A Fenton Mechanism and an Oxochromium(IV) Intermediate in Reactions of the Hydroperoxochromium(III) Ion

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The covalently bound hydroperoxo complex $(H_2O)_5CrOOH^{2+}$ is reduced by Fe^{2+} in aqueous solution by a Fenton mechanism. The reaction is second-order, with k_{298} = 48.4 L mol^{-1} s^{-} ($\Delta H^{\ddagger}$ = 30.0 ± 0.7 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −110 ± 2 J mol^{-1} K^{-1}). These values are close to those for the H_2O_2/Fe^{2+} reaction. In the Fenton mechanism, if it applies to the reaction between $CrOOH^{2+}$ and Fe^{2+}, CrO^{2+} would be an intermediate. It was identified by trapping with $HC_2O_4^-$ and with a water-soluble phenol, [2-methyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]ammonium chloride. The new products formed, and their yields, support a scheme in which CrO^{2+} occurs as an intermediate. This could be tested directly, since the properties and reactivity of this species are independently known. The reaction of CrO^{2+} with Fe^{2+} has k = 3.8 × 10^3 L mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 28.3 ± 1.8 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −81 ± 2 J mol^{-1} K^{-1}.

Introduction

The reaction of Cr_{aq}^{2+} with O_2 produces the superoxochromium(III) ion, $(H_2O)_5CrO_2^{2+}$, as the first observable intermediate.[1,2] Our recent resonance Raman study supports an end-on geometry for this molecule.[1d] The reaction of $(H_2O)_5CrO_2^{2+}$ with certain one-electron donors yields a species for which we proposed an end-on hydroperoxo structure, $(H_2O)_5CrOOH^{2+}$ (henceforth $CrOOH^{2+}$) (eq 1). Species D in eq 1 represents

$$Cr_{aq}^{2+} \xrightarrow{O_2} (H_2O)_5CrO_2^{2+} \xrightarrow{+D,\,+H^+} (H_2O)_5CrOOH^{2+} + D^+ \quad (1)$$

outer-sphere reductants, such as $Ru(NH_3)_6^{2+}$ or $V(H_2O)_6^{2+}$.[1c,2] Some of the evidence supporting the end-on structure for $CrOOH^{2+}$ comes from the reversibility of the redox process: the one-electron oxidation of the purported $CrOOH^{2+}$ by Ce(IV) results in a clean recovery of CrO_2^{2+} in >75% yield.[2] This reaction resembles the oxidation of hydrogen peroxide and alkyl hydroperoxides by Ce(IV) as shown in eq 3.[3]

$$CrOOH^{2+} + Ce^{4+} \rightarrow CrO_2^{2+} + Ce^{3+} + H^+ \quad (2)$$

$$ROOH/H_2O_2 + Ce^{4+} \rightarrow ROO^{\bullet}/HOO^{\bullet} + Ce^{3+} + H^+ \quad (3)$$

Additional evidence concerning the structure of $CrOOH^{2+}$ is provided by the kinetic results obtained in this work (see later). The long-lived $CrOOH^{2+}$ (half-life of approximately 15 min under typical conditions) and several hydroperoxocobalt compounds[4] are the only known examples of metal hydroperoxides in aqueous solution.

Considerable data on the reduction of hydrogen peroxide and alkyl hydroperoxides by transition metal ions have been reported,[5,6] but very little is known about the reactivity of transition-metal hydroperoxides, L_nMOOH^{n+}.[4,7] The long lifetime of $CrOOH^{2+}$ has provided us with an opportunity to compare directly the reactivity of a metal hydroperoxide with that of H_2O_2 and ROOH. Also, if we find a pattern to the chemistry that is typical of free peroxides, it would lend additional support to our structural assignment for the peroxochromium ion as an end-on species.

The present kinetic study for the reaction of Fe^{2+} with $CrOOH^{2+}$ was undertaken to examine the mechanism of reactions of a peroxide anion covalently attached to a chromium(III) center. Specifically we wanted to know whether coordination to Cr^{3+} deactivates the peroxide and whether CrO^{2+} is involved as intermediate in these reactions.

