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# Electrochemical Properties of the Unstable Complexes of Chromium(III) with Superoxide and Hydroperoxide Anions and with Dioxygen

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The electrochemical behavior of the metastable $(H_2O)_5CrOO^{2+}$ and $(H_2O)_5CrOOH^{2+}$ cations is reported. Reproducible, irreversible cathodic responses were obtained for both ions at suitable electrodes. The formal potential of the $(H_2O)_5CrOO^{2+}/(H_2O)_5CrOOH^{2+}$ couple at pH 1 was estimated as 0.97 V vs NHE on the basis of voltammetric measurements at an oxidatively activated rotating pyrolytic graphite electrode and of the kinetics of cross-reactions with suitable, stable redox couples. The two-electron reduction of $(H_2O)_5CrOOH^{2+}$ was observed at –0.07 V vs NHE at mercury electrodes. Comparison with the potential where $H_2O_2$ is reduced at mercury electrodes (–0.7 V vs NHE) indicates that a substantial change in the electrochemical reactivity of the peroxo ligand is produced by its coordination to the $(H_2O)_5Cr^{3+}$ center. The possible relevance of the observed behavior to transition metal activation of $O_2$ toward electroreduction is discussed.

The reaction between $Cr(OH_2)_6^{2+}$ and a large excess of $O_2$ produces the $(H_2O)_5CrOO^{2+}$ cation, which subsequently decomposes to other products. However, the half-life of the complex is ample to permit its electrochemical behavior to be observed. The cation was first studied by Ilan *et al.*[1] and spectroscopically by Sellers and Simic.[2] More recently, Espenson, Bakac, and co-workers described preparative procedures for the generation of this cation,[3,4] characterized a number of aspects of its redox chemistry,[4,5] and proposed mechanisms for its decomposition.[3,6] We became interested in examining the electrochemical behavior of the cation because of the insights that might result into the mechanisms by which transition metal centers can activate oxygen–oxygen bonds toward reduction as, for example, in the catalysis of the electrochemical reduction of $O_2$ by metalloporphyrins.[7]

In the present study, the electroreduction of $(H_2O)_5CrOO^{2+}$ (hereafter $CrOO^{2+}$) is shown to proceed in two steps with $(H_2O)_5CrOOH^{2+}$ (hereafter $CrOOH^{2+}$) as the first reduction product. The electrochemistry of this hydroperoxide complex was also characterized, and the effects of coordination to Cr(III) on the electrochemical reactivity of the coordinated ligands were investigated. The results provide additional information on the electron-transfer chemistry of this interesting pair of complexes.

## Experimental Section

**Materials.** Reagent grade chemicals were used as received from commercial sources: $Cr(ClO_4)_3$ and $Fe(phen)_3(ClO_4)_2$ (phen = 1,10-phenanthroline) (G. F. Smith), $Ru(bpy)_3Cl_2$ (bpy = 2,2′-bipyridine, Alfa Products), $Ru(NH_3)_6Cl_3$ (Strem Chemical Co.), $CF_3COOH$ and $CH_3OH$ (E & M Chemical Co.). $Os(bpy)_3(ClO_4)_2$ and $Fe(5,6\text{-}(CH_3)_2phen)_3(ClO_4)_2$ ($5,6\text{-}(CH_3)_2phen$ = 5,6-dimethyl-1,10-phenanthroline) were prepared as described in the literature.[8,9] Laboratory-deionized water was further purified by passage through a purification train (Milli-Q from Millipore Co.). Triply distilled mercury (Bethlehem Apparatus Co.) was used for polarographic experiments. Prepurified argon was used to remove $O_2$ from solutions by bubbling. Solutions of $CrOO^{2+}$ were prepared by the procedure described in ref 4: 10 mL of a 2.5 mM solution of $Cr^{2+}$ in 0.1 M $CF_3COOH$ was rapidly injected into 40 mL of an $O_2$-saturated solution containing 0.1 M $CF_3COOH$ and 0.02 M $CH_3OH$. Solutions of $CrOOH^{2+}$ were prepared by mixing equimolar quantities of $CrOO^{2+}$ and $Ru(NH_3)_6^{2+}$ and were used within 2 min.[10] Solutions of $Cr^{2+}$ and $Ru(NH_3)_6^{2+}$ were prepared by zinc amalgam reduction of $Cr^{3+}$ and $Ru(NH_3)_6^{3+}$, respectively. Solutions of $Ru(bpy)_3^{3+}$, $Fe(phen)_3^{3+}$, and $Fe(5,6\text{-}(CH_3)_2phen)_3^{3+}$ were obtained by electrolytic oxidation of solutions of the reduced complexes.

**Apparatus and Procedures.** Electrochemical measurements were performed in a conventional two-compartment cell closed with a Teflon cap through which the electrodes and gas bubbling system were fitted. The working electrode (dropping mercury, hanging mercury drop (Brinkman Model 410), or pyrolytic graphite) and the platinum foil counter electrode were in the same cell compartment. The Ag/AgCl reference electrode was in the second cell compartment which was separated from the main compartment by a fritted glass disk. A rotating platinum disk electrode (Pine Instrument Co.) was used to obtain current–potential curves for the oxidation of $H_2O_2$.

A Pine Instrument Co. potentiostat (Model RDE 3) was used to record cyclic and rotating-disk voltammograms. Normal and dc polarographic experiments were carried out with a PAR Model 174 instrument. Rotating disk electrodes were rotated with a Pine Instrument Co. Model ASR rotator. Current–potential responses were recorded with a Kipp and Zonen X-Y recorder. Spectral and kinetic measurements were made with a Hewlett-Packard Model 8450 spectrophotometer.

Kinetic measurements were carried out by monitoring changes in absorbance at wavelengths selected to give optimal sensitivity. For the reductions of $Ru(bpy)_3^{3+}$, $Fe(phen)_3^{3+}$, and $Fe(5,6\text{-}(CH)_3)_2phen)_3^{3+}$ by $CrOOH^{2+}$, pseudo-first-order reaction conditions were employed with 10- to 20-fold excesses of $CrOOH^{2+}$. Absorbances, $A$, of the reduced forms of the complexes were measured at 448, 510, and 520 nm, respectively. Observed rate constants, $k_{obs}$, were obtained from plots of $\ln[1 - (A/A_\infty)]$ vs time. For the oxidations of $Fe(5,6\text{-}(CH_3)_2phen)_3^{2+}$ and $Os(bpy)_3^{2+}$ by $CrOO^{2+}$, decreases in the absorbance were monitored at 520 and 480 nm, respectively, under pseudo-first-order reaction conditions with 10- to 20-fold excesses of $CrOO^{2+}$. Values of $k_{obs}$ were obtained from plots of $\ln(A/A_0)$ vs time for absorbance changes measured during the first 100 s after the reactants were mixed. The concentrations of $CrOO^{2+}$ and $CrOOH^{2+}$ were assumed to be constant. The spontaneous decomposition of these species was always less than 10%. Contributions from the back-reaction were also assumed to be negligible during the 100

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s required for the kinetic measurements. The concentration of $CrOO^{2+}$ was evaluated from its absorbance at 246 nm at the time the two reactants were mixed. The concentration of $CrOOH^{2+}$ was obtained by calculation from its known decomposition rate (see next section).

