2592 *Inorg. Chem.* **1988**, *27*, 2592-2595

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Reactions of the Superoxochromium(III) Ion with Transition-Metal Complexes

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The reactions of the superoxochromium(III) ion, CrO_2^{2+}, with a number of one-electron-reducing agents have been examined in acidic aqueous solutions at 25 °C and 0.10 M ionic strength. The results are consistent with an outer-sphere mechanism for $Ru(NH_3)_6^{2+}$ ($k = 9.5 \times 10^5$ M^{-1} s^{-1}), $Co(sep)^{2+}$ (8.5×10^5 M^{-1} s^{-1}), and $V(H_2O)_6^{2+}$ (2.3×10^5 M^{-1} s^{-1}). The reactions with $Fe(H_2O)_6^{2+}$, $Co([14]aneN_4)(OH_2)_2^{2+}$, and $Co([15]aneN_4)(OH_2)_2^{2+}$ take place by an inner-sphere mechanism characterized by the formation and subsequent decomposition of binuclear intermediates. The rate constants for these reactions have values 4.5×10^3, $\sim 7 \times 10^6$, and 6.2×10^5 M^{-1} s^{-1}, respectively.

Introduction

Oxidations that depend on dioxygen are of fundamental importance to many chemical and biological processes.[1] Although dioxygen is an integral part of many redox systems, it is known to be sluggish in many of its reactions, often utilizing a transition-metal complex to activate it in redox processes. The triplet ground state of dioxygen provides a considerable kinetic barrier to the autoxidation of normally diamagnetic organic molecules. This barrier is associated with generally very slow reactions involving a change of spin or formation of unstable triplet-state products. This problem can be avoided by the reaction of dioxygen coordinated to a transition metal, where greater spin-orbit coupling considerably reduces the kinetic barrier to a change of spin. In addition, the formation of a metal dioxygen complex may provide sufficient energy to pair the spins.[1b] Thus the coordination of O_2 to *reduced* transition metals often yields potent and efficient *oxidants*.

Little is known about the reactivity patterns of transition-metal-dioxygen adducts in aqueous solution since the lifetimes of these adducts vary from moderately long to extremely short. One dioxygen adduct that has been studied in some detail is $Co([14]aneN_4)(OH_2)O_2^{2+}$.[2] The report on the reactivity of this species represents much of what is known about the chemistry of transition-metal-dioxygen adducts. The complex, which readily decomposes in aqueous solutions, is a moderately strong oxidant (estimated $E° \sim 0.3 \pm 0.1$ V).[2b] The oxidations of several transition-metal complexes with the in situ generated $Co([14]aneN_4)(OH_2)(O_2)^{2+}$ proceed with high rate constants and utilize all three oxidizing equivalents provided by the coordinated superoxide.

Another transition-metal-oxygen adduct, CrO_2^{2+},[3] has been characterized recently.[4] This is a semistable species with a half-life of ~15 min in 0.10 M aqueous $HClO_4$ at 25 °C under anaerobic conditions. Owing to its relative stability, pronounced spectral features, and known high reactivity toward one reductant (Cr^{2+}), it appeared to be an interesting candidate for a kinetic and mechanistic study of its reactions with a series of reducing complexes. This paper reports the results of that study.

Experimental Section

Materials. Dilute aqueous solutions of CrO_2^{2+} were prepared according to the literature procedure.[4] The ligands[5] $[14]aneN_4$ and $[15]aneN_4$ were obtained from Strem Chemical Co. Samples of $Co(\textit{meso}\text{-}Me_6[14]aneN_4)(OH_2)_2(ClO_4)_2$ and $Co(tmc)(OH_2)(ClO_4)_2$ were available in our laboratory reserves, and $Co(sep)Cl_3$ was a gift from A. M. Sargeson. $Ru(NH_3)_6Cl_3$ was obtained from Aldrich Chemical Co.

Solutions of $Co([14]aneN_4)(OH_2)_2^{2+}$ were prepared by mixing a 10% stoichiometric excess of the ligand with deaerated solutions of $Co(ClO_4)_2$. Sufficient $HClO_4$ was added after the reaction was complete to make the solution 0.10 M in H^+. The UV-vis spectrum of anaerobic $Co([14]aneN_4)(OH_2)_2^{2+}$ agreed well with the published one ($\lambda_{max} = 465$ nm, $\epsilon = 22$ M^{-1} cm^{-1}).[6] Solutions of $Co([15]aneN_4)(OH_2)_2^{2+}$ were prepared similarly and used at the natural pH owing to the low stability of the complex in acidic solutions. The concentrations of the anaerobic stock solutions of $Co([15]aneN_4)(OH_2)_2^{2+}$ were determined spectrophotometrically at 497 nm ($\epsilon = 13.9$ M^{-1} cm^{-1}).[7] The concentrations of the stock solutions of $Co(\textit{meso}\text{-}Me_6[14]aneN_4)(OH_2)_2^{2+}$ and $Co(tmc)(OH_2)^{2+}$ were determined from the mass of the cobalt complex taken.

Solutions of $Co(sep)^{2+}$ and $Ru(NH_3)_6^{2+}$ were prepared by a zinc amalgam reduction of $Co(sep)(ClO_4)_3$ and $Ru(NH_3)_6Cl_3$, respectively, in H_2O. Solutions of Fe^{2+} were prepared by a zinc amalgam reduction of acidic aqueous solutions of $Fe(ClO_4)_3$. The concentrations of the reduced species was considered to be equal to that of the parent species. The concentration of the $Co(sep)^{3+}$ solution was determined spectrophotometrically at 470 nm ($\epsilon = 110$ M^{-1} cm^{-1}).[8]

The stock solution of vanadium(IV) perchlorate was prepared by ion exchange (Dowex 50W-X8) of the sulfate salt. Vanadium(IV) was eluted with 1 M perchloric acid and standardized spectrophotometrically ($\lambda = 760$, $\epsilon = 17.2$ M^{-1} cm^{-1}).[9] The $V(H_2O)_6^{2+}$ used in the experiments was prepared by a zinc amalgam reduction of $VO(ClO_4)_2$ in 0.10 M $HClO_4$.

Instrumentation. Routine UV-visible spectra were recorded by use of a Perkin-Elmer Lambda Array 3840 UV/VIS spectrophotometer. The kinetic measurements were made with a Durrum stopped-flow spectrophotometer interfaced to an OLIS 3820 data system. Multiwavelength stopped-flow experiments used a George W. Gates Co. GID-25 rapid-scan monochromator, which served as the light source when interfaced to the Durrum stopped-flow spectrophotometer. Unless stated otherwise, all the stopped-flow experiments were done under anaerobic conditions at 25 °C and with a cell path length of 2 cm. The single-wavelength kinetic measurements for the outer-sphere electron-transfer reactions were done at one of the two maxima of CrO_2^{2+}, 247 nm ($\epsilon = 7400$ M^{-1} cm^{-1}) and 290 nm ($\epsilon = 3100$ M^{-1} cm^{-1}).[3e] The reductants were present in a pseudo-first-order excess relative to $[CrO_2^{2+}]$. The ionic strength was kept constant in all experiments at 0.10 M ($HClO_4$ + $LiClO_4$). The kinetic traces were analyzed by use of the first-order, second-order, and biexponential fitting routines on the OLIS computer system.

Results

Reaction between CrO_2^{2+} and Outer-Sphere-Electron-Transfer Reductants. The reactions are first-order in $[CrO_2^{2+}]$ and [R]

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(4) Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579.

(5) $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane; tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

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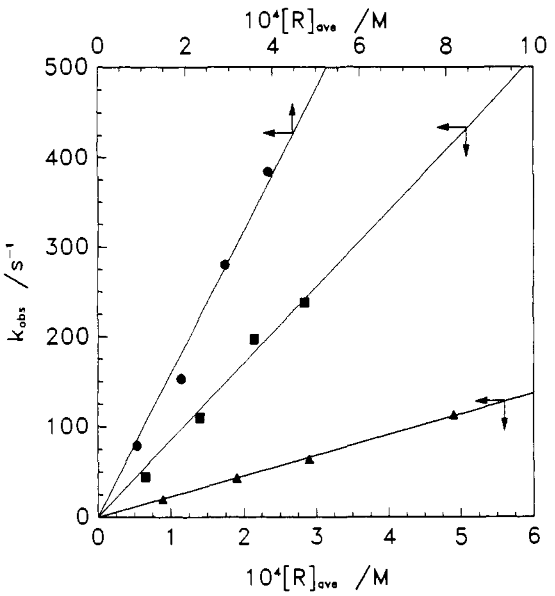

Figure 1. Dependence of k_{obsd} on $[R]_{av}$ ($[HClO_4] = \mu = 0.10$ M, $T = 25.0$ °C). R = $Ru(NH_3)_6^{2+}$ (circles), $Co(sep)^{2+}$ (squares), $V(OH_2)_6^{2+}$ (triangles).

(R = $Ru(NH_3)_6^{2+}$, $Co(sep)^{2+}$, and $V(H_2O)_6^{2+}$). Chloride ion in the concentration range 3×10^{-4}-0.05 M has no effect on the reactions of CrO_2^{2+} with $Ru(NH_3)_6^{2+}$. It was assumed that the reactions with $Co(sep)^{2+}$ and V^{2+} are also chloride independent. No spectroscopic evidence for an intermediate was obtained in any of the reactions.

The absorbances at 290 and 247 nm decreased during the reaction of CrO_2^{2+} with $Ru(NH_3)_6^{2+}$ and V^{2+}. The decreasing absorbance–time traces represent directly the consumption of CrO_2^{2+} during the reaction, since the other solutes absorb relatively little compared to CrO_2^{2+} at 247 and 290 nm. $Co(sep)^{3+}$ absorbs strongly at 247 nm ($\epsilon \sim 14000$ M^{-1} cm^{-1}), and the absorbances increased in the reaction of CrO_2^{2+} with $Co(sep)^{2+}$. The absorbance change at 247 nm suggests a 1:1 stoichiometry for this reaction. The UV spectrum of the products is consistent with the formation of $Co(sep)^{3+}$.

The results of the kinetic experiments are consistent with an outer-sphere reaction mechanism, eq 1–3. Figure 1 illustrates

$$CrO_2^{2+} + R \rightarrow CrO_2^{+} + R^{+} \quad (1)$$

$$-d[CrO_2^{2+}]/dt = k_1[CrO_2^{2+}][R] \quad (2)$$

$$k_{obsd} = k_1[R] \quad (3)$$

the three plots of k_{obsd} vs $[R]_{av}$ suggested by eq 3. A least-squares analysis yielded second-order rate constants k_1 for the three reagents $Ru(NH_3)_6^{2+}$, $Co(sep)^{2+}$, and V^{2+} as (9.5 ± 0.2) × 10^5, (8.5 ± 0.2) × 10^5, and (2.28 ± 0.05) × 10^5 M^{-1} s^{-1}, respectively.

Reaction between CrO_2^{2+} and Fe^{2+}. A biexponential reaction is observed with a rapid consumption of CrO_2^{2+} signaled by the absorbance changes. Once the effect of $HCrO_4^-$ is allowed for (see next paragraph), it became evident that the reaction of interest gives rise to a decrease in the absorbance at 290 nm (first stage) and a slower increase in the absorbance at 240 nm (second stage). The consumption of CrO_2^{2+} was monitored at 290 nm, and the formation of Fe^{3+} at 240 nm (Figure 2). The experiments were done with Fe^{2+} in pseudo-first-order excess under both aerobic and anaerobic conditions. Oxygen had no effect on the reaction and later experiments utilized air-saturated solutions.

In the anaerobic experiments CrO_2^{2+} was degassed for 5 min. This time is sufficient for a buildup of $\leq 5 \times 10^{-6}$ M $HCrO_4^-$.[4] The amount of $HCrO_4^-$ in solution at a given time depends on the age of the CrO_2^{2+} solution and initial concentrations of dioxygen and CrO_2^{2+}.[4] The presence of $HCrO_4^-$ can account for the second of the two reaction stages observed at 290 nm and the first of the two reaction stages at 240 nm. This assignment, based on a previous study of the $HCrO_4^-$/Fe(II) system,[10] was confirmed by blank experiments with genuine $HCrO_4^-$.