Experimental Section

Reagents. $[Ru(NH_3)_6]Cl_3$ was purchased from Alfa and used without purification. Solutions of $[Ru(NH_3)_6]^{2+}$ were prepared by reduction of $[Ru(NH_3)_6]Cl_3$ in H_2O with Zn/Hg and used within 4 h. The concentration of Ru(II) was determined spectrophotometrically (ϵ_{275nm} = 620 L mol^{-1} cm^{-1}).[8] Solutions of Fe^{2+} were prepared by reduction of $Fe(ClO_4)_3$ with Zn/Hg in 0.1 M $HClO_4$ solution under Ar. The concentrations of Fe^{3+} were determined spectrophotometrically (ϵ_{240nm} = 4160 L mol^{-1} cm^{-1}).[9] $Cr(ClO_4)_3 \cdot nH_2O$ was prepared by reduction of CrO_3 by H_2O_2 in dilute perchloric acid and recrystallized twice. The concentration of Cr^{3+} was determined spectrophotometrically (ϵ_{408nm} = 15.6 L mol^{-1} cm^{-1}). Solutions of Cr^{2+} were prepared by reduction of a known amount of Cr^{3+} with Zn/Hg in 0.10 M H^+. $LiClO_4$ was prepared from Li_2CO_3 and $HClO_4$ and recrystallized three times. Solutions of $LiClO_4$ were standardized by ion exchange on Dowex 50W-X4 in acid form, followed by the titration of the replaced H^+ by a standard solution of NaOH. Dilute solutions of H_2O_2 were standardized iodometrically. Solutions of $CrOOH^{2+}$ were prepared by reduction of CrO_2^{2+} with $Ru(NH_3)_6^{2+}$.[2] The concentration of $CrOOH^{2+}$ was determined by adding an excess of NaI to the solution and measuring the absorbance of I_3^- at

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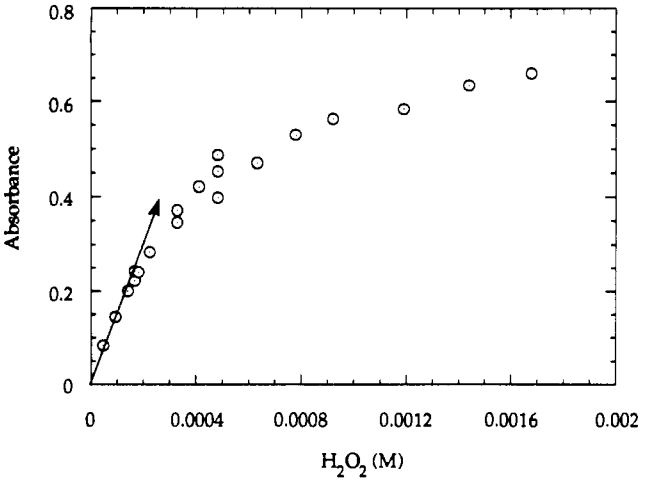

Figure 1. Plot of Δ(absorbance) versus $[H_2O_2]$ for the determination of the molar absorption coefficient of ArO•. Conditions: λ = 400 nm, [ArOH] = 3 mM, $[VO^{2+}]$ = 7.6 mM, $[HClO_4]$ = 0.1 M.

350 nm ($\epsilon_{350nm} = 2.5 \times 10^4$ L mol^{-1} cm^{-1}).[10] Sodium oxalate from Baker was used without further purification. [2-Methyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]ammonium chloride, ArOH, was synthesized by a published procedure[11] and characterized by ^{1}H NMR.

The molar absorption coefficient of ArO• was determined by the reaction of excess VO^{2+} with a known amount of H_2O_2 in the presence of ArOH according to eqs 4 and 5. Neither VO^{2+} nor VO_2^+ reacts with ArOH

$$VO^{2+} + H_2O_2 \rightarrow VO_2^+ + {}^{\bullet}OH + H^+ \quad (4)$$

$$^{\bullet}OH + ArOH \rightarrow H_2O + ArO^{\bullet} \quad (5)$$

to yield the ArO• radical on the time scale used here. Therefore the molar absorptivity could be obtained from the absorbance change for the reaction of VO^{2+}, H_2O_2, and ArOH at 400 nm. Experiments were conducted with VO^{2+} in excess over H_2O_2, and the absorbance changes were plotted against the concentration of H_2O_2 added. The plot is linear at low $[H_2O_2]$, as expected, but deviates from the straight line at higher H_2O_2 (Figure 1). From the initial linear portion we obtain ϵ(ArO•) = 1440 ± 40 L mol^{-1} cm^{-1} at λ = 400 nm. The deviation from linearity at higher $[H_2O_2]$ can be accounted for by the known reaction[12] of •OH with H_2O_2, eq 6. The $HO_2^{\bullet}/O_2^{\bullet-}$ produced is much less oxidizing than

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (6)$$

•OH and is not expected to oxidize ROH to RO•. Instead, superoxide will disproportionate to O_2 and H_2O_2. The net effect of reaction 6 is to decrease the yield of RO• at high $[H_2O_2]$, causing the curvature in Figure 1. A direct reaction between RO• and H_2O_2 could also play a role.[13] The electronic absorption spectrum of the 2,4,6-tri-*tert*-butylphenoxyl radical has been measured by generating the radical by chemical oxidation and flash photolysis methods[14a] in hexane and by an electrochemical method[14b] in ethanol solution. In ethanol, the molar absorption coefficient at 400 nm was cited as $\epsilon_{400nm} = 2.45 \times 10^3$ L mol^{-1} cm^{-1}.[14c]

Kinetics. All the kinetic experiments were carried out at 25.0 ± 0.2 °C by use of a Cary 219 or a Shimazu UV-3101PC spectrophotometer equipped with an internal timer and a thermostated cell-holder. The kinetics were monitored directly at a wavelength giving the best absorbance change. 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.

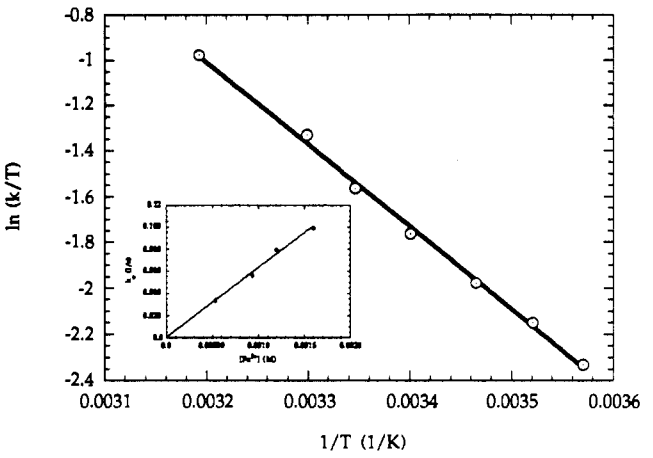

Figure 2. Plot of $\ln(k/T)$ vs $1/T$ according to transition state theory for the reaction of $CrOOH^{2+}$ with Fe^{2+} at 0.10 M H^+ and μ = 0.42 M. The inset is the plot of k_{obs} vs $[Fe^{2+}]$ at 25 °C.

The activation parameters for the reactions of $CrOOH^{2+}$ with Fe^{2+} and of CrO^{2+} with Fe^{2+} were calculated from the Eyring equation. The kinetic measurements were conducted in the temperature ranges 6.9–40.0 and 5.1–25.0 °C, respectively.

The kinetics of the reaction of Fe^{2+} with ArO• were determined by allowing H_2O_2 to react with a large excess of Fe^{2+} in the presence of ArOH. The rapid formation of ArO• was followed by the slower reduction of ArO• by Fe^{2+}. In a different experiment, ArO• was prepared from VO^{2+}, H_2O_2, and ArOH, as described earlier. The reaction of interest was then initiated by injecting Fe^{2+}. The agreement between the two methods was good and yielded k_{17} = 35.0 ± 1.2 L mol^{-1} s^{-1}.

The stoichiometry of the reaction of $CrOOH^{2+}$ with Fe^{2+} was calculated from the absorbance changes at 240 nm after the appropriate corrections for the absorption of Fe^{2+}, $Ru(NH_3)_6^{3+}$, and Cr^{3+} were made.

The CO_2 from the reaction of 0.05 mM $CrOOH^{2+}$ with 0.15 mM Fe^{2+} in the presence of 5.7 mM oxalate at 0.10 M H^+ was detected in the following way. After the reaction was completed (10 min), the CO_2 was displaced from solution with a stream of argon and bubbled into a basic solution of $Ba(ClO_4)_2$, forming a fine precipitate of $BaCO_3$. A control experiment having all the same components except $CrOOH^{2+}$ yielded no precipitate.

Results

Reaction with Iron(II). Ferrous ion reduces $CrOOH^{2+}$ according to the stoichiometry of eq 7, independent of $[H^+]$ in the

$$CrOOH^{2+} + 2Fe^{2+} + 3H^+ \rightarrow Cr^{3+} + 2Fe^{3+} + 2H_2O \quad (7)$$

range 0.10–0.50 M. The kinetics were conducted under pseudo-first-order conditions with Fe^{2+} in excess over $CrOOH^{2+}$. Typically, 0.06 mM $CrOOH^{2+}$ was used to react with 0.8–4 mM Fe^{2+}. Experiments under Ar and O_2 showed no difference in the kinetics or stoichiometry. The rate constant increased with the ionic strength. For example, at 0.10 M H^+, the rate constants of 48 and 81 L mol^{-1} s^{-1} were measured for the reactions at μ = 0.10 M and μ = 0.50 M, respectively.

Kinetic studies in the temperature range 6.9–40.0 °C yielded $\Delta H^{\ddagger}$ = 30.0 ± 0.7 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −110 ± 2 J mol^{-1} K^{-1} (Figure 2 and Table I).

The Trapping of CrO^{2+}. Oxalate ions were found previously[15] to reduce CrO^{2+} according to eq 8. The rate constant k_{ox} has a

$$C_2O_4^{2-} + CrO^{2+} + 2H^+ \rightarrow Cr^{2+} + 2CO_2 + H_2O \quad (8)$$

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Table I. Activation Parameters for the Reductions of $CrOOH^{2+}$ and HOOH with Fe^{2+}

peroxide	k_{298}[a]	$\Delta H^{\ddagger}$/kJ mol^{-1} [b]	$\Delta S^{\ddagger}$/kJ mol^{-1} K^{-1} [b]
$CrOOH^{2+}$	48.4 ± 0.7	30.0 ± 0.7	−110 ± 2
HOOH	58	37	−86

[a] At $\mu = [H^+] = 0.10$ M. [b] Values for H_2O_2 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. The data for $CrOOH^{2+}$ were obtained at $\mu = 0.42$ M and $[H^+] = 0.10$ M.

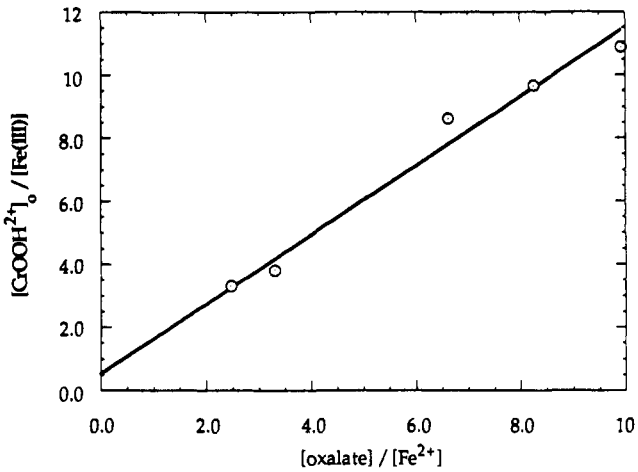


Figure 3. Plot of $[CrOOH^{2+}]_0/[Fe(ox)_3^{3-}]$ as a function of [oxalate]/$[Fe^{2+}]$ showing a linear relationship with an intercept of 0.52 and a slope of 1.08. $[CrOOH^{2+}]_0 = (8.1\text{–}11.1) \times 10^{-5}$ M; $[Fe^{2+}] = 2.52 \times 10^{-4}$ M; $T = 25$ °C; $\mu = [H^+] = 0.10$ M.

value of 1.07×10^3 L mol^{-1} s^{-1} at 0.10 M H^+, this being the composite value for $C_2O_4^{2-}$ and $HC_2O_4^-$ at this acidity.

The reaction of $CrOOH^{2+}$ with Fe^{2+} in the presence of oxalate ions evolves considerable quantities of CO_2. The kinetics are, however, unaffected by oxalate ions. A rate constant of $k = 51.0 \pm 1.8$ L mol^{-1} s^{-1} was measured in the presence of 1.8 mM oxalate, compared to 48.4 ± 0.7 L mol^{-1} s^{-1} in its absence. We assumed that the reaction takes place according to Scheme I and have measured the amounts of $Fe(C_2O_4)_3^{3-}$ produced as a function of the initial reactant concentrations.

Scheme I

$$Fe^{2+} + CrOOH^{2+} + H^+ \rightarrow CrO^{2+} + Fe^{3+} \quad (9)$$

$$CrO^{2+} + Fe^{2+} + 2H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O \quad k_{Fe} \quad (10)$$

$$Fe^{3+} + 3C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-} \quad (11)$$

$$CrO^{2+} + C_2O_4^{2-} + 2H^+ \rightarrow Cr^{2+} + 2CO_2 + H_2O \quad k_{ox} \quad (8)$$

$$Cr^{2+} + Fe(C_2O_4)_3^{3-} \rightarrow Cr^{3+} + Fe^{2+} + 3C_2O_4^{2-} \quad (12)$$

By mixing known amounts of oxalate and Fe^{3+} in a 0.10 M H^+ solution, one can obtain a constant molar absorption coefficient only when the ratio [oxalate]/$[Fe^{3+}]$ is larger than 40. On the other hand, to get a meaningful absorbance change in the experiments having Fe^{2+}, oxalate, and $CrOOH^{2+}$, the ratio [oxalate]/$[Fe^{2+}]$ has to be kept within 10. These two requirements have limited the concentration variations in these experiments. The results are shown in Figure 3.

The yields of $Fe(C_2O_4)_3^{3-}$ produced are given in Table II. Although the reactions of Cr^{2+} with CrO^{2+} and $CrOOH^{2+}$ very likely have large rate constants, they were ignored in Scheme I, owing to the kinetic and concentration advantage of $Fe(C_2O_4)_3^{3-}$.

Table II. Summary of the Trapping Experiments with Oxalate

$[CrOOH^{2+}]_0/10^{-5}$ M	$[Fe^{2+}]$/mM	[oxalate]/mM	$[Fe(ox)_3^{3-}]/10^{-5}$ M
11.5	1.08	0	22.7[a]
11.1	0.252	2.08	1.15
11.1	0.252	0.833	2.92
11.1	0.252	0.625	3.35
8.4	0.506	0	16.6[a]
8.1	0.252	1.67	0.934
8.1	0.252	2.50	0.759

[a] Calculated from the absorbance change at 240 nm.

The fact that three different oxalate species were present in solution ($C_2O_4^{2-}$, $HC_2O_4^-$, and $H_2C_2O_4$) was ignored since all of the experiments were carried out at a constant $[H^+]$ of 0.10 M.

The presence of oxalate has a profound effect on the reaction. The total amount of Fe^{3+} produced in the absence of oxalate is 0.227 mM, i.e. close to twice the amount of initial $[CrOOH^{2+}]$ (0.115 mM); this factor of 2 is expected from eqs 9–11. Even a small amount of oxalate (0.625 mM) drastically reduces the amount of Fe(III) found (0.0335 mM) due to the participation of reactions 8 and 12. In the presence of 2.5 mM oxalate, the amount of Fe(III) is only 5% of that found in the absence of oxalate.

According to Scheme I the yield of $Fe(C_2O_4)_3^{3-}$ is related to the relative concentrations of $[Fe^{2+}]$ and oxalate (eqs 13 and 14).

$$[Fe(ox)_3^{3-}]_\infty = [CrOOH^{2+}]_0 + [CrOOH^{2+}]_0 \frac{k_{Fe}[Fe^{2+}] - k_{ox}[C_2O_4^{2-}]}{k_{Fe}[Fe^{2+}] + k_{ox}[C_2O_4^{2-}]} \quad (13)$$

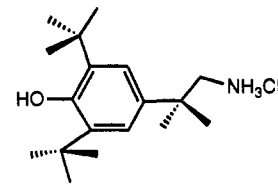
$$\frac{[CrOOH^{2+}]_0}{[Fe(C_2O_4)_3^{3-}]_\infty} = 0.5 + \frac{k_{ox}[C_2O_4^{2-}]}{2k_{Fe}[Fe^{2+}]} \quad (14)$$

The data fit the proposed scheme well, as illustrated by the plot of the left-hand side of eq 14 against the ratio [oxalate]/$[Fe^{2+}]$, Figure 3. The values of the intercept and slope are 0.58 ± 0.05 and 1.0 ± 0.1, respectively. According to the proposed scheme, the slope represents the ratio of the rate constants for the reduction of CrO^{2+} by oxalate and Fe^{2+}. After the substitution for k_{ox}, the value of $k_{Fe} = 500$ L mol^{-1} s^{-1} is obtained. This rate constant applies to the reaction of (oxalato)iron(II) complexes with the chromyl ion; it is not the same as that reported later for the reaction of $Fe(H_2O)_6^{2+}$ with the chromyl ion.

We attempted to use $ABTS^{2-}$ as a trap for CrO^{2+} (eq 15),[15] but quantitative determinations were thwarted by the side reaction between the product, Fe^{3+}, and $ABTS^{2-}$ that also yields $ABTS^-$.

$$CrO^{2+} + ABTS^{2-} + 2H^+ \rightarrow Cr^{3+} + ABTS^- \quad (15)$$

To confirm the formation of the chromyl intermediate a water-soluble phenol, [2-methyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]ammonium chloride, ArOH, was also used as a trap.



ArOH

It was shown independently that CrO^{2+} reacts with ArOH to yield ArO$^{\bullet}$, an aryloxyl radical that is persistent and reasonably intensely colored ($\epsilon_{400} = 1.44 \times 10^3$ L mol^{-1} cm^{-1}) (eq 16). Controls showed that neither the separate reactants nor the spent reaction solution generated ArO$^{\bullet}$ upon addition of ArOH. The $CrOOH^{2+}$–

$$ArOH + CrO^{2+} \xrightarrow{H^+} ArO^{\bullet} + Cr^{3+} \quad k_{ArOH} \qquad (16)$$

Fe^{2+} reaction, on the other hand, when conducted with ArOH added, did yield $ArO^{\bullet}$. Unfortunately, the spectrum of $ArO^{\bullet}$ faded with time owing to the subsequent reduction of $ArO^{\bullet}$ by Fe^{2+} (eq 17), for which we have determined independently the

$$ArO^{\bullet} + Fe^{2+} \xrightarrow{H^+} ArOH + Fe^{3+} \qquad (17)$$

rate constant $k_{17} = 35$ L mol^{-1} s^{-1}. As expected, the higher the ratio $[Fe^{2+}]/[ArOH]$, the faster the disappearance of $ArO^{\bullet}$ formed in reaction 16. The ratio of the yield of Fe^{3+} ($=[CrOOH^{2+}]_0 - [ArO^{\bullet}]_\infty$) and $[ArO^{\bullet}]_\infty$ is predicted to be a linear function of the ratio of the concentrations of the competing reagents (eq 18).

$$\frac{[CrOOH^{2+}]_0 - [ArO^{\bullet}]_\infty}{[ArO^{\bullet}]_\infty} = \frac{k_{Fe}[Fe^{2+}]}{k_{ArOH}[ArOH]} \qquad (18)$$

The absorbance changes at 400 nm could not be used to determine quantitatively the amounts of $ArO^{\bullet}$ produced, because of the side reaction of $ArO^{\bullet}$ with Fe^{2+}, eq 17. Only an estimate of $k_{Fe}/k_{ArOH} \sim 37$ was obtained. When solutions of authentic CrO^{2+} were added to a mixture of Fe^{2+} and ArOH, the yield of $ArO^{\bullet}$ corresponded to $k_{Fe}/k_{ArOH} = 21$ (Figure 4). The two values, 37 and 21, are reasonably close, given that the time scales for the two experiments differ appreciably. In the former case, $CrOOH^{2+}$ and Fe^{2+} react over a period of approximately 10 min to yield the chromyl ion, which is then rapidly trapped by ArOH. During this time Fe^{2+} reduces some of the $ArO^{\bullet}$ formed, which thus escapes detection. The reaction between the chromyl ion and ArOH is, of course, the rapid trapping step in the reaction between $CrOOH^{2+}$ and Fe^{2+}. When it occurs independently, it takes only a few seconds. The yield of $ArO^{\bullet}$ is thus nearly quantitative, and the determined ratio k_{Fe}/k_{ArOH} smaller. The reasonable agreement between the two values supports our contention that CrO^{2+} is the intermediate in the reaction of $CrOOH^{2+}$ with Fe^{2+}. A more detailed analysis is given in the Discussion.

Direct kinetic measurements were performed on the reaction of Fe^{2+} with CrO^{2+} in the absence of oxalate. For these experiments, CrO^{2+} was prepared by oxidation of Cr^{2+} with Tl(III) to avoid the side reaction of Fe^{2+} with CrO_2^{2+} (a natural impurity in solutions of CrO^{2+} that are prepared from O_2 and Cr^{2+}). Without oxalate, the reaction of Tl(III) with Fe^{2+} was slow and did not interfere with the reaction of CrO^{2+} with Fe^{2+}. Figure 5 shows the plot of k_{obs} versus $[Fe^{2+}]$ and the Eyring plot for this reaction. The activation parameters $\Delta H^{\ddagger} = 28.3 \pm 1.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -81 \pm 6$ J K^{-1} mol^{-1} were obtained. The rate constant is 3800 L mol^{-1} s^{-1} at 25 °C and 0.10 M H^+, which is significantly larger than the value extracted from the competition experiments with oxalate. However, the presence of a strongly coordinating ligand, such as oxalate, may have changed the nature of the metal ions involved. The value of the rate constant for the CrO^{2+}/Fe^{2+} reaction in the presence of oxalate is thus needed. Unfortunately, the determination of this rate constant was not successful because of the interference from side reactions. As mentioned earlier, the CrO^{2+} prepared from Cr^{2+} and O_2 contains significant amounts of CrO_2^{2+}, which also reacts with Fe^{2+} and thus interferes with the reaction of interest. When CrO^{2+} was prepared from Cr^{2+} and Tl(III), the reaction of excess Tl(III) with Fe^{2+} in the presence of oxalate interfered with the measurement of the CrO^{2+}/Fe^{2+} reaction.

The reported rate constants for the reaction of H_2O_2 with Fe^{2+}

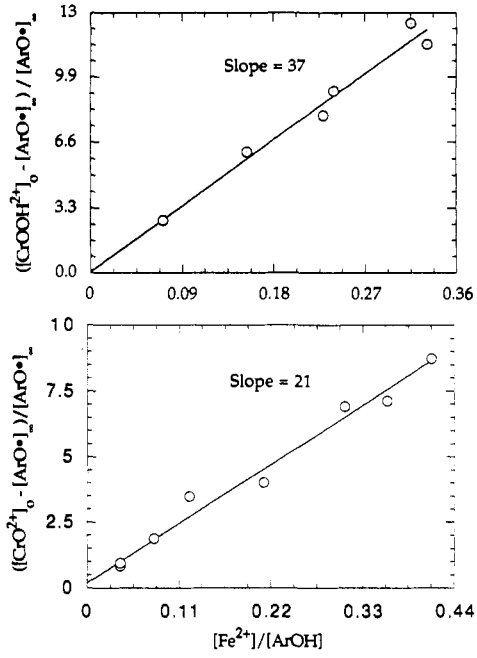


Figure 4. Linear relationship of the product distribution, $([CrO^{2+}]_0 - [ArO^{\bullet}]_\infty)/[ArO^{\bullet}]_\infty$ or $([CrOOH^{2+}]_0 - [ArO^{\bullet}]_\infty)/[ArO^{\bullet}]_\infty$, vs the ratio $[Fe^{2+}]/[ArOH]$ according to eq 18. $T = 25$ °C; $\mu = [H^+] = 0.10$ M.

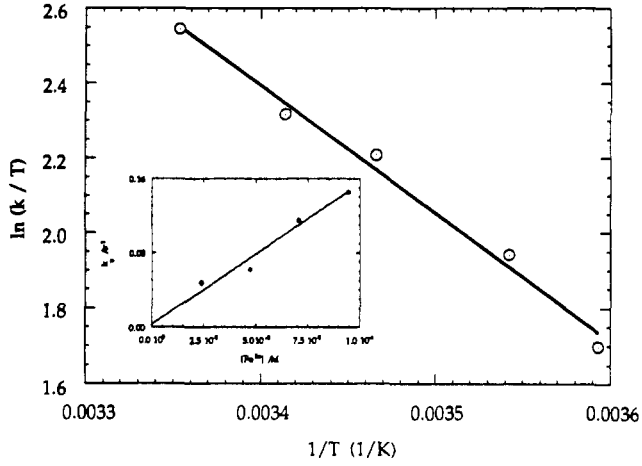


Figure 5. Eyring plot for the reaction of CrO^{2+} with Fe^{2+}. The inset is the plot of k_{obs} versus $[Fe^{2+}]$ at 25 °C ($\mu = [H^+] = 0.10$ M).

cover a rather wide range, 40–80 L mol^{-1} s^{-1}.[16] We have therefore redetermined this rate constant and obtained a value of 58 L mol^{-1} s^{-1} in 0.10 M $HClO_4$, in good agreement with some of the reported data[16c-e] (Table I).

Discussion

Mechanism. As shown in Table I, the reactions of Fe^{2+} with H_2O_2 and $CrOOH^{2+}$ have strikingly similar rate constants and activation parameters. The salt effects differ, in agreement with expectations based on the charge types involved. The reaction with H_2O_2 is unaffected by changes in ionic strength, whereas that with $CrOOH^{2+}$ shows a positive salt effect. Indirectly, this ionic strength effect also serves as evidence that these are indeed two different reactions. Given that the rate constants at $\mu = 0.10$ M are comparable (see Table I), it is important to be able to ascertain that reaction 7 is indeed a genuine reaction of Fe^{2+} with $CrOOH^{2+}$, and not that of Fe^{2+} with H_2O_2 formed by decomposition of $CrOOH^{2+}$.

(16) (a) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125. (b) Wells, C. F.; Salam, M. A. *Trans. Faraday Soc.* **1967**, *63*, 620. (c) Hardwick, T. J. *Can. J. Chem.* **1957**, *35*, 428. (d) Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. *Trans. Faraday Soc.* **1951**, *47*, 462. (e) Po, H. N.; Sutin, N. *Inorg. Chem.* **1968**, *7*, 621.

Since reactions of H_2O_2 with transition metal complexes require a precoordination of the peroxide to the metal, the kinetics of redox reactions are a function of both the reduction potentials and the rates of ligand substitution. From the data in Table I, we infer that the reaction of $CrOOH^{2+}$ with Fe^{2+} also proceeds by an inner-sphere mechanism, eq 19. The binuclear intermediate $CrOO(H)Fe^{2+}$ can then cleave in either a one-electron (eq 20a) or a two-electron process (eq 20b). Both pathways are consistent with the kinetics and stoichiometry, and both feature a metal–oxo intermediate, the oxochromium(IV) or chromyl ion in eq 20a and an oxoiron(IV) or ferryl ion in eq 20b. The Fe^{2+} reduction of FeO^{2+}, produced in eq 20b, would take place in a reaction analogous to eq 10.

$$CrOOH^{2+} + Fe^{2+} \rightarrow [CrOO(H)Fe^{4+}] \qquad (19)$$

$$[CrOO(H)Fe^{4+}] \rightarrow CrO^{2+} + FeOH^{2+} \qquad (20a)$$

$$[CrOO(H)Fe^{4+}] \rightarrow CrOH^{2+} + FeO^{2+} \qquad (20b)$$

The trapping experiment with oxalate showed that an intermediate, reacting competitively with Fe^{2+} and $HC_2O_4^-$, is clearly involved. However, the unavailability of the rate constant for the reaction of Fe^{2+} with CrO^{2+} in the presence of oxalate makes it difficult to identify the intermediate unambiguously on the basis of the oxalate trapping experiments alone.