Most measurements were performed in 0.1 M $CF_3COOH$ as supporting electrolyte, but tests showed that the results were the same in 0.1 M $HClO_4$. Potentials were measured and are reported with respect to an Ag/AgCl, 3 M NaCl electrode which had a potential of 0.20 V vs the normal hydrogen electrode, NHE. Experiments were conducted at the ambient laboratory temperature (21 ± 2 °C).

## Results and Discussion

**Preparation of $(H_2O)_5CrOO^{2+}$.** Espenson and co-workers have shown that much higher yields of the $CrOO^{2+}$ cation result when the reaction between $Cr^{2+}$ and $O_2$ is carried out in the presence of alcohols.[4] In the absence of alcohols, larger portions of the $Cr^{2+}$ are converted to $Cr^{3+}$ and $HCrO_4^-$ during the reaction with $O_2$. Even in the presence of alcohols, some of these side products are formed.[4] In the present experiments, the concentration of $CrOO^{2+}$ in the solutions resulting from the reaction of 25 $\mu$mol of $Cr^{2+}$ with 48 $\mu$mol of $O_2$ in the presence of 0.02 M methanol was monitored spectrophotometrically at 246 and 290 nm, where the molar absorbances of the cation are $7 \times 10^3$ and $3.1 \times 10^3$ $M^{-1}$ $cm^{-1}$, respectively.[2,3]

The concentration of $CrOO^{2+}$ decreased slowly as the reactions responsible for its spontaneous decomposition proceeded.[3] However, the rate of the decomposition was sufficiently slow that the excess $O_2$ could be removed from the reactant solutions by bubbling with argon for a few minutes, after which the electrochemical responses from dioxygen-free solutions of $CrOO^{2+}$ and its decomposition products were recorded.

The total chromium content of test solutions was determined iodometrically after oxidation to Cr(VI) with $H_2O_2$.[11] The (relatively small) quantities of $HCrO_4^-$ present in the solutions were estimated by means of electrochemical measurements as described below.

**Electrochemical Responses from Solutions of $CrOO^{2+}$.** In Figure 1A is shown a set of dc polarograms recorded in a solution of $CrOO^{2+}$.[12] The time indicated by each polarogram is the elapsed time since the $Cr^{2+}$ was injected into the initially dioxygen-saturated solution. The removal of the $O_2$ by bubbling with argon consumed the first 7 min of the experiment. The polarograms obtained after 7 and 19 min exhibit a cathodic current plateau immediately adjacent to the anodic background arising from the oxidation of the Hg electrode (the oxidation of Hg begins near 0.4 V vs Ag/AgCl in 1 M $H^+$). No similar plateau is present in polarograms recorded separately in solutions of $O_2$ or $Cr^{2+}$. The observed behavior is characteristic of oxidants whose reduction potential is more positive than the potential of the $Hg^{2+}$/Hg couple. If the formal potential for half-reaction 1 is more

$$CrOO^{2+} + H^+ + e = CrOOH^{2+};\quad E_1^f \qquad (1)$$

positive than the potential where the oxidation of Hg proceeds, the beginning of the electroreduction of $CrOO^{2+}$ will not be observable at Hg electrodes unless significant overpotentials are required for the reduction to occur. The presence of the cathodic currents immediately adjacent to 0.4 V in Figure 1A indicates that the reduction of $CrOO^{2+}$ begins at potentials positive of 0.4 V. The current plateau between the anodic background and 0.2 V in the polarograms in Figure 1A provides a measure of the sum of the concentrations of all of the reactants present which are reduced at potentials positive of 0.2 V. The reduction of $O_2$ does not commence until ca. 0.15 V (Figure 1B), so the only likely sources of the plateau currents at potentials positive of 0.2 V are the reductions of $CrOO^{2+}$ and $HCrO_4^-$. It was possible to estimate the concentration of $HCrO_4^-$ in mixtures of this ion with $CrOO^{2+}$ by recording cyclic voltammograms at a gold electrode from an initial potential of 0.85 V. A reduction peak for $HCrO_4^-$ appeared at 0.54 V, while no cathodic response from the $CrOO^{2+}$ cation was observed at gold electrodes at this potential. Calibration (nonlinear except at low concentrations) of the voltammetric response at the gold electrode with pure solutions of $HCrO_4^-$ showed that the $HCrO_4^-$ present in solutions such as the one employed in Figure 1A typically amounted to 5–10% of the concentration of $CrOO^{2+}$. The concentrations of both species slowly decreased as the $HCrO_4^-$ was consumed by reaction with the $Cr^{2+}$ generated during the homolytic decomposition of $CrOO^{2+}$.[3] The lack of $HCrO_4^-$ in the fully decomposed solution of $CrOO^{2+}$ is evident in the featureless polarogram shown in Figure 1A for the solution of $CrOO^{2+}$ which had been allowed to decompose for 53 min.

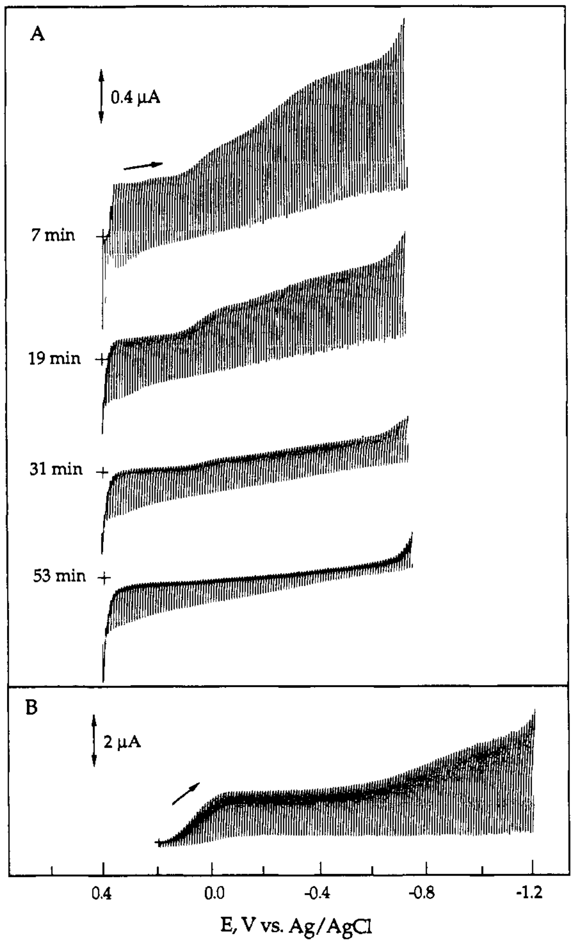

**Figure 1.** (A) Dc polarograms recorded with a dropping mercury electrode in a solution of $CrOO^{2+}$ containing 0.5 mM total chromium. The time elapsed since the cation was formed by reaction between $Cr^{2+}$ and excess $O_2$ is indicated for each polarogram. Argon was bubbled through the solution during the intervals between the recording of the polarograms. Mercury flow rate: 0.95 mg $s^{-1}$. Drop time: 5 s. Scan rate: 2 mV $s^{-1}$. Supporting electrolyte: 0.1 M $CF_3COOH$. The crosses mark the initial potential and zero current. (B) DC polarogram for 0.1 M $CF_3COOH$ saturated with air ($[O_2]$ = 0.28 mM).

