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Reactions of some chromium-oxygen complexes containing superoxo, hydroperoxo, oxo, and [mu]-peroxo ligands

Susannah Lesley Scott
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Scott, Susannah Lesley, Ph.D.

Iowa State University, 1991

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Reactions of some chromium-oxygen complexes containing superoxo, hydroperoxo, oxo, and μ-peroxo ligands

by

Susannah Lesley Scott

A Dissertation Submitted to the
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DEDICATION

This thesis is dedicated to Earl Laird Smith, whose faith in me made this work possible.

GENERAL INTRODUCTION

The reaction of reduced metal ions with molecular oxygen is a fundamental chemical process. Atmospheric oxygen can destroy expensive industrial catalysts, or it can be vital to their catalytic action. Oxygen is necessary for the functioning of some metalloenzymes, but its reaction with others leads to highly toxic products. Enzymes exist whose principle function is believed to be removal of these toxic products, and the reaction usually requires a coordinated metal ion. Finally, the presence or absence of oxygen can be crucial to chemical synthesis.

Oxidations by molecular oxygen are complex, multistep reactions. Oxygen requires four electrons to become water; also, an O-O bond must be cleaved. Neither of these processes can be accomplished by a single metal ion, therefore intermediates must be formed. The intermediates may be partially-reduced but unbound oxygen species, such as superoxide, hydrogen peroxide or hydroxyl radical. All of these have been prepared independently and their properties are well-known. Sometimes the metal ion is directly involved in the intermediates, and occasionally novel metallic species can be isolated.

This work concerns the nature and properties of the metallic intermediates formed during the reaction of $Cr(H_2O)_6^{2+}$ with O_2. The reaction is extremely rapid, a feature which has hindered efforts to identify intermediates and elucidate the mechanism. The overall reaction is represented by equation 1.

$$4\,Cr(H_2O)_6^{2+} \;+\; O_2 \;\rightarrow\; 2\,(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+} \;+\; 6\,H_2O \quad (1)$$

The metallic product, $Cr(OH)_2Cr^{4+}$, is a bis-μ-hydroxo dimer of Cr(III) identified by ion-exchange and isotopic-labelling studies. Since the d^3 electron configuration makes Cr(III) complexes extremely inert towards substitution, it was proposed that the dimer must arise from oxidation of Cr^{2+} by a Cr(IV) intermediate. The electron transfer event in the precursor complex creates two Cr(III) centers whose ligand environments, including two μ-hydroxo bridges, are frozen. The Cr(IV) intermediate was never isolated, and was presumed highly unstable and far too reactive for direct study.

Recently, a stable adduct between Cr^{2+} and O_2 which has the spectral and thermodynamic characteristics of a superoxochromium(III) ion was identified. Kinetic studies showed this species to be a fairly good oxidant, with both outer-sphere and inner-sphere electron transfer capabilities. Its principal mode of decomposition is homolysis, equation 2, followed by reaction of CrO_2^{2+} with Cr^{2+}.

$$CrO_2^{2+} \rightleftharpoons Cr^{2+} + O_2 \qquad (2)$$

Thus the superoxochromium(III) ion is a good candidate for first intermediate in the reaction of Cr^{2+} with O_2. The reaction of CrO_2^{2+} with Cr^{2+} is too fast for conventional mixing techniques, so further information about the mechanism was not accessible from kinetic studies. A product of this reaction which has been overlooked until this study is the aquachromium(IV) ion, a potent oxidant which reacts rapidly with Cr^{2+}.

Oxidation of most organic substrates by O_2 is slow because of the spin mismatch between its triplet ground state and the closed valence shells of most stable organic molecules. When O_2 is coordinated to (and perhaps reduced by) a metal ion, the spin barrier is removed, and the reaction rate may be substantially enhanced. When the reduced metal ion is regenerated as a product of the oxidation reaction, it may react with O_2 again, thus creating a catalytic cycle. Metal complexes which undergo these reactions are oxygen carriers as well as activators. In this work, the reactions of Cr complexes as oxygen carriers and activators was investigated.

The reactivity of the various intermediate oxometal species also bears on the mechanism of oxidation of organic substrates by chromic acid, a widely-used organic synthetic technique.

This reaction has been investigated by many workers for over five decades, however, their efforts were limited by lack of direct information about the intermediates involved. It is now accepted that chromic acid reacts with alcohols to form an ester, which then decomposes by a concerted two-electron path to give Cr(IV). The fate of Cr(IV) has been variously proposed as oxidation by chromic acid, disproportionation, or reaction with the substrate. Recent work focused on the last possibility, and it was concluded that Cr(IV) oxidizes organic substrates to alkyl radicals. In the present work, the independent preparation of aquachromium(IV) permitted a direct investigation of this reaction, and the results, which are not in agreement with previous conclusions about the reactivity of Cr(IV), are discussed.

One of the proposed intermediates in the reaction of Cr^{2+} with O_2, $CrOCr^{4+}$, has never been observed under reaction conditions. In particular, the reaction between CrO^{2+} and Cr^{2+} does not yield the species described in the literature as $CrOCr^{4+}$. The intense color and oxidizing ability of the proposed complex was claimed to be the result of strong electronic interactions in the μ-oxo bridge. In fact, both properties are due to a bridging semiquinone radical, which is reversibly reduced to bridging hydroquinone. The incorrect previous characterization of this species highlights the difficulties involved in interpreting the reaction chemistry of all of the highly soluble and unstable chromium-oxygen compounds.

Explanation of Dissertation Format

The dissertation is organized into three sections following the "Alternate Thesis Format". Each section corresponds to a manuscript submitted for publication in either *J. Am. Chem. Soc.* or *Inorg. Chem.* Each section is self-contained with its own tables, figures, schemes and references. All the work described here was performed by S. L.Scott.

SECTION I

CATALYTIC OXIDATION OF THE HYDROXYMETHYLCHROMIUM(III) ION BY THE SUPEROXOCHROMIUM(III) ION

ABSTRACT

The superoxochromium(III) ion, CrO_2^{2+}, is an efficient catalyst for autoxidation of the hydroxymethylchromium(III) ion, $CrCH_2OH^{2+}$, in aqueous solution. The reaction involves one-electron oxidation of $CrCH_2OH^{2+}$ by CrO_2^{2+}, $k = 137$ L mol^{-1} s^{-1}, to yield Cr^{2+}, CH_2O and a novel hydroperoxochromium(III) ion, CrO_2H^{2+}. The Cr^{2+} produced reacts rapidly with O_2 to regenerate the catalyst CrO_2^{2+}. When O_2 is depleted, the Cr^{2+} reacts instead with CrO_2^{2+} to produce the aquachromium(IV) ion, CrO^{2+}. This initiates a chain reaction that rapidly consumes the remaining CrO_2^{2+} and a stoichiometric amount of $CrCH_2OH^{2+}$.

INTRODUCTION

Molecular oxygen is a powerful oxidant if not always a rapid one. Recent studies of the complexes formed between metal ions and molecular oxygen[1] have shown that coordination and partial reduction activate O_2 towards many organic and inorganic substrates. Such reactions, important both industrially and biologically, involve a number of intermediates, whose lifetime and reactivity depend dramatically on the metal and ligands. Macrocycles, especially porphyrins, have a strong stabilizing effect on such intermediates, and the literature abounds with examples of metal-porphyrin complexes containing oxygen in the superoxo, peroxo or oxo forms, and the metal in any of a number of unusual oxidation states.[2]

Much less information is available on similar chemistry in non-porphyrin systems, and especially in aqueous solution, mostly because the intermediates involved are usually too short-lived to be observed directly. With a few exceptions[1,3-5] the work reported in this area deals almost exclusively with oxygen-carrying properties of metal-oxygen adducts,[1,6] and not with mechanistic studies of their electron-transfer chemistry.

The reaction of Cr^{2+} with O_2 yields a long-lived superoxochromium(III) ion,[7] CrO_2^{2+}, eq 1 (here and elsewhere the coordinated water molecules are omitted).

$$Cr^{2+} + O_2 \rightleftharpoons CrO_2^{2+} \qquad (1)$$

The CrO_2^{2+} has been identified and characterized as a complex of chromium(III) with superoxide.[5] Unlike most of the other transition metal-oxygen adducts, CrO_2^{2+} can be handled at room temperature even under air-free conditions since the reverse reaction is so slow, $k_{-1} = 2.5 \times 10^{-4}\ s^{-1}$.[5] This makes it possible to study its chemistry without interference from free O_2 and in the absence of rapid oxygen binding/release equilibria. The thermal decomposition of CrO_2^{2+} and its reactions with inorganic reductants such as hydrazine,

$Ru(NH_3)_6^{2+}$, $Co(sep)^{2+}$, V^{2+}, Fe^{2+}, etc. have been studied.[5] Based on the kinetic and spectral evidence obtained in that work it was proposed that one-electron outer-sphere reduction of CrO_2^{2+} yields a long-lived hydroperoxochromium(III) ion, CrO_2H^{2+}, which could not, however, be characterized owing to the extremely low concentrations of its immediate precursor, CrO_2^{2+}, available at that time (typically ≤ 40 μM).

In this chapter, kinetic results are reported for the autoxidation of $CrCH_2OH^{2+}$, consisting of an uncatalyzed path and a path catalyzed by CrO_2^{2+}. A mechanistic interpretation for the catalysis is presented, as well as conclusive evidence for the formation of CrO_2H^{2+} as a product at millimolar concentrations.

This chapter also contains an improved method for the preparation of CrO_2^{2+}. This procedure permits 10-fold higher concentrations of the desired product (up to 0.5 mM) than was previously possible, with no undesirable chromium side-products such as chromate. Also, the presence of alcohols in the reaction medium stabilizes CrO_2^{2+} towards spontaneous decomposition in aerated solutions.

EXPERIMENTAL SECTION

Dilute solutions ($\leq$ 40 μM) of CrO_2^{2+} were initially prepared by injecting Cr^{2+} into 0.1 M aqueous $HClO_4$ saturated with O_2, as described previously.[5] Higher concentrations could not be prepared in this way, because the yield of CrO_2^{2+} decreases and those of Cr(III) and $HCrO_4^-$ increase as the total concentration of Cr increases.[5] As described later in greater detail, it was found that much higher concentrations of CrO_2^{2+} can be prepared by essentially the same method, provided the solution contains a small amount of an alcohol. Later preparations typically had 0.1 - 1 M CH_3OH. Concentrations of CrO_2^{2+} were determined spectrophotometrically (λ_{max} 290 nm, $\varepsilon = 3.1 \times 10^3$ M^{-1} cm^{-1}; λ_{max} 245 nm, ε 7.4×10^3 M^{-1} cm^{-1}).[5,7]

The yellow hydroxymethylchromium ion, $CrCH_2OH^{2+}$, was prepared in solution[8] from 0.02 M Cr^{2+}, 0.01 M H_2O_2 and 1 M CH_3OH, and was standardized spectrophotometrically (λ_{max} 392 nm, $\varepsilon = 570$ M^{-1} cm^{-1}; λ_{max} 282 nm, $\varepsilon = 2.4 \times 10^3$ M^{-1} cm^{-1}).[8,9] In several cases the complex was purified by ion-exchange on a 10 cm column of Sephadex SP C-25 cation-exchange resin, from which it was eluted with 0.2 M $HClO_4$. The behavior of the purified and unpurified complexes was identical in all of the reactions studied and in most preparations the ion-exchange step was omitted. The deuterated complex $CrCD_2OD^{2+}$ was prepared by the same method as $CrCH_2OH^{2+}$, except that D_2O and CD_3OD were substituted for H_2O and CH_3OH. The preparation of $CrCD_2OH^{2+}$ used H_2O and CD_3OD. The preparation of $CrCH_2OCH_3$ used CH_3OCH_3 (as a saturated aqueous solution) instead of CH_3OH.

$[Co(NH_3)_5F](ClO_4)_2$ was prepared from $[Co(NH_3)_5F](NO_3)_2$[10] and $HClO_4$. Solutions of $Co(NH_3)_5F^{2+}$ were prepared daily. Dilute solutions of H_2O_2 were prepared from commercially-available 30 % H_2O_2 and were standardized by $I^-/S_2O_3^{2-}$ titration daily. Alcohols were purchased from commercial suppliers and used as received.

Spectrophotometric titration curves and kinetic traces were obtained by measuring the change in absorbance at 290 nm, using a Cary 219 UV-visible spectrophotometer equipped with an internal timer and a thermostatted cell-holder. At 290 nm, both CrO_2^{2+} and $CrCH_2OH^{2+}$ contribute to the total absorbance. All reagents except $CrCH_2OH^{2+}$ were mixed in a spectrophotometer cell capped with a septum and saturated with either oxygen or argon. Air-free $CrCH_2OH^{2+}$ was injected by syringe and the solution was shaken gently to commence the reaction. For the determination of the kinetic isotope effect in the catalyzed autoxidation of $CrCH_2OH^{2+}$, the kinetics were also determined on $CrCD_2OD^{2+}$ in D_2O and $CrCD_2OH^{2+}$ in H_2O. The total deuterium content in the former system was > 96%. All the kinetic experiments were performed at 25.0 ± 0.1 °C. Pseudo-first-order rate constants were obtained graphically as the negative of the slope of $\ln(A_t - A_\infty)$ versus time, or as a parameter from the nonlinear least-squares fit to a single exponential rate law. Oxygen concentrations were measured with a dissolved-oxygen electrode from Hach Chemical Company.

Inorganic products were identified and their concentrations determined spectrophotometrically. Oxidizing titer was evaluated by deaerating the product solution with argon, then adding an excess (ca. 1 g) of solid sodium iodide. The absorbance at 350 nm due to triiodide ($\varepsilon = 2.54 \times 10^4\ M^{-1}\ cm^{-1}$)[11] was measured to determine the concentration of iodine in solution. Formaldehyde was determined by the chromotropic acid analysis.[12]

RESULTS

Qualitative observations

The reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} in the presence of excess O_2 was accompanied by an exponential decrease in absorbance at 290 nm. When O_2 was not in excess, the reaction profile showed a dramatic break, Figure I-1. In the absence of O_2, the reaction was fast and autocatalytic, Figure I-2.

Effect of CH_3OH on the yield and stability of CrO_2^{2+}

As already noted in earlier work,[5] the reaction of Cr^{2+} with O_2 in dilute aqueous $HClO_4$ (0.01 - 0.10 M) yielded CrO_2^{2+} quantitatively only at very low concentrations of Cr^{2+} ($\leq 40\ \mu M$). At higher concentrations, large amounts of Cr(III) and $HCrO_4^-$ ($\lambda_{max} = 345$ nm, $\varepsilon = 1.45 \times 10^3\ M^{-1}\ cm^{-1}$) formed at the expense of CrO_2^{2+}. The addition of as little as 0.01 M CH_3OH to the reaction mixture prior to or immediately after the injection of Cr^{2+} resulted in greatly improved yields of CrO_2^{2+}. Up to 0.5 mM CrO_2^{2+} was prepared in this way, with no contamination by $HCrO_4^-$. Other alcohols, such as CH_3CH_2OH and $(CH_3)_2CHOH$, had the same effect on the yield of CrO_2^{2+}. In addition, the decomposition of CrO_2^{2+} was slower in oxygenated solutions that contained alcohol than in those that did not.

Catalyzed reaction of O_2 with $CrCH_2OH^{2+}$

When CrO_2^{2+} (0.008 - 0.12 mM) and $CrCH_2OH^{2+}$ (0.13 - 0.93 mM), are mixed in the presence of excess O_2 (0.26 - 1.27 mM), a straightforward catalytic process takes place, eq 2. The CrO_2^{2+} is recovered fully at the end of the reaction, and CH_2O is produced quantitatively, i.e., $[CH_2O]_\infty \geq 0.9\ [CrCH_2OH^{2+}]_0$.

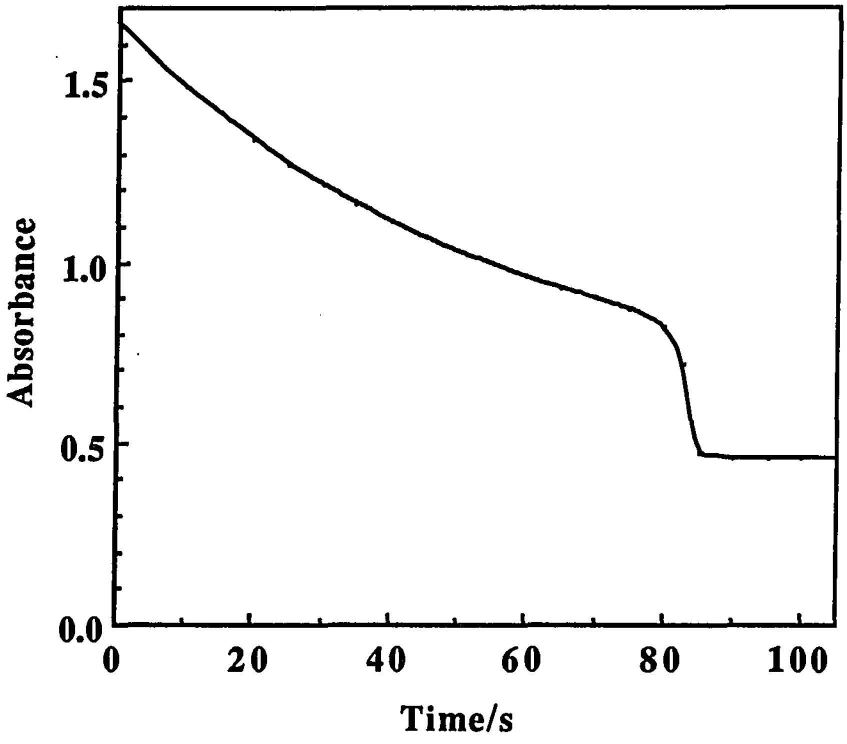

Figure I-1. Kinetic trace at 290 nm for the reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} in the presence of a limiting amount of O_2. Experimental conditions: 0.10 mM CrO_2^{2+}, 0.42 mM $CrCH_2OH^{2+}$, 0.2 M CH_3OH, 0.10 M $HClO_4$, 0.34 mM O_2. Optical pathlength: 1 cm.

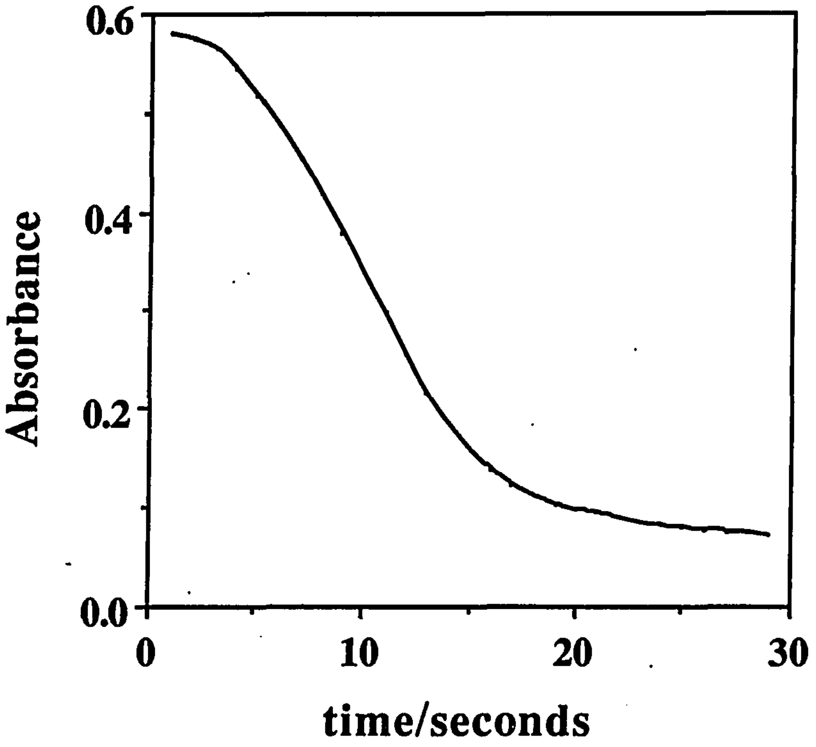

Figure I-2. Kinetic trace at 290 nm for the reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} in the absence of O_2. Experimental conditions: 0.043 mM CrO_2^{2+}, 0.098 mM $CrCH_2OH^{2+}$, 0.02 M CH_3OH, 0.013 M $HClO_4$. Optical pathlength: 2 cm.

$$CrCH_2OH^{2+} + O_2 \xrightarrow[k_2]{CrO_2^{2+}} CrO_2H^{2+} + CH_2O \qquad (2)$$

$$-d[CrCH_2OH^{2+}]/dt = k_{obs}\,[CrCH_2OH^{2+}] \qquad (3)$$

$$k_{obs} = k_o + k_2[CrO_2^{2+}] \qquad (4)$$

The kinetics obey the first-order rate law of eq 3 to >90% completion. The rate constant k_2, eq 4, is linearly dependent on $[CrO_2^{2+}]$ and independent of $[O_2]$, $[H^+]$, and $[CH_3OH]$. The rate constant k_2 increases with increasing ionic strength ($HClO_4 + LiClO_4$) at constant $[HClO_4]$ = 0.10 M. The data in Figure I-3 yield $k_2 = 137 \pm 5$ L mol^{-1} s^{-1} at $\mu = 0.10$ M. The intercept k_o is a summation of terms corresponding to the known hydrolysis of $CrCH_2OH^{2+}$ [8-10] and direct autoxidation of $CrCH_2OH^{2+}$, discovered in this work and described subsequently. As seen in Figure I-3, the k_o terms contributes little to the overall rate constant under the experimental conditions.

In one experiment the change in oxygen concentration was monitored by use of a dissolved-oxygen electrode. The data yielded $k_2 = 140$ L mol^{-1} s^{-1}, in excellent agreement with the value determined spectrophotometrically.

The value of k_2 is virtually unaffected by deuteration at carbon. For the reaction between $CrCD_2OH^{2+}$ and CrO_2^{2+}, $k_2 = 122$ L mol^{-1} s^{-1} for a primary isotope effect k_H/k_D = 1.1. However, the value of k_2 for the reaction of $CrCD_2OD^{2+}$ in D_2O is 76 L mol^{-1} s^{-1}; therefore for O-deuteration, the kinetic isotope effect is 1.8.

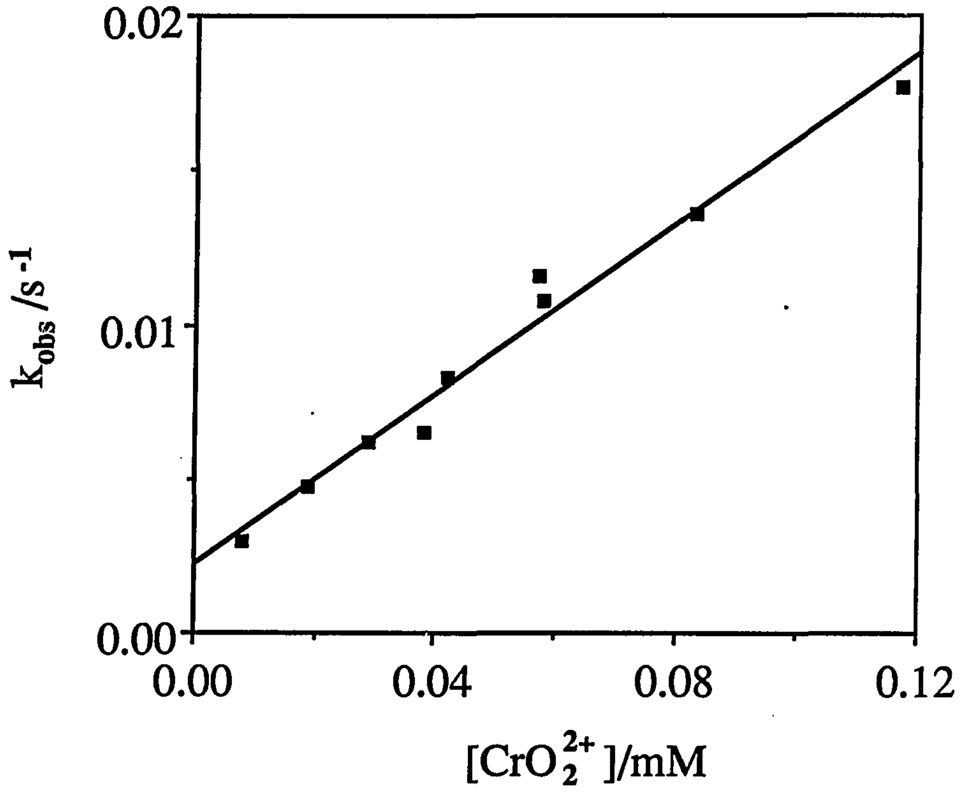

Figure I-3. Dependence of the pseudo-first-order rate constant for the reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} on the concentration of CrO_2^{2+}. Experimental conditions: 0.42 mM $CrCH_2OH^{2+}$, 0.2 M CH_3OH, 0.10 M $HClO_4$, 0.3 - 1.2 mM O_2, 25.0 °C.

The reaction of the O-methylated complex, $CrCH_2OCH_3^{2+}$, with CrO_2^{2+} is much slower than the reaction of $CrCH_2OH^{2+}$. Also, the first-order plots for the former reaction conducted in the presence of a large excess of O_2 are non-linear.

The hydroperoxochromium(III) ion

The identification of the chromium product as CrO_2H^{2+} is based on the following evidence. After completion of reaction 2 the iodometric analysis of spent solutions confirmed the presence of two oxidizing equivalents per mole of initial $CrCH_2OH^{2+}$ in addition to the oxidizing equivalents present due to the catalyst, CrO_2^{2+}. The reaction of the oxidizing product with iodide under a given set of conditions (0.10 M H^+, 5.0 mM I^-) is over in a few seconds. The product is thus clearly not free H_2O_2, whose reaction with iodide was measured under identical conditions, and took several hours to go to completion.

The most convincing evidence for this product species being an intact one-electron reduction product of CrO_2^{2+} comes from its reaction with Ce(IV). When one equivalent of the latter is added to the solution after completion of reaction 2, CrO_2^{2+} is produced in a concentration comparable to (~ 75%) that of $CrCH_2OH^{2+}$ consumed, consistent with eq 5.

$$CrO_2H^{2+} + Ce(IV) \rightarrow CrO_2^{2+} + Ce(III) + H^+ \qquad (5)$$

Some decay of CrO_2H^{2+} takes place on the time scale of the experiment, see later.

Independent experiments showed that the stoichiometric reaction of CrO_2^{2+} with $Ru(NH_3)_6^{2+}$ also yields CrO_2H^{2+}, eq 6, as proposed previously.[5c] Subsequent reoxidation by Ce(IV) again restores the spectrum of CrO_2^{2+}.

$$CrO_2^{2+} + Ru(NH_3)_6^{2+} + H^+ \rightarrow CrO_2H^{2+} + Ru(NH_3)_6^{3+} \qquad (6)$$

After reaction 2 is over, the absorbance in the visible range decreases with a simultaneous loss of the oxidizing titer of the solution. This result is reasonably attributed to the decomposition of CrO_2H^{2+}. The final spectrum is that of Cr^{3+}, although the presence of some other low-absorbing Cr products has not been ruled out. Figure I-4 shows the spectrum measured immediately after completion of reaction 2, the final spectrum obtained 1.5 hours later, and a difference spectrum of CrO_2H^{2+}. A study of the decomposition and reactivity of CrO_2H^{2+} will be reported separately.[13]

Uncatalyzed reaction of O_2 with $CrCH_2OH^{2+}$

Air-free solutions of $CrCH_2OH^{2+}$ slowly decompose by acid-dependent acidolysis to yield Cr^{3+} and CH_3OH.[8-10] The decomposition of $CrCH_2OH^{2+}$ is strongly accelerated by O_2 and yields HCHO. In 0.1 M H^+ the respective rate constants for decomposition of 0.23 mM $CrCH_2OH^{2+}$ in argon-saturated and O_2-saturated solutions are $1 \times 10^{-3}\ s^{-1}$ and $8 \times 10^{-3}\ s^{-1}$. The reaction in the presence of O_2 appears to have a minor autocatalytic component, and the rate constant evaluated near the end of the reaction was ~10% greater than that obtained from the initial portion of the trace. The final spectrum showed the presence of some CrO_2^{2+} ($\leq$ 0.06 μM) among the reaction products. Oxidation of the spent solution by Ce(IV), eq 5, produced a clean spectrum of 0.16 mM CrO_2^{2+}, indicating that CrO_2H^{2+} is a major chromium product. The overall reaction can thus be written as in eq 7.

$$CrCH_2OH^{2+} + O_2 \rightarrow CH_2O + CrO_2H^{2+} \ (+ \ CrO_2^{2+} + Cr^{3+}) \qquad (7)$$

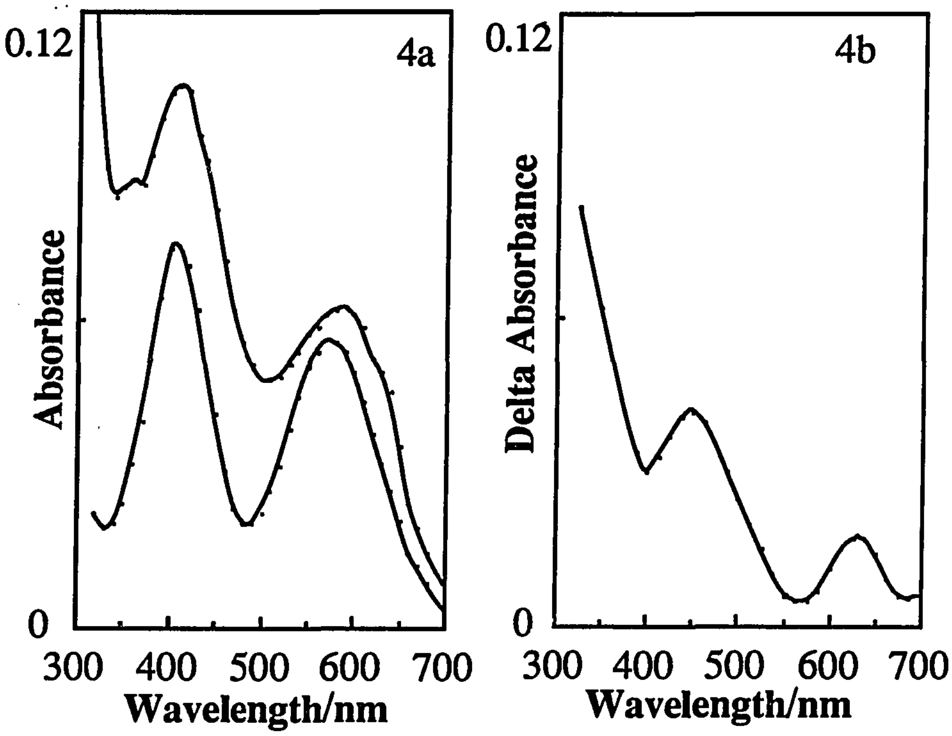

Figure I-4. (a) Spectrum of reaