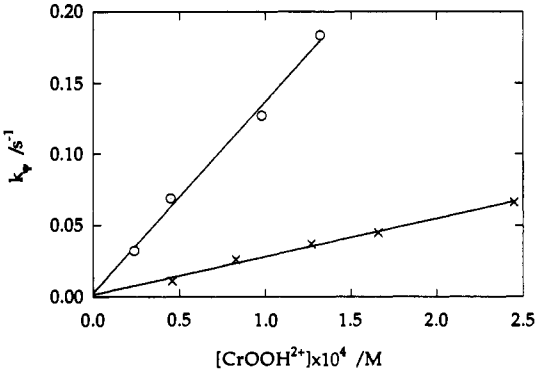

Figure 4. Dependence of the observed rate constants on the concentration of CrO_2H^{2+} in H_2O (open circles) and in D_2O (crosses) for the reaction of CrO_2H^{2+} with CrO^{2+} in 0.10 M $H(D)ClO_4$ at 25 °C.

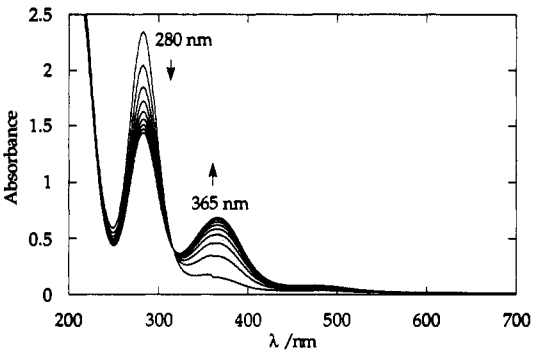

Figure 5. Repetitive scan spectra (every 100 s) for the reaction of 0.16 mM CrO_2H^{2+} with 0.19 mM $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, showing the disappearance of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ at 280 nm and the growth of the product at 365 nm.

is a linear function of $\Delta S^{\ddagger}$ not only for CrO_2H^{2+} but for H_2O_2 as well. The slope of the line yields the isokinetic temperature of 400 ± 30 K or 130 ± 10 °C. The activation parameters for the reactions of H_2O_2 and CrO_2H^{2+} are given in Table III, and the data for the reactions of H_2O_2 with $Co(CN)_5^{3-}$ and with Fe^{2+} were obtained from the literature.[15]

Oxidation of CrO_2H^{2+}. Addition of Cr^{2+} (0.2 mM) to an air-saturated solution of methanol-free CrO_2H^{2+} (0.05 mM) caused the absorbance in the UV to increase. The spectrum of the product matches exactly that of CrO_2^{2+}. The chemistry involved is shown in eqs 9 and 10.

$$Cr^{2+} + O_2 \rightarrow \{CrO^{2+} + CrO_2^{2+}\}$$

$$k_9 = 1.6 \times 10^8\ M^{-1}\ s^{-1}\ [16] \quad (9)$$

$$CrO^{2+} + CrO_2H^{2+} \xrightarrow{H^+} Cr^{3+} + CrO_2^{2+} \quad (10)$$

With CrO_2H^{2+} present in a large excess over CrO^{2+}, the formation of CrO_2^{2+} follows first-order kinetics. The observed rate constants vary linearly with the concentration of CrO_2H^{2+} and yield $k_{10} = (1.34 \pm 0.06) \times 10^3\ M^{-1}\ s^{-1}$ at 25 °C and 0.10 M H^+. When all of the solutions (Cr^{2+}, $DClO_4$, $Ru(NH_3)_6^{2+}$, CrO_2D^{2+}) were prepared in D_2O, the rate constant was significantly smaller, 266 ± 10 M^{-1} s^{-1}, giving $k_H/k_D = 5.0$, as shown in Figure 4.

There was no reaction between CrO_2H^{2+} (0.15 mM) and $HCrO_4^-$ (0.03–0.08 mM) in 10 min at 0.1 M H^+.

Reactions with Nucleophiles. $(en)_2CoSCH_2CH_2NH_2^{2+}$ reacts with CrO_2H^{2+} according to eq 11. The rate constant $k_{11} = 20.5$

$$(en)_2CoSCH_2CH_2NH_2^{2+} + CrOOH^{2+} \xrightarrow{H^+} (en)_2Co\overset{O}{S}CH_2CH_2NH_2^{2+} + Cr^{3+} + H_2O \quad (11)$$

± 0.4 M^{-1} s^{-1} at 0.10 M H^+ was obtained from a plot of k_ψ vs $[(en)_2CoSCH_2CH_2NH_2^{2+}]$. The formation of $(en)_2CoS(O)CH_2CH_2NH_2^{2+}$, an oxygen transfer product, is clearly indicated by the growing absorption maximum at 365 nm.[17] The reaction is clean with an isosbestic point at 310 nm as shown in the repetitive-scan spectra in Figure 5.