The magnitude of the polarographic reduction currents (corrected for contributions from $HCrO_4^-$) in freshly prepared solutions of the $CrOO^{2+}$ cation corresponded to a diffusion coefficient of ca. 1 (±0.5) × $10^{-5}$ $cm^2$ $s^{-1}$ for a one-electron reduction. This value is similar to the diffusion coefficient of the $Cr(OH_2)_6^{3+}$ cation, ca. 0.6 × $10^{-5}$ $cm^2$ $s^{-1}$.[13]

A plot of the polarographic current measured at 0.2 V as a function of time is shown in Figure 2 along with spectral measurements of the absorbance of the solution of $CrOO^{2+}$ at

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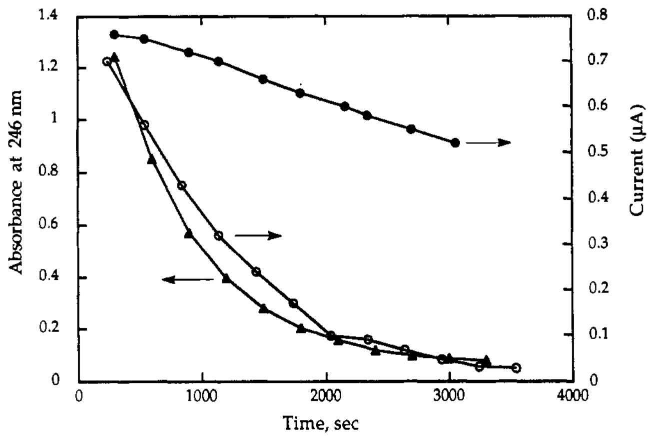

**Figure 2.** Time dependence of dc polarographic currents measured at 0.2 V and of absorbance at 246 nm for a solution of CrOO$^{2+}$. The measurements began 4 min after preparation of the CrOO$^{2+}$ solution: (○) current and (▲) absorbance for a deaerated solution; (●) current for a solution saturated with O$_2$.

246 nm. The correlation between the decreases in the polarographic reduction current and the concentration of CrOO$^{2+}$ is apparent. (The small deviation evident between 1000 and 2000 s arises from the contribution of $HCrO_4^-$ reduction to the polarographic currents.) The decomposition of the CrOO$^{2+}$ complex is not a simple first-order process,[3,6] and no attempt was made to fit the data to a kinetic rate law. One pathway for the decomposition involves the homolytic dissociation of CrOO$^{2+}$ into Cr$^{2+}$ and O$_2$, followed by reaction of the Cr$^{2+}$ with additional CrOO$^{2+}$.[6] The rate of this decomposition pathway is diminished by the presence of excess O$_2$, which reacts with the Cr$^{2+}$, thus diverting it from reacting with a second molecule of CrOO$^{2+}$.[3] The cathodic current at 0.2 V would therefore be expected to decrease more slowly in the presence of O$_2$. The upper curve in Figure 2 demonstrates the expected behavior.

**Rotating-Disk Voltammetry of CrOO$^{2+}$.** In order to observe the initial portion of current–potential curves for the reduction of CrOO$^{2+}$, its behavior was examined at solid electrodes. Poorly defined responses were obtained with platinum, gold, and untreated pyrolytic graphite electrodes. However, reasonably well-formed current–potential curves were obtained at rotating pyrolytic graphite electrodes which were pretreated by cycling between 0.8 and 1.5 V in 0.1 M CF$_3$COOH for 2 min. Such pretreatment of graphite electrodes to improve their behavior in voltammetric experiments is a well-known tactic.[14] A current–potential curve recorded with a preoxidized electrode is shown in Figure 3. The wave with a half-wave potential near –0.3 V in Figure 3 corresponds to the reduction of O$_2$. In order to obtain as large a plateau current as possible for the reduction of CrOO$^{2+}$ (and to diminish the extent of its decomposition), the O$_2$ present in the initial solution was only partially removed by restricting the bubbling with argon to no more than 4 or 5 min. A small wave at –0.3 V remained even after more extended argon bubbling because O$_2$ is generated continuously by the homolytic decomposition of CrOO$^{2+}$.[3] If argon was not bubbled through solutions of CrOO$^{2+}$ as it decomposed, the magnitude of the wave at –0.3 V increased as that of the one at 0.4 V diminished.

The plateau currents of the wave at 0.4 V in current–potential curves such as that in Figure 3 were measured as a function of the electrode rotation rate to obtain an estimate of the diffusion coefficient for CrOO$^{2+}$. The resulting value, $(0.8 \pm 0.3) \times 10^{-5}$ cm$^2$ s$^{-1}$, assuming a one-electron reduction, was in reasonable agreement with the value obtained from the polarographic current at 0.2 V in Figure 1A. Thus, the electrochemical reduction of CrOO$^{2+}$ corresponds to half-reaction 1, which proceeds irreversibly at pyrolytic graphite electrodes.

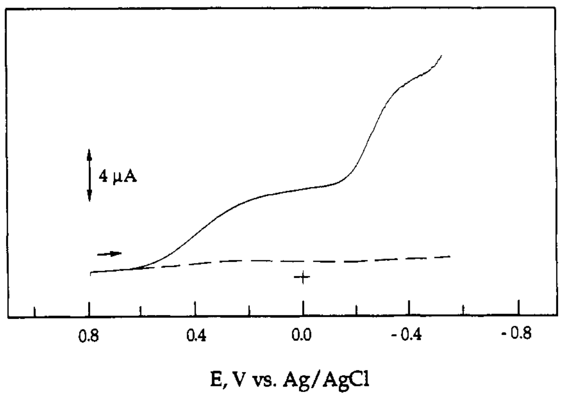

**Figure 3.** Current–potential curve for the reduction of 0.1 mM CrOO$^{2+}$ at a preoxidized pyrolytic graphite disk electrode rotated at 400 rpm. Supporting electrolyte: 0.1 M CF$_3$COOH. Electrode area: 0.4 cm$^2$. Scan rate: 10 mV s$^{-1}$.