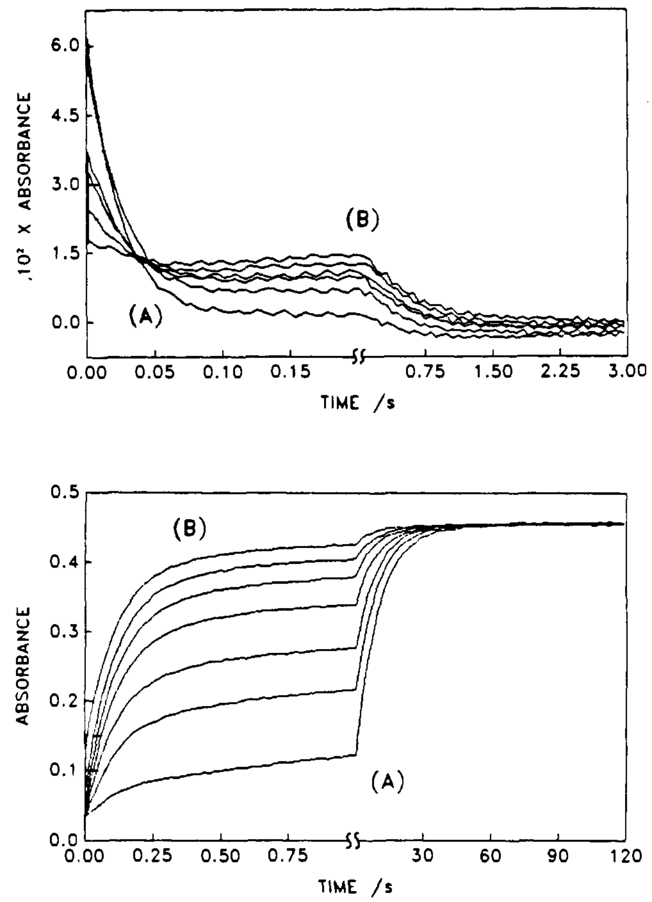

Figure 2. The reaction between CrO_2^{2+} and Fe^{2+} illustrated by a family of absorbance–time profiles at 290 nm (upper figure) and 240 nm (lower figure). All experiments were performed on the same solution at various times over a 2-h period (t = 0 h, A; t = 2 h, B). The first stage at 240 nm and the second stage at 290 nm are caused by the presence of small amounts of $HCrO_4^-$ (see text).

The first stage at 290 nm and the second stage at 240 nm can be assigned to the reaction of CrO_2^{2+} with Fe^{2+}. The overall absorbance change at 240 nm suggests that one molecule of CrO_2^{2+} oxidizes three molecules of Fe^{2+} to Fe^{3+} (eq 4).

$$CrO_2^{2+} + 3Fe^{2+} + 4H^{+} \rightarrow Cr^{3+} + 3Fe^{3+} + 2H_2O \quad (4)$$

The reaction initially produces an intermediate wtih an absorption maximum at 320 nm. The increase in absorbance at 320 nm coincides with the loss of CrO_2^{2+} at 290 nm (eq 5). The data

$$-d[CrO_2^{2+}]/dt = d[Int]/dt = k_{Fe}[CrO_2^{2+}][Fe^{2+}] \quad (5)$$

in Figure 3 yield the rate constant k_{Fe} = (2.45 ± 0.05) × 10^4 M^{-1} s^{-1}, independent of $[H^+]$ in the range 0.010–0.10 M. There is no absorbance change at 240 nm in this stage.

In a subsequent slower reaction the absorbance decreases at 320 nm and increases at 240 nm (Figure 4), according to the rate law of eq 6. The absorbance increase at 240 nm is consistent

$$-d[Int]/dt = k[Int][Fe^{2+}] \quad (6)$$

with the formation of two Fe^{3+} ions per intermediate ion. From the data in Figure 3 one calculates k_6 = 60 ± 2 M^{-1} s^{-1}, independent of $[H^+]$ in the range 0.010–0.10 M. A mechanism consistent with all the observations is shown in eq 7–10. The

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(10) Espenson, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 1880.

$$CrO_2^{2+} + Fe^{2+} \xrightarrow{k_{Fe}} CrO_2Fe^{4+} \qquad (7)$$

$$CrO_2Fe^{4+} \xrightarrow[H^+]{\text{fast}} CrO_2H^{2+} + Fe^{3+} \qquad (8)$$

$$CrO_2H^{2+} + Fe^{2+} \xrightarrow[H^+]{k_{int}} Fe^{3+} + CrO^{2+} + H_2O \qquad (9)$$

$$CrO^{2+} + Fe^{2+} \xrightarrow[2H^+]{\text{fast}} Fe^{3+} + Cr^{3+} + H_2O \qquad (10)$$

$$\text{net:}\quad CrO_2^{2+} + 3Fe^{2+} \xrightarrow{4H^+} Cr^{3+} + 3Fe^{3+} + 2H_2O \qquad (4)$$

binuclear intermediate produced in eq 7 is analogous to CrO_2Cr^{4+} formed in the reaction of CrO_2^{2+} and Cr^{2+}.[4] CrO_2Fe^{4+} is proposed to decompose as in eq 8, owing to the substitutional lability of Fe(III).[11] Thus, the intermediate observed at 320 nm is assigned to CrO_2H^{2+}.[12] The reduction of CrO_2H^{2+} by Fe^{2+} in eq 9 and 10 is consistent with the formation of 2 equiv of Fe^{3+} in the second stage of the reaction.

On the basis of the 1:1 stoichiometry for the formation of the intermediate (eq 7 and 8) and the absorbance changes in the kinetic experiments, the molar absorptivity of CrO_2H^{2+} is 1300 M^{-1} cm^{-1} at 320 nm and (2–3) × 10^3 M^{-1} cm^{-1} at 240 nm.

Reactions of CrO_2^{2+} with $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([15]aneN_4)(OH_2)_2^{2+}$. The UV–vis reaction profiles recorded in the multiwavelength stopped-flow experiments indicated multiphasic kinetics for both reactions. A rapid rise in the absorbance of the reaction mixture in the range 240–400 nm is followed by a slower absorbance decrease in the same wavelength range.

The reactions were monitored spectrophotometrically in single-wavelength stopped-flow experiments at 320 nm, the wavelength of the maximum absorbance change. The first stage for the reaction of CrO_2^{2+} with $Co([14]aneN_4)(OH_2)_2^{2+}$ is very fast. Efforts to lower the observed rate by lowering the concentration of the excess reagent, $Co([14]aneN_4)(OH_2)_2^{2+}$, were not feasible owing to the experimental uncertainty associated with the handling of the extremely oxygen-sensitive $Co([14]aneN_4)(OH_2)_2^{2+}$ at the very low (10^{-5} M) concentration levels. A single kinetic measurement at 25 °C yielded the rate constant $k_{Co[14]} \sim 7 \times 10^6$ M^{-1} s^{-1}. The second stage has an observed rate constant of 2.5 s^{-1}, and the third, a rate constant of 0.064 s^{-1}. It is possible that some of the absorbance changes in the $Co[n]aneN_4)(H_2O)_2^{2+}$ reactions are caused by trace amounts of chromate, like the reaction with Fe^{2+}.

The first stage for the reaction of $Co([15]aneN_4)(OH_2)_2^{2+}$ is first-order in $[CrO_2^{2+}]$ and first-order in $[Co([15]aneN_4)(OH_2)_2^{2+}]$. Figure 3 illustrates a plot of k_{obsd} vs $[Co([15]aneN_4)(OH_2)_2^{2+}]_{av}$. A least-squares analysis yields a rate constant $k_{co[15]} = (6.2 \pm 0.3) \times 10^5$ M^{-1} s^{-1}. The second stage is independent of $[CrO_2^{2+}]$, $[Co([15]aneN_4)(OH_2)_2^{2+}]$, and $[H^+]$. An average value for the first-order rate constant for the second stage is 0.48 ± 0.02 s^{-1}.

The data for both cobalt(II) complexes are consistent with an inner-sphere mechanism, eq 11 and 12, analogous to that proposed

$$CrO_2^{2+} + Co([n]aneN_4)^{2+} \xrightarrow{k_{Co[n]}} CrO_2Co([n]aneN_4)^{4+} \qquad (11)$$

$$n = 14, 15$$

$$CrO_2Co([n]aneN_4)^{4+} \rightarrow \text{products} \qquad (12)$$

for the reaction with Fe^{2+}. The binuclear intermediates produced in these reactions are not expected to dissociate as readily as CrO_2Fe^{4+} owing to the substitutional inertness of Co(III). The absorption maximum at 320 nm is thus assigned to the binuclear complexes. The similarity in the spectral features between CrO_2H^{2+} and $[CrO_2Co([n]aneN_4)]^{4+}$ seems reasonable, since CrO_2^+ is the chromophore in both species.

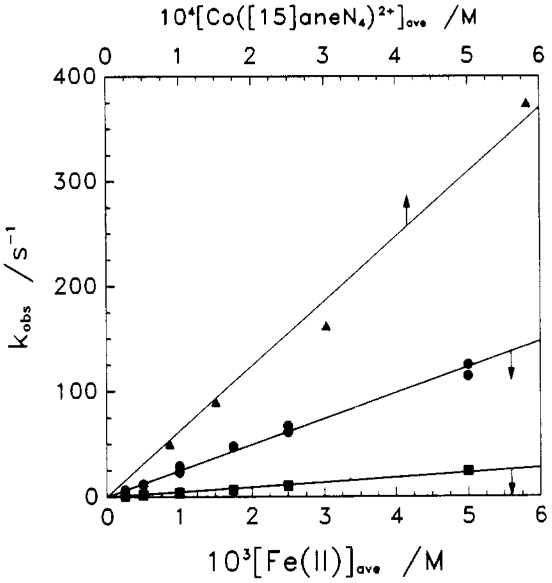

Figure 3. Dependence of k_{obsd} on $[Fe^{2+}]_{av}$ (first stage, circles; second stage, squares) and of k_{obsd} on $[Co([15]aneN_4)^{2+}]_{av}$ (triangles) (25 °C, $[H_3O^+] = \mu = 0.10$ M). The data symbolized by squares were multiplied by 10^2.

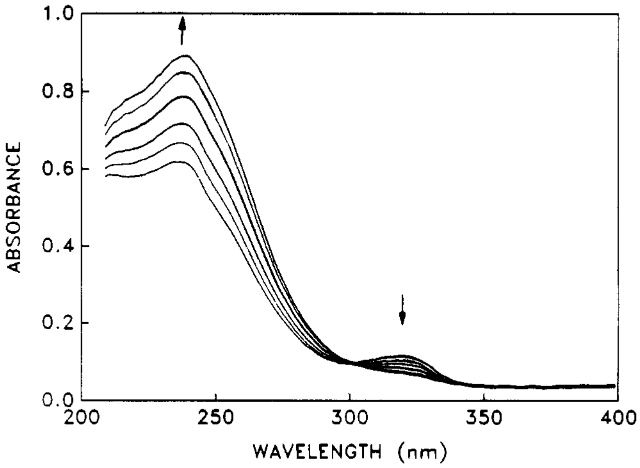

Figure 4. Absorbance–wavelength profiles for the loss of the intermediate formed in the reaction of CrO_2^{2+} and Fe^{2+}. The absorbance decreases at 320 nm ($k = 0.012$ s^{-1}) and increases at 240 nm ($k = 0.011$ s^{-1}). The total collection time is 430 s ($[H_3O^+] = \mu = 0.10$ M, $[CrO_2^{2+}]_0 = 3.2 \times 10^{-5}$ M, $[Fe^{2+}]_0 = 2.5 \times 10^{-4}$ M).

Other Reactions of CrO_2^{2+}. The reaction with $Co(meso\text{-}Me_6[14]aneN_4)^{2+}$ did not conform to the general pattern observed with other reductants studied. No reaction was detected between CrO_2^{2+} and $Co(tmc)^{2+}$, apart from the rapid decomposition of $Co(tmc)^{2+}$ in acidic medium.

Discussion

Reactions with $V(H_2O)_6^{2+}$, $Ru(NH_3)_6^{2+}$, and $Co(sep)^{2+}$. An outer-sphere electron transfer seems to be the most reasonable mechanistic assignment for the reactions of CrO_2^{2+} with substitutionally inert $V(H_2O)_6^{2+}$, $Ru(NH_3)_6^{2+}$, and $Co(sep)^{2+}$. The treatment of the data according to the Marcus theory is not feasible since neither the reduction potential nor the self-exchange rate constant for $CrO_2^{2+/+}$ is known. The similarity in the observed rate constants for the three reductants, as well as the mild trend within the series ($k_{Co(sep)^{2+}} > k_{Ru(NH_3)_6^{2+}} > k_{V^{2+}}$), has been well established in other outer-sphere reactions,[2b,13-21] supporting the

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(11) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967.

(12) The protonated form of the peroxochromium complex, CrO_2H^{2+}, is probably dominant under our experimental conditions, like the related cobalt complex $(H_2O)([14]aneN_4)CoO_2H^{2+}$.[2b]

(13) Ramasami, T.; Endicott, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 389.