Triphenylphosphine. Because of the low solubility of Ph_3P in H_2O, the reaction of PPh_3 with hydroperoxides was studied in 1:1 CH_3CN/H_2O (v/v) at 0.10 M H^+. Under these conditions the reaction of H_2O_2 with PPh_3 took place with a 1:1 stoichiometry and a rate constant 2.94 ± 0.08 M^{-1} s^{-1}. The reaction with CrO_2H^{2+} gave k = 75 ± 3 M^{-1} s^{-1}.

$$Ph_3P + CrO_2H^{2+} \rightarrow Ph_3P{=}O + CrOH^{2+} \quad (12)$$

Bromide Ions. The absorbance increase at 260 nm, corresponding to the formation of Br_3^-, was used to follow the reaction of CrO_2H^{2+} with Br^-. To obtain sufficient absorbance change, >30 mM Br^- was used to react with CrO_2H^{2+} (0.05–0.1 mM). The acid dependence was studied in the range 0.10–0.75 M H^+ at 2.0 M ionic strength. The second-order rate constants are 0.063, 0.19, 0.31, and 0.41 M^{-1} s^{-1} at 0.10, 0.25, 0.50, and 0.75 M H^+, respectively. A plot of the second-order rate constants against $[H^+]$ yields a straight line described by the equation $k_2/M^{-1}\ s^{-1} = 0.035 + 0.52[H^+]$. The oxidation of bromide by H_2O_2 takes

(15) (a) For the reaction of Fe^{2+} with H_2O_2, values were calculated from the data in: Hardwick, T. J. *Can. J. Chem.* **1957**, *35*, 428. Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. *Trans. Faraday Soc.* **1951**, *47*, 462. (b) For the reaction of $Co(CN)_5^{3-}$ with H_2O_2, see: Chock, P. B.; Dewar, R. B. K.; Halpern, J.; Wong, L.-Y. *J. Am. Chem. Soc.* **1969**, *91*, 82.

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place according to the same general rate law with $k = 3.8 \times 10^{-7} + 2.3 \times 10^{-4}[H^+]$.[18]

Discussion

Mechanism. The reduction of H_2O_2 and ROOH by transition metal complexes requires precoordination of peroxide to the metal. The reaction rate is therefore governed not only by the driving force for these reactions but also by the ligand substitution rates of the metal complexes. For example, V^{2+} reduces H_2O_2 more slowly than Fe^{2+} does ($k_V = 17\ M^{-1}\ s^{-1}$, compared to $k_{Fe} = 58\ M^{-1}\ s^{-1}$), even though the reduction potential of V^{3+}/V^{2+} ($E° = -0.255$ V) is over 1 V more negative than that of Fe^{3+}/Fe^{2+} ($E° = 0.77$ V). The same reactivity order is found in the reactions of CrO_2H^{2+} with transition metal reductants, Table III.

The most striking feature of the data in Table III is the similarity of rate constants for the reactions of H_2O_2 and CrO_2H^{2+} with common reductants. As a rule, the reactions of CrO_2H^{2+} are slower, but the difference is small. The most obvious interpretation is that the two peroxides react by the same mechanism and that the replacement of one H^+ by Cr^{3+} has little influence on the reduction potential of H_2O_2.

With the possible exception of Cu^+,[2f] the aqueous reactions of H_2O_2 with transition metal complexes in Table III are believed[2,3] to proceed by a one-electron, Fenton-type mechanism, eq 1b. As for the reactions of CrO_2H^{2+}, the trapping experiments with ArOH and oxalate reported previously strongly support the intermediacy of CrO^{2+} in the reaction with Fe^{2+}.[4] Similarly, the formation of $ArO^·$ in the reaction of CrO_2H^{2+} with VO^{2+} in the presence of ArOH provides evidence for the intermediacy of CrO^{2+} in this system as well. The observed reactivity order for the series of reductants and the isokinetic relationship in Figure 3 suggest that the rest of the reactions in Table III also take place by a modified Fenton mechanism, shown for Fe^{2+} in eqs 13 and 14.

$$CrO_2H^{2+} + Fe^{2+} \rightarrow CrO^{2+} + FeOH^{2+} \qquad (13)$$

$$CrO^{2+} + Fe^{2+} \xrightarrow{2H^+} Cr^{3+} + Fe^{3+} + H_2O \qquad (14)$$

The reaction of L^2Co^{2+} with H_2O_2 has a 1:1 stoichiometry, whereas the corresponding reaction with CrO_2H^{2+} has $\Delta[CrO_2H^{2+}]/\Delta[L^2Co^{2+}] = 0.50$. It was proposed previously[2c] that the H_2O_2 reaction starts out with a Fenton-type step, but the product $OH^·$ is captured by the macrocyclic ligand, possibly in a single step. The chromyl ion, on the other hand, is much less reactive toward C–H bonds[1d] and is therefore released into solution.