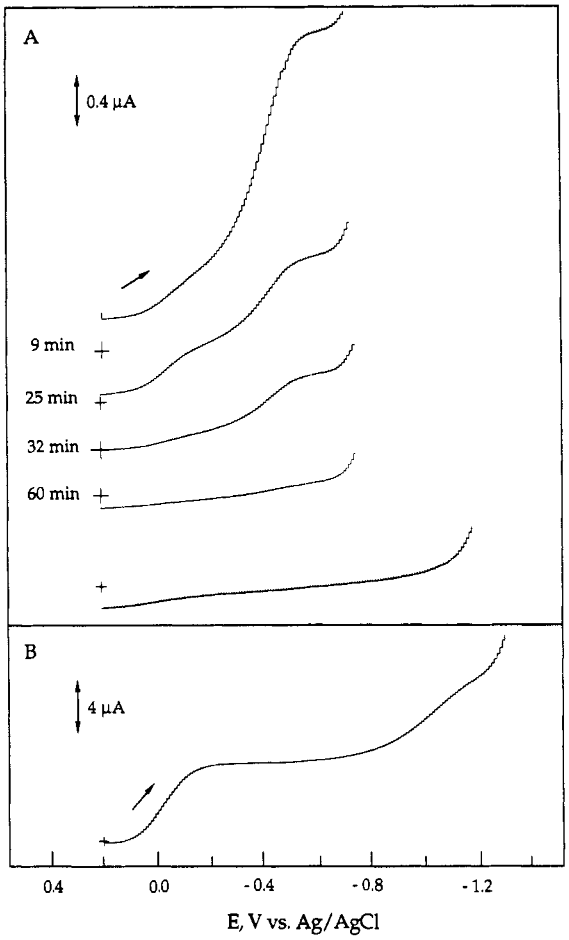

**Figure 4.** (A) Normal pulse polarograms recorded at a dropping mercury electrode in a solution of CrOO$^{2+}$. The indicated times have the same significance as in Figure 1A. The lowest curve is the response obtained in the pure supporting electrolyte. Mercury flow rate: 0.95 mg s$^{-1}$. Drop time: 2 s. Current was measured 48 ms after pulse application; the pulse amplitude was increased at 5 mV s$^{-1}$. Initial potential: 0.2 V. Supporting electrolyte: 0.1 M CF$_3$COOH. The crosses mark the initial potential and zero current. (B) Normal pulse polarogram for 0.1 M CF$_3$COOH saturated with air.

**Electroreduction of CrOOH$^{2+}$.** The CrOOH$^{2+}$ complex produced in half-reaction 1 can be further reduced at more negative potentials. The clearest responses were obtained at mercury electrodes using the normal pulse polarographic technique.[15]

A typical set of normal pulse polarograms recorded with a solution of CrOO$^{2+}$ is shown in Figure 4A. As with the dc polarograms (Figure 1), there is substantial cathodic current at

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(15) Reference 12, p 183 ff.

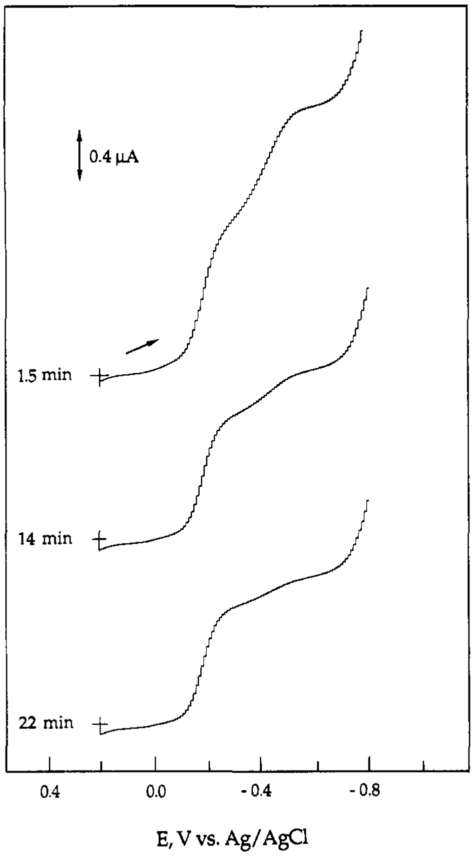

**Figure 5.** Normal pulse polarograms recorded with a solution prepared by adding an approximately equimolar quantity of $Ru(NH_3)_6^{2+}$ to a deaerated solution containing 0.12 mM $CrOO^{2+}$. The time elapsed since the addition of the $Ru(NH_3)_6^{2+}$ is indicated for each polarogram. Other conditions were as in Figure 4.

the initial potential of 0.2 V with the freshly prepared solution and this current decreases with time as do those for the two reduction waves evident at –0.04 and –0.43 V. The smaller wave at –0.04 V appears at the potential where $O_2$ is reduced (Figure 4B). The likely source of the $O_2$ was explained earlier in connection with Figure 3. Although this wave is more evident in the normal pulse polarograms in Figure 4A, close inspection of the dc polarograms in Figure 1A reveals the presence of the same wave.

The prominent wave near –0.43 V in Figure 4A corresponds to the prominent wave in Figure 1A, and it shows the same decrease in magnitude with time. In the dc polarograms in Figure 1A the wave appears at –0.27 V, while its half-wave potential is –0.43 V in the normal pulse polarograms. This shift in $E_{1/2}$ values between dc and pulse polarograms is commonly observed with irreversible electrode reactions and is the result of the shorter effective measurement time in normal pulse polarography ($\sim$50 ms vs a few seconds). In pulse polarograms recorded with longer measurement times, the half-wave potential shifted to more positive values, as expected. Thus, the wave at –0.43 V in Figure 4A can be assigned to the reduction of $CrOOH^{2+}$.

The hydroperoxo complex, $CrOOH^{2+}$, has been shown to result from the chemical reduction of $CrOO^{2+}$ by outer-sphere reductants such as $Ru(NH_3)_6^{2+}$.[5,10] We therefore recorded normal pulse polarograms for a solution prepared by adding an equimolar quantity of $Ru(NH_3)_6^{2+}$ to a solution of $CrOO^{2+}$. Three such polarograms are shown in Figure 5. Note the absence of cathodic current at the initial potential and the presence of a new cathodic wave near –0.17 V. The second cathodic wave near –0.4 V matches the one in Figure 4A. The elimination of the cathodic current at 0.2 V shows that the $Ru(NH_3)_6^{2+}$ reduced all of the oxidants (i.e., $HCrO_4^-$ and $CrOO^{2+}$) which are present in solutions of $CrOO^{2+}$ and are reduced at potentials positive of 0.4 V. The cathodic wave at –0.17 V corresponds to the reduction of the $Ru(NH_3)_6^{3+}$ produced by the reaction of $Ru(NH_3)_6^{2+}$ with $CrOO^{2+}$ and $HCrO_4^-$. The second cathodic wave must arise from the product of the reduction of $CrOO^{2+}$ because any $Cr^{3+}$ present would be reduced only at much more negative potentials. The absence of any anodic current in Figure 5 at 0 V, where $Ru(NH_3)_6^{2+}$ would be oxidized, indicates that all of the $Ru(NH_3)_6^{2+}$ was chemically oxidized by reaction with $CrOO^{2+}$ and the other oxidants present. This result is consistent with the report of Espenson and co-workers[5,10] that $Ru(NH_3)_6^{2+}$ reduces $CrOO^{2+}$ by one electron to produce $CrOOH^{2+}$. The product obtained from the chemical reduction of $CrOO^{2+}$ is apparently the same as the product of the electrochemical reduction because both complexes give rise to the same polarographic wave near –0.4 V (compare Figures 4 and 5), which diminishes as the metastable $CrOOH^{2+}$ decomposes (Figure 5).