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Table I. Summary of Kinetic Data for Reductions of CrO_2^{2+} and $Co([14]aneN_4)(OH_2)O_2^{2+}$

		oxidant $k/M^{-1}\ s^{-1}$	
reductant	E^f, V (vs NHE)	$(H_2O)_5CrO_2^{2+}$ [a]	$Co([14]aneN_4)(OH_2)O_2^{2+}$ [b]
$Ru(NH_3)_6^{2+}$	0.06[c]	$(9.5 \pm 0.2) \times 10^5$	$(2.3 \pm 0.1) \times 10^5$ [a]
$Co(sep)^{2+}$	−0.30[d]	$(8.5 \pm 0.3) \times 10^5$	$\sim 10^6$ [j]
$V(OH_2)_6^{2+}$	−0.226[e]	$(2.3 \pm 0.1) \times 10^5$	$(1.8 \pm 0.3) \times 10^5$ [a]
$Co([14]aneN_4)^{2+}$	0.421[f]	$\sim 7 \times 10^6$	$(4.9 \pm 0.4) \times 10^5$ [a]
$Co([15]aneN_4)^{2+}$	0.65[b]	$(6.2 \pm 0.3) \times 10^5$	$(3.7 \pm 0.4) \times 10^4$ [j]
$Fe(OH_2)_6^{2+}$	0.74[g]	$(4.5 \pm 0.2) \times 10^3$	$(1.1 \pm 0.1) \times 10^3$ [i]
$Cr(OH_2)_6^{2+}$	−0.41[g]	$\sim 8 \times 10^8$ [h]	

[a] $[HClO_4] = \mu = 0.10$ M. [b] Reference 2b. [c] Reference 12. [d] Sargeson, A. M. *Chem. Ber.* **1979**, *15*, 23. [e] Latimer, W. M. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952. [f] Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431. [g] Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. [h] Reference 4. [i] $[HClO_4] = 0.1$ M, $[NaClO_4] = 0.2$ M. [j] $[HClO_4] + [NaClO_4] = 0.1$ M.

assignment in the present system.

In none of the reactions was there any evidence obtained for the reverse of eq 1. All the reactions obeyed pseudo-first-order kinetics cleanly, and no appreciable intercepts are noted in Figures 1 and 3. Thus the reduction potential for $CrO_2^{2+/+}$ in 0.10 M $HClO_4$ must be at least as high as the reduction potential of the mildest reductant, $Ru(NH_3)_6^{2+}$ (0.06 V).[22] This is consistent with the estimated $E°$ for $Co([14]aneN_4)O_2^{2+/+}$ of 0.3 V,[2b] since the two oxygen adducts react at similar rates with all the complexes studied (Table I).

Reactions with $Co([n]aneN_4)^{2+}$ (n = 14, 15) and Fe^{2+}. Since these reducing agents feature ligand substitution rate constants in excess of the observed rate constants for reduction of CrO_2^{2+}, they can react by inner-sphere pathways. The direct observation of intermediates in all three reactions strongly indicates the formation of μ-peroxo complexes.[2b,23] This conclusion is strengthened by the similarity in the chemistry of CrO_2^{2+} and $Co([14]aneN_4)O_2^{2+}$. Detailed product analysis of the reactions of the latter complex with several reductants has shown that these reactions form metastable μ-peroxo complexes. The formation of the μ-peroxo adducts makes a large contribution to the overall free energy change, making adduct formation (inner-sphere pathway) the preferred reaction pathway.[2b,24] This is also expected to be true for the inner-sphere reactions of CrO_2^{2+}.

The intermediates observed in the reactions of CrO_2^{2+} with all three reductants exhibit absorption maxima at 320 nm. A species with a similar spectrum has been observed in a previous study of the reaction of CrO_2^{2+} with $N_2H_5^+$.[25] It was presumed to be a feature of the subsequent chromium chemistry and not directly related to the reaction of interest. A similar spectrum is observed when $Cr(OH_2)_6^{3+}$ and H_2O_2 are allowed to react for a long time. Given the complexity of the chemistry involved[26] in all of these reactions, it is likely that some common intermediates are formed.

The decomposition of the unstable intermediates, CrO_2H^{2+} (formed in the reaction with Fe^{2+}) and $CrO_2Co([n]aneN_4)^{4+}$, take place by different mechanisms. The sterically hindered bimetallic complexes decompose in unimolecular processes, whereas CrO_2H^{2+} shows a typical reactivity of a peroxide toward Fe^{2+}. Owing to the very low concentrations of CrO_2^{2+} in solution, the detailed product analysis was not feasible.

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