Let us assume that the much lower reactivity of CrO^{2+}, relative to $HO^·$, in redox reactions and hydrogen atom abstractions is thermodynamic in origin. If this is true, then the similarity of the kinetic data for H_2O_2 and CrO_2H^{2+} has an interesting implication: the substitution of H^+ by Cr^{3+} lowers the free energy content of H_2O_2 and $HO^·$ by an approximately equal amount. Thus despite the larger absolute reduction potentials of the hydrogen species relative to the chromium-substituted ones, the free energy *change* in reactions 1a and 1b is approximately the same. Additional data are required to test this proposal.

Effect of H^+. The kinetics of the reaction of Fe^{2+} with H_2O_2 is acid independent at $[H^+] > 0.01$ M.[15a] Below this concentration the rate constant increases with decreasing acidity, probably because of the pH dependence of the Fe^{III}/Fe^{II} reduction potential.[19] Similar observations were made in the reactions of H_2O_2 with Ti^{3+} and VO^{2+} at 0.003–1 M $HClO_4$.[20]

The rate law for the reaction of CrO_2H^{2+} with Fe^{2+} has a major acid independent term ($k = 37\ M^{-1}\ s^{-1}$) and a term inversely proportional to $[H^+]$ in the range 0.011–0.41 M, eq 15. All the other reactions in Table III are acid independent, except the reaction with VO^{2+}.

$$k_{Fe} = k_o + k'[H^+]^{-1} \qquad (15)$$

The precise value of the pK_a of $Cr(H_2O_2)^{3+}$ is not known, although one can reasonably place it in the range 1–3.[1c] Both forms, $Cr(H_2O_2)^{3+}$ and CrO_2H^{2+}, might therefore be present under our experimental conditions. The pH independence of most of the reactions in Table III indicates that the reactivities of the two forms are similar or that the pK_a lies outside the estimated limit.

The detailed mechanism for the reduction of CrO_2H^{2+} by transition metal complexes is shown in eqs 16 and 17. The

$$CrO_2H^{2+} + M^n \rightleftarrows CrO_2(H)M^{n+2} \qquad (16)$$

$$CrO_2(H)M^{n+2} \rightarrow CrO^{2+} + MOH^n \qquad (17)$$

formation and dissociation of the binuclear peroxo intermediate, reaction 16, may or may not be acid dependent. Note that in the reductions of H_2O_2 by low-valent transition metal complexes there is typically no acid dependence associated with this step. VO^{2+} is a notable exception.[20] However, the substitution of CrO_2H^{2+} for H_2O_2 causes an increase in the charge on the peroxo intermediate by two units, which will certainly cause a dramatic change in its pK_a. Thus the reverse reaction, eq –16, and the electron-transfer/product forming step, eq 17, may be acid catalyzed. As long as the kinetic order in H^+ is the same for reactions –16 and 17, the overall kinetics will be acid independent, eq 18, as observed experimentally. The $1/[H^+]$ term in the iron(II) case may indicate that $FeOH^+$ is much more reactive than Fe^{2+}.

$$k_{obs} = k_{16}k_{17}/(k_{-16} + k_{17}) \qquad (18)$$

Oxygen Transfer Reactions. As shown in Table IV, the reactions of CrO_2H^{2+} with nucleophiles are about 20 times faster than the corresponding reactions with H_2O_2. Oxidations of coordinated[17a] and free thiols[21] by H_2O_2 take place by nucleophilic attack at the O–O bond[17a,21] with the kinetics described by eq 19.

$$\text{rate} = (k_1 + k_2[H^+])[H_2O_2][\text{Nuc}] \qquad (19)$$

It has been shown[17a] that the energetics of the O–O bond cleavage control the oxidation of coordinated thiols. For the reaction of CrO_2H^{2+} with the (thiolato)cobalt complex, the addition of ArOH has no effect on the kinetics or on the yield of the (sulfenato)-cobalt product. Also no $ArO^·$ was observed in this reaction, which indicates that CrO^{2+} was not produced. We believe that the oxidation of $(en)_2CoSCH_2CH_2NH_2^{2+}$ by CrO_2H^{2+} proceeds by the same mechanism as the H_2O_2 reaction. The weaker O–O bond and the positive charge on CrO_2H^{2+} may be the reason for the 20-fold acceleration compared to the hydrogen peroxide reaction. Unlike H_2O_2, CrO_2H^{2+} does not oxidize $(en)_2CoS(O)CH_2CH_2NH_2^{2+}$ to the sulfinato complex $(en)_2CoS(O)_2CH_2CH_2NH_2^{2+}$ at appreciable rates.