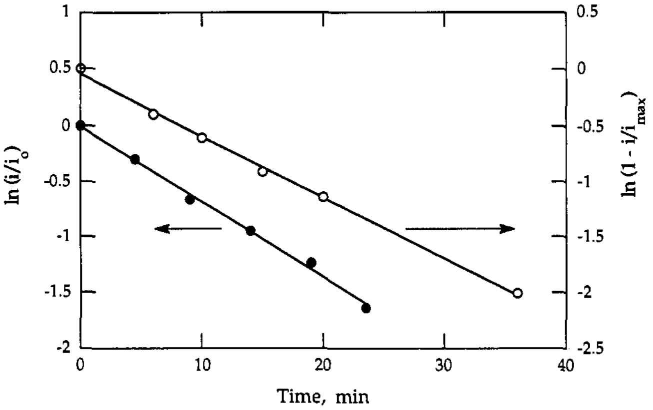

**Figure 6.** First-order kinetic plots of (●) plateau currents for the wave near –0.4 V in normal pulse polarograms, such as that in Figure 5, and (○) $\ln[1 - (i/i_{max})]$ from the data obtained with a rotating platinum disk electrode where $i$ is the anodic plateau current for the oxidation of $H_2O_2$ and $i_{max}$ is the corresponding value after the decomposition of $CrOOH^{2+}$ was complete.

The foot of the wave in Figure 5 corresponding to the reduction of the $CrOOH^{2+}$ complex overlaps somewhat with the upper portion of the wave for the reduction of $Ru(NH_3)_6^{3+}$. By measuring the plateau current of the latter wave after most of the $CrOOH^{2+}$ had decomposed and subtracting this value from the plateau current for the second wave measured 1.5 min after the $Ru(NH_3)_6^{2+}$ was added to the solution, we found the ratio of the plateau currents for the two waves to be ca. 1.7. A value of 2.0 would be expected if the first, one-electron reduction of $Ru(NH_3)_6^{3+}$ were followed by a two-electron reduction of the $CrOOH^{2+}$ complex present at equal concentration (and having the same diffusion coefficient as $Ru(NH_3)_6^{3+}$). Some of the $Ru(NH_3)_6^{2+}$ added to the solutions of $CrOO^{2+}$ is consumed in the reduction of $HCrO_4^-$ (produced during the generation of $CrOO^{2+}$; *vide supra*) and in the reduction of any $O_2$ present to yield products ($Cr^{3+}$ and $H_2O_2$) which are not reduced before –0.8 V. For this reason, the magnitude of the two plateau currents in Figure 5 at 1.5 min would not be expected to have a ratio of precisely 2.0. The observed ratio of 1.7 provides a reasonable basis for concluding that the second wave in Figure 5 corresponds to a two-electron reduction of the metastable hydroperoxide complex, $CrOOH^{2+}$, according to half-reaction 2.

$$CrOOH^{2+} + 2e + 3H^+ \rightarrow Cr^{3+} + 2H_2O \qquad (2)$$

The spontaneous decomposition of the $CrOOH^{2+}$ complex was monitored by measuring the magnitude of the second reduction wave in solutions similar to that employed in Figure 5. The decomposition follows first-order kinetics (solid points in Figure 6) with a rate constant of ca. $1.2 \times 10^{-3}$ s$^{-1}$. The decomposition was presumed to involve aquation of the hydroperoxo complex:[4]

$$(H_2O)_5CrOOH^{2+} \xrightarrow{H_3O^+} Cr(OH_2)_6^{3+} + H_2O_2 \qquad (3)$$

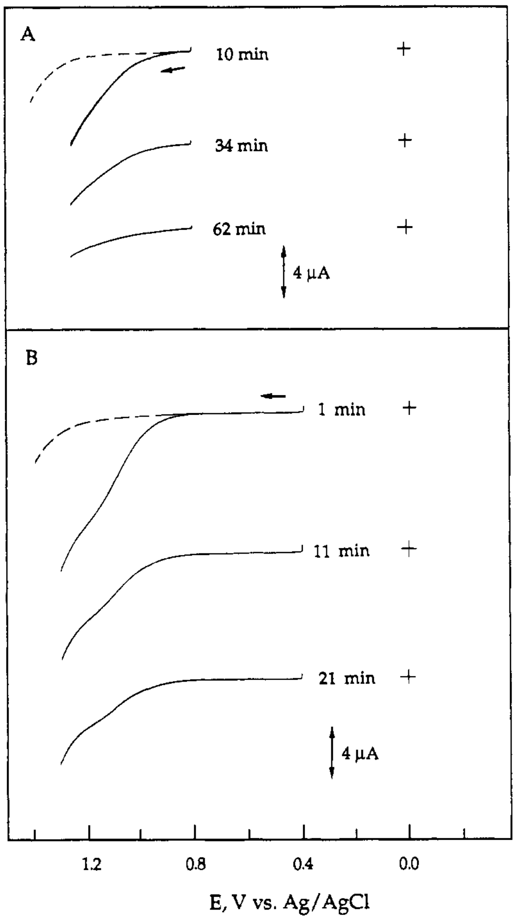

**Figure 7.** (A) Current–potential curves for the oxidation of 0.1 mM $CrOO^{2+}$. The indicated times have the same significance as in Figure 1A. (B) Current–potential curves for the oxidation of $CrOOH^{2+}$ prepared by adding an equimolar quantity of $Ru(NH_3)_6^{2+}$ to a deaerated 0.09 mM solution of $CrOO^{2+}$. The indicated times have the same significance as in Figure 5. Other conditions were as in Figure 3. The dashed curves are the responses obtained in the pure supporting electrolyte (0.1 M $CF_3COOH$).

To check this supposition, the decomposition was also followed by determining the concentration of $H_2O_2$ in solutions of $CrOOH^{2+}$ from the magnitude of the wave for its oxidation near 0.8 V at a rotating platinum disk electrode. (No response attributable to the oxidation of the $O_2H^-$ ligand coordinated to the Cr(III) center was observed at any potential within the accessible range.) A first-order kinetic plot of the resulting data is shown by the open points in Figure 6. The slopes of the two linear plots in Figure 6 are similar, as expected if the rate of appearance of $H_2O_2$ matched the rate of disappearance of $CrOOH^{2+}$. These results support the identification of reaction 3 as the decomposition reaction.

The specific rate estimated for reaction 3 is ca. 400 times greater than the rate of exchange of $H_2O$ ligands with solvent $H_2O$ in $Cr(OH_2)_6^{3+}$.[16] Thus, the $Cr^{3+}$–$O_2H^-$ bond or, more likely, the $Cr^{3+}$–$O_2H_2$ bond (a p$K_a$ in the range 1–3 has been estimated for $Cr(O_2H_2)^{3+}$ [4]) is apparently more readily activated toward dissociation than is the $Cr^{3+}$–$OH_2$ bond, perhaps because the $O_2H^-$ ligand has a larger number of exposed electron pairs available for interaction with protons in the reaction solution.