The model with ArOH as a trap predicts that the yield ratio should be a linear function of the ratio $[Fe^{2+}]/[ArOH]$, which passes through the origin. As shown in Figure 4, this is indeed the case.

The complete reaction scheme, taking into account all the competing and side reactions, is shown in Scheme II. Computer simulations based on this scheme and using known rate constants for the reactions of CrO^{2+} with Fe^{2+} (k = 3800 L mol^{-1} s^{-1}) and ArOH (k = 240 L mol^{-1} s^{-1})[17] were carried out. As shown in Figure 6, the calculated and experimental data agree well and support the assignment of CrO^{2+} as the intermediate. The possible oxidation of $CrOOH^{2+}$ by CrO^{2+} was not considered in Scheme II. It is unlikely to occur in the presence of a large excess of Fe^{2+} and ArOH over $CrOOH^{2+}$.

The formation of CrO^{2+} rather than FeO^{2+} in reaction 20 indicates that the driving force for reaction 20a is greater than that for reaction 20b. This is consistent with the known trend of decreasing strength of the M=O bonds toward the right in the periodic table. Also, Ce(IV) ($E°$ = 1.72 V) oxidizes Cr^{3+}, but not Fe^{3+}, supporting our contention that $E°(Fe^{IV/III}) > E°(Cr^{IV/III})$.

The similarity of the rate constants for the reductions of $CrOOH^{2+}$ and H_2O_2 by Fe^{2+} may be taken as additional support for the end-on (η^1) structure for $CrOOH^{2+}$. It would appear highly unlikely, although not impossible, that the η^2 coordination of H_2O_2 to chromium would not change its reactivity significantly.

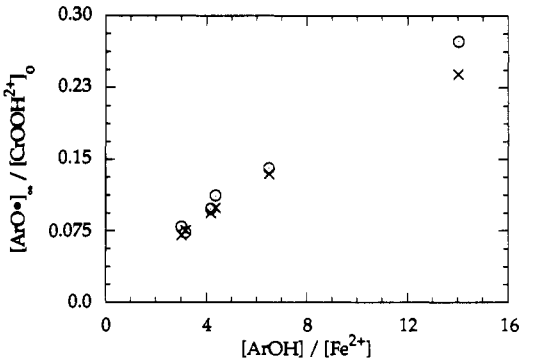


Figure 6. Experimental data (circles) and computer simulation (crosses, based on Scheme II) for the reaction of $CrOOH^{2+}$ with Fe^{2+} in the presence of ArOH. The rate constants k_9 (48 L mol^{-1} s^{-1}), k_{10} (3800), k_{ArOH} (240), and k_{17} (35) were set in the simulation at their independently measured values.

Scheme II

$$CrOOH^{2+} + Fe^{2+} \xrightarrow{k_9} CrO^{2+} + FeOH^{2+} \qquad (9)$$

$$CrO^{2+} + Fe^{2+} \xrightarrow{k_{10},\,2H^+} Cr^{3+} + Fe^{3+} + H_2O \qquad (10)$$

$$CrO^{2+} + ArOH \xrightarrow{k_{ArOH}} CrOH^{2+} + ArO^{\bullet} \qquad (16)$$

$$ArO^{\bullet} + Fe^{2+} \xrightarrow{k_{17},\,+H^+} ArOH + Fe^{3+} \qquad (17)$$

The reactions of H_2O_2 with both Cr^{2+} and Fe^{2+} (eq 21) yield OH radicals and metals in the 3+ oxidation state. If we accept that the potentials for both $M^{IV/III}$ couples are significantly lower

$$M^{2+} + H_2O_2 \rightarrow M(OH)^{2+} + {}^{\bullet}OH \qquad (21)$$

$$M^{2+} + H_2O_2 \rightarrow MO^{2+} + H_2O \qquad (22)$$

than that for the $^{\bullet}OH/H_2O$ couple (+2.7 V),[18] then it becomes obvious that the thermodynamic products would be MO^{2+} and H_2O (eq 22). There is apparently no facile pathway for the observed, kinetic products (MOH^{2+} and $^{\bullet}OH$) to be converted to the thermodynamic ones during the short lifetime of $^{\bullet}OH$.

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(17) Al-Ajlouni, A.; Bakac, A.; Espenson, J. H. Unpublished results.

(18) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1713.