Table IV. Comparison of the Kinetic Data for the Reactions of Nucleophiles with CrO_2H^{2+} and with H_2O_2 (25 °C, 0.10 M H^+)

	k_{298} ($M^{-1}\ s^{-1}$)		
reagent	PPh_3	Br^-	$CoSR^{2+}$
CrO_2H^{2+}	75	0.063	20.5
H_2O_2	3	0.000 23[a]	1.36[b]

[a] Reference 18. [b] Reference 17a.

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The oxidation of tertiary phosphines by H_2O_2 has been used to synthesize tertiary phosphine oxides,[22] but no detailed kinetic studies have been carried out. To compare the reactivities of H_2O_2 and CrO_2H^{2+}, the reactions of both hydroperoxides with PPh_3 were studied kinetically in 1:1 CH_3CN/H_2O. Similar to the case for other nucleophiles in Table IV, the reaction of H_2O_2 with PPh_3 is about 20 times slower than the corresponding CrO_2H^{2+} reaction.

The oxidation of halides by H_2O_2 has been known to follow the same kinetic expression as shown in eq 19.[18] The acid-dependent kinetics found in the reaction of Br^- with CrO_2H^{2+} resemble those observed in the corresponding H_2O_2 reaction, suggesting the same mechanism for the two peroxides.

Oxidation of CrO_2H^{2+}. Hydrogen peroxide and alkyl hydroperoxides can be oxidized by strong oxidizing agents, such as Ce^{IV} and Mn^{III}.[23] Oxidation of CrO_2H^{2+} by Ce^{IV} to produce CrO_2^{2+} has been used initially to characterize CrO_2H^{2+} as an intact product of the one-electron reduction of CrO_2^{2+}.[1c,4] In this work we studied the oxidation of CrO_2H^{2+} by CrO^{2+}, eq 10. The experimentally observed stoichiometry of eq 10 and the kinetic isotope effect $k_H/k_D = 5.0$ are consistent with hydrogen atom abstraction by CrO^{2+}. However, the isotope effect is a combination of contributions from solvent and coordinated water in addition to that from the hydroperoxo group, which makes the mechanistic assignment less than definitive.

The two peroxides, H_2O_2 and CrO_2H^{2+}, have similar reactivities toward both oxidants and reductants examined in this work. The CrO_2H^{2+} is a somewhat better reductant and H_2O_2 a better oxidant, but differences are generally small and can probably be rationalized by charge effects and minor differences in the redox potentials and O–O bond strengths.

Decomposition of CrO_2H^{2+}. At 0.4 M H^+ and <0.1 mM CrO_2H^{2+}, the hydroperoxochromium ion has a half-life of ca. 15 min at 25 °C. Our preliminary work indicates that the decomposition becomes faster at higher initial concentrations, indicating a greater than first-order dependence on CrO_2H^{2+}. This kinetic behavior and the formation of O_2 as one of the decomposition products indicate that the coordinated peroxide may be decomposing by disproportionation (eq 20), similar to

$$2CrO_2H^{2+} \rightarrow 2CrOH^{2+} + O_2 \quad (20)$$

$$CrO_2H^{2+} + H^+ \rightarrow Cr^{3+} + H_2O_2 \quad (21)$$

$$3CrO_2H^{2+} + 2H_2O \rightarrow 2HCrO_4^- + Cr^{3+} + 5H^+ \quad (22)$$

the parent H_2O_2. The effect of H^+ on the kinetics and the increased yields of H_2O_2 at higher H^+ are consistent with acidolysis of eq 21 being also a major pathway. This type of decomposition has been observed in other metal hydroperoxide systems as well.[24] At 0.10 M H^+, the UV–vis spectra of the decomposed solutions and the kinetic result are consistent with both $HCrO_4^-$ and H_2O_2 being present in the decomposed solution. Equation 22 is proposed to account for this decomposition route, which is also a disproportionation reaction; however, this time it occurs between Cr(III) and coordinated peroxide. At high concentration of H^+, eq 21 is dominant but eq 22 becomes a major path when the concentration of H^+ is low. The kinetic traces for the decomposition of CrO_2H^{2+} were complicated by the generation of gas bubbles, which precluded the detailed analysis of the three processes.

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