**Electro-Oxidation of $CrOO^{2+}$ and $CrOOH^{2+}$.** We were unable to find conditions where the electro-oxidation of the $O_2^-$ ligand coordinated to the $Cr^{3+}$ center in $CrOO^{2+}$ gave rise to a clearly defined anodic wave. However, it was possible to observe the initial portion of an anodic response attributable to this oxidation. The current–potential curves in Figure 7A show that in solutions of $CrOO^{2+}$ anodic current begins to flow at a rotating pyrolytic graphite electrode at potentials less positive than those at which the oxidation of the background electrolyte begins (dashed line in Figure 7A). We believe the current shown by the solid line in Figure 7A for the 10-min-old solution can be assigned to the electro-oxidation of $CrOO^{2+}$, which appears to begin near 1.1 V. The oxidation, half-reaction 4, is likely to be followed by rapid

$$CrOO^{2+} - e \rightarrow CrOO^{3+} \qquad (4)$$

dissociation to yield $Cr^{3+}$ and $O_2$,[17] which would account for the lack of any evidence of reversibility for the reaction. The observation that the oxidation of $CrOO^{2+}$ begins near 1.1 V provides a rough estimate of the upper limit on the formal potential of the $CrOO^{3+/2+}$ couple. If the electrode reaction were Nernstian, the rapid dissociation of the $CrOO^{3+}$ complex would produce a negative shift in the potential where $CrOO^{2+}$ is oxidized. However, the highly non-Nernstian behavior exhibited by the $CrOO^{2+}/CrOOH^{2+}$ couple makes it unlikely that the $CrOO^{3+/2+}$ couple is Nernstian. Thus, it may be surmised that the formal potential of the $CrOO^{3+/2+}$ couple is probably no greater than ca. 1.2 V vs Ag/AgCl or 1.4 V vs NHE. A lower bound on the potential is provided by the formal potential of the $CrOO^{2+}/CrOOH^{2+}$ couple. If the formal potential of the $CrOO^{3+}/CrOO^{2+}$ couple were less positive than that of the $CrOO^{2+}/CrOOH^{2+}$ couple, the $CrOO^{2+}$ complex would be unstable with respect to disproportionation to $CrOO^{3+}$ and $CrOOH^{2+}$, and no disproportionation of the $CrOO^{2+}$ complex has been observed.

The irreversible electro-oxidation of the $CrOOH^{2+}$ complex at the rotating graphite disk electrode is shown in Figure 7B. The oxidation wave with a half-wave potential near 1.05 V is poorly resolved because the product of the oxidation, $CrOO^{2+}$, is oxidized at only slightly more positive potentials and the oxidation of the background electrolyte begins soon after that (Figure 7A). However, the magnitude of the plateau current estimated for the wave in Figure 7B that was recorded 1 min after the solution of $CrOOH^{2+}$ was prepared, 4.4 μA, is not far from the value calculated for a one-electron oxidation, 4.6 μA, using the diffusion coefficient for $CrOO^{2+}$ obtained from its one-electron reduction at graphite electrodes (*vide supra*). The rate of decrease of the anodic wave in Figure 7B matches the rate of decrease of the reduction wave for $CrOOH^{2+}$ in Figure 6, which supports the attribution of the wave in Figure 7B to the oxidation of $CrOOH^{2+}$ to $CrOO^{2+}$.

**Estimation of the Formal Potential of the $CrOO^{2+}/CrOOH^{2+}$ Couple from Rotating-Disk Voltammetry.** The current–potential curves for the reduction of $CrOO^{2+}$ and the oxidation of $CrOOH^{2+}$ at oxidized pyrolytic graphite rotating disk electrodes in Figures 3 and 7B, respectively, provide a basis for estimating the formal potential of the $CrOO^{2+}/CrOOH^{2+}$ couple. Currents on the rising portions of the current–potential curves were measured and used to construct the plots of log $k$ vs potential shown in Figure 8A. To obtain the values of the heterogeneous electron-transfer rate constant, $k$, the measured currents were used to calculate a set of kinetic currents, $i_k$, given by eq 5, where $i$ is the measured

$$i_k = \frac{i i_p}{i_p - i} \qquad (5)$$

current at each potential and $i_p$ is the potential-independent plateau current. The rate constant, $k$, was then calculated from eq 6,

$$k = \frac{i_k}{FAC} \qquad (6)$$

where $F$ is Faraday's constant, $A$ is the electrode area, and $C$ is the concentration of the reactant undergoing reduction or

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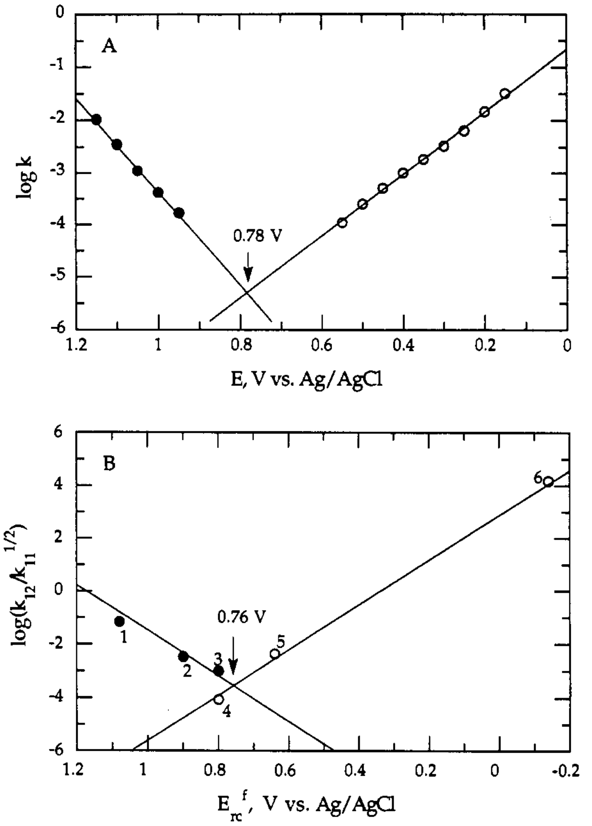

**Figure 8.** (A) Potential dependence of the heterogeneous rate constants for the reduction of $CrOO^{2+}$ (○) and the oxidation of $CrOOH^{2+}$ (●) at rotating pyrolytic graphite disk electrodes. (B) Plot of the left-hand side of eq 8 vs the formal potential of the redox couples using the kinetic data from Table 1. The numbered points correspond to cross-reactions with (1) $Ru(bpy)_3^{3+}$, (2) $Fe(phen)_3^{3+}$, (3) $Fe(5,6\text{-}(CH_3)_2phen)_3^{3+}$, (4) $Fe(5,6\text{-}(CH_3)_2phen)_3^{2+}$, (5) $Os(bpy)_3^{2+}$, and (6) $Ru(NH_3)_6^{2+}$.

oxidation at the electrode. The value of $k$ at each potential is given by eq 7a or 7b, where $k_s$ is the standard heterogeneous rate

$$\text{for the reduction of } CrOO^{2+}\text{:}\quad k = k_s \exp\left[\frac{-\alpha F}{RT}(E - E_1^f)\right] \tag{7a}$$

$$\text{for the oxidation of } CrOOH^{2+}\text{:}\quad k = k_s \exp\left[\frac{(1-\alpha)F}{RT}(E - E_1^f)\right] \tag{7b}$$

constant at the formal potential of half-reaction 1 and $\alpha$ is the transfer coefficient.[18] The plots in Figure 8A exhibit the expected linearity with slopes that correspond to $\alpha = 0.35$ and $1 - \alpha = 0.52$. The deviation of the sum of $\alpha$ and $1 - \alpha$ from unity may reflect uncertainties in the measurements as well as the sensitivity of the reaction to the nature of the electrode material. Comparable responses were not obtained at platinum or gold electrodes or at pyrolytic graphite electrodes which had not been preoxidized. It is likely that the functional groups present on the oxidized graphite surface are involved in promoting the coupled electron and proton transfers that are involved in the electrode reaction.[14] The intersection of the two lines in Figure 8A corresponds to a formal potential for the $CrOO^{2+}/CrOOH^{2+}$ couple of 0.78 V vs Ag/AgCl (0.98 V vs NHE). The corresponding value of $k_s$ is $5.0 \times 10^{-6}$ cm s$^{-1}$.

**Estimation of the Formal Potential of the $CrOO^{2+}/CrOOH^{2+}$ Couple from the Kinetics of Redox Cross-Reactions.** Espenson *et al.*[5] have measured the kinetics of the outer-sphere oxidation of transition metal complexes by $CrOO^{2+}$ in homogeneous solutions. We carried out a series of similar measurements with both $CrOO^{2+}$ and $CrOOH^{2+}$ using transition metal complexes chosen to have formal potentials reasonably close to that of the $CrOO^{2+}/CrOOH^{+}$ couple and known electron self-exchange rate constants. The $CrOOH^{2+}$ complex was oxidized to $CrOO^{2+}$ by $Ru(bpy)_3^{3+}$, $Fe(phen)_3^{3+}$, and $Fe(5,6\text{-}(CH_3)_2phen)_3^{3+}$ and $CrOO^{2+}$ was reduced to $CrOOH^{2+}$ by $Os(bpy)_3^{2+}$ and $Fe(5,6\text{-}(CH_3)_2phen)_3^{2+}$ using procedures described in the Experimental Section. The kinetic data obtained are summarized in Table 1 along with a previously reported value[5] for the reduction of $CrOO^{2+}$ by $Ru(NH_3)_6^{3+}$. It is instructive to display the data in Table 1 in a format suggested by the Marcus relation[19a]

**Table 1.** Kinetic Data for Electron-Transfer Cross-Reactions Involving the Reduction of $CrOO^{2+}$ or the Oxidation of $CrOOH^{2+}$

A. Reduction of $CrOO^{2+}$

| reductant | $E^f$, V[a] (vs NHE) | $k_{11}$, $M^{-1}\,s^{-1}$ [b] | $k_{12}$, $M^{-1}\,s^{-1}$ [c] |
|---|---|---|---|
| $Ru(NH_3)_6^{2+}$ | 0.06 | $4.0 \times 10^3$ [d] | $9.5\ (\pm 0.2) \times 10^5$ [e] |
| $Os(bpy)_3^{2+}$ | 0.84 | $2.2 \times 10^7$ [f] | 21 (±3) |
| $Fe(5,6\text{-}(CH_3)_2phen)_3^{2+}$ | 1.00 | $3.3 \times 10^8$ [g] | 1.6 (±0.4) |

B. Oxidation of $CrOOH^{2+}$

| oxidant | $E^f$, V[a] (vs NHE) | $k_{11}$, $M^{-1}\,s^{-1}$ [b] | $k_{12}$, $M^{-1}\,s^{-1}$ [c] |
|---|---|---|---|
| $Fe(5,6\text{-}(CH_3)_2phen)_3^{3+}$ | 1.00 | $3.3 \times 10^8$ [g] | 18 (±1) |
| $Fe(phen)_3^{3+}$ | 1.10 | $3.3 \times 10^8$ [h] | 62 (±10) |
| $Ru(bpy)_3^{3+}$ | 1.28 | $4.2 \times 10^8$ [i] | $1.4\ (\pm 0.1) \times 10^3$ |

[a] Formal potentials were measured by cyclic voltammetry or potentiometry. [b] Electron self-exchange rate constants for the reductants and oxidants. [c] $[CF_3COOH] = 0.1$ M. [d] Reference 20. [e] Reference 5. [f] Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542. [g] Assumed to be the same as $Fe(phen)_3^{2+/3+}$. [h] Ruff, I.; Zimonyi, M. *Electrochim Acta* **1973**, *18*, 515. [i] Young, R. C.; Keen, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468.

$$\log(k_{12}/k_{11}^{1/2}) = \log(k_{22}^{1/2}) \pm 8.47(E_1^f - E_{rc}^f) \tag{8}$$

where $k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2}$, $K_{eq}$ is the equilibrium constant for the cross-reaction, $f$ is approximated as unity, $E_1^f$ is the formal potential of the $CrOO^{2+}/CrOOH^{2+}$ couple (half-reaction 1), and $E_{rc}^f$ is the formal potential of the redox couple involved in the cross-reaction. The plus sign in eq 8 applies to the reduction of $CrOO^{2+}$ and the minus sign to the oxidation of $CrOOH^{2+}$.

A plot of $\log(k_{12}/k_{11}^{1/2})$ vs $E_{rc}^f$ based on eq 8 is shown in Figure 8B for the experimental systems of Table 1. The lines are drawn with the theoretical slope of $\pm 8.47$ V$^{-1}$, and all six of the data points fall reasonably close to the best-fit lines. The intersection of the lines occurs at 0.76 V (0.96 V vs NHE), which should correspond to the formal potential of the $CrOO^{2+}/CrOOH^{2+}$ couple. This value justifies the approximation of regarding $f$ as unity in the Marcus relation except for the case of the $Ru(NH_3)_6^{3+/2+}$ couple. Recalculation of this point in Figure 8B produces a somewhat larger deviation from the line, but the best estimate of $E_1^f$ remains as 0.78–0.74 V vs Ag/AgCl (0.98–0.94 V vs NHE). The average value of 0.96 V vs NHE is in reasonable agreement with the value of 0.98 V vs NHE obtained from the independent voltammetric measurements (Figure 8A). The average of the two values, 0.97 V vs NHE, is our best estimate of the formal potential of the $CrOO^{2+}/CrOOH^{2+}$ couple in 0.1 M $H^+$. The rate constant for electron self-exchange for the $CrOO^{2+}/CrOOH^{2+}$ couple calculated from the point of intersection of the lines in Figure 8B is $6 \times 10^{-8}$ $M^{-1}\,s^{-1}$. This rate constant compares favorably with the value of $2.5 \times 10^{-8}$ $M^{-1}\,s^{-1}$ that can be calculated from the Marcus theory[19b] using the heterogeneous rate constant for the $CrOO^{2+}/CrOOH^{2+}$ couple estimated in Figure 8A.

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(18) Reference 12, p 290 ff.

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A different value of the formal potential of the $CrOO^{2+}$/$CrOOH^{2+}$ couple was reported recently by Espenson *et al.*[21] These authors attempted to equilibrate a redox indicator having a known formal potential with the $CrOO^{2+}$/$CrOOH^{2+}$ couple in solution. A formal potential of 0.82 V vs NHE was obtained in 1 M $H^+$, corresponding to 0.76 V vs NHE in 0.1 M $H^+$, 0.21 V less positive than the value obtained in the present study. In comparison experiments with the same redox indicator, we found its reduced form to be quantitatively oxidized by $CrOO^{2+}$; an equilibrium mixture of oxidized and reduced forms of the indicator was not produced. The quantitative oxidation was consistent with the formal potential of 0.97 V vs NHE obtained in the present study. Although the value of the formal potential given in ref 21 is apparently too small, most of the interesting chemical comparisons examined in that paper remain valid.

**Effect of the Cr(III) Center on the Redox Chemistry of $O_2^-$ and $O_2H^-$.** It is of interest to consider the effects of coordination of $O_2^-$ and $O_2H^-$ to the $(H_2O)_5Cr^{3+}$ center on the redox properties of the two ligands. Despite the positive values of the standard potentials of the $H_2O_2/H_2O$ and $H_2O_2/OH$ couples ($E° = 1.76$ and 0.8 V vs NHE, respectively[22] ), $H_2O_2$ is not reduced at significant rates at most electrode surfaces. The reduction of $H_2O_2$ does proceed at mercury electrodes but only near –0.7 V vs NHE in acidic electrolytes.[23] The reduction of $CrOOH^{2+}$ at –0.27 V vs Ag/AgCl (–0.07 V vs NHE) (Figure 1A) might be taken as an indication that the replacement of one proton in $H_2O_2$ by $(H_2O)_5Cr^{3+}$ significantly enhances the reactivity of the peroxo group toward electrochemical reduction. However, the driving forces involved in the electrochemical reductions of the two oxidants also need to be considered. The formal potentials for the reductions of $CrOOH^{2+}$ according to half-reactions 9 and 10 can be calculated from the equilibrium constant for the

$$CrOOH^{2+} + 2e + 3H^+ = Cr^{3+} + 2H_2O \qquad (9)$$

$$CrOOH^{2+} + e + H^+ = CrO^{2+} + H_2O \qquad (10)$$

formation of $CrOO^{2+}$ and related data on its redox chemistry reported by Espenson *et al.*,[21] the known standard potentials of the $Cr^{3+}/Cr^{2+}$, $H_2O_2/H_2O$, and $O_2/H_2O$ couples, and the formal potential of the $CrOO^{2+}/CrOOH^{2+}$ couple evaluated in this study. (Espenson *et al.*[21] carried out essentially the same calculation using their smaller value for the formal potential of the $CrOO^{2+}$/$CrOOH^{2+}$ couple.). The calculated values at $[H^+] = 0.1$ M are $E_9^f = 1.79$ V and $E_{10}^f = \leq 2.02$ V vs NHE. Both of these potentials are inflated because the oxidant being reduced is thermodynamically unstable with respect to dissociation of the unique ligand while the same is not true of the reduced products, but it is not clear how to introduce this feature into comparison of relative reactivities. Comparison of these calculated formal potentials with the experimental reduction potentials shows that the reduction of $CrOOH^{2+}$ at –0.07 V vs NHE involves an overvoltage of $\leq 2.1$ V if half-reaction 10 is rate limiting and the corresponding overvoltage for the reduction of $H_2O_2$ to OH is ca. 1.4 V. Thus, the electrochemical reactivity of the peroxide group toward one-electron reduction is evidently greater for $H_2O_2$ than for $CrOOH^{2+}$. However, the opposite ordering is obtained if the two reduction potentials, –0.7 and –0.07 V vs NHE, are compared with the formal potentials for the two-electron reductions of $H_2O_2$ and $CrOOH^{2+}$ at $[H^+] = 0.1$ M, 1.70 V and 1.79 vs NHE, respectively. An appropriate and satisfying comparison of relative reactivities would require more mechanistic information than is presently available.

A significant change in the electrochemical reactivity of $H_2O_2$ produced by its coordination to a $(H_2O)_5Cr^{3+}$ center would contrast with the recent report of Espenson and co-workers, who observed similar kinetic parameters for the reduction by $Fe^{2+}$ of $H_2O_2$ and $CrOOH^{2+}$.[10] However , the reduction by $Fe^{2+}$ is believed to follow an inner-sphere pathway with both oxidants while the electrochemical reduction may involve an outer-sphere mechanism because of the absence on either $H_2O_2$ or $CrOOH^{2+}$ of a suitable lead-in group for the mercury electrode surface.

Changes in reactivity resulting from the coordination of $O_2H^-$ to transition metal centers may also be relevant to the behavior of transition metal complexes which serve as catalysts for the direct four-electron electroreduction of $O_2$ to $H_2O$. Various complexes of both Co(II) and Cu(II) catalyze the four-electron electroreduction of $O_2$ under conditions where the same complexes do not catalyze the electroreduction of $H_2O_2$ at comparable rates.[7,24,25] In all cases, the catalyzed reductions of $O_2$ commence with its coordination to the transition metal center. The first stage of the subsequent electroreduction is believed to lead to a hydroperoxo complex which may exhibit the type of enhanced reactivity toward the further one-electron electroreduction of the coordinated ligand as does the analogous $CrOOH^{2+}$ complex examined in this study. The much slower reaction rates observed when $H_2O_2$ instead of $O_2$ is the substrate[7,25] may simply reflect the much lower concentrations of the more reactive hydroperoxide complex which are present in acidic or neutral solution when this intermediate must be formed by substitution on the metal center rather than by electroreduction of an already coordinated $O_2$ molecule.

The electro-oxidation of $CrOOH^{2+}$ to $CrOO^{2+}$ at 1.05 V vs Ag/AgCl in (Figure 7B) (1.25 V vs NHE) involves an overvoltage of only 0.28 V, since the $CrOO^{2+}/CrOOH^{2+}$ couple has a formal potential of 0.97 V vs NHE at $[H^+] = 0.1$ M. The electro-oxidation of $H_2O_2$ in aqueous acid proceeds in a two-electron step and typically requires both an oxidatively activated platinum electrode and an overvoltage of 0.4–0.5 V. The replacement of one proton in $H_2O_2$ by the $Cr(OH_2)_5{}^{3+}$ center apparently activates the $O_2H^-$ group toward release of an electron and stabilizes the resulting $O_2^-$ ligand sufficiently to avoid the immediate protonation and disproportionation steps which occur with the uncoordinated ligand. The unusual ability of $Cr^{3+}$ to stabilize the coordinated $O_2^-$ ligand was also pointed out by Espenson *et al.*[21]

The same factor is reflected in the remarkable difference between the formal potentials of the $O_2/O_2H$ couple, $E^f = 0.06$ V (vs NHE; pH = 1), and the $CrOO^{3+/2+}$ couple, $\sim 1.4 > E^f > 0.97$ V. The extraction of an electron from $O_2^-$ bound to $Cr^{3+}$ is evidently much more difficult than is the extraction from $O_2H$. Although our estimate of the formal potential of the $CrOO^{3+/2+}$ couple is very approximate, it may be of interest to use it to estimate the stability of the short-lived $CrOO^{3+}$ complex. Combining the equilibrium constant for the heterolytic dissociation of $CrOO^{2+}$, $3.3 \times 10^{-8}$ M,[3] the formal potential of the $O_2/O_2^-$ couple, –0.16 V ($[O_2] = 1$ M as standard state), and the approximate value of the formal potential of the $CrOO^{3+}/CrOO^{2+}$ couple, $E^f = \sim 1.4$–0.97 V, one calculates an equilibrium constant of $8 \times 10^{18}$–$4 \times 10^{11}$ M for

$$CrOO^{3+} = Cr^{3+} + O_2 \qquad (11)$$

Despite the large uncertainty in the quantitative value of this equilibrium constant, the lack of affinity of the $Cr^{3+}$ cation for $O_2$ is evident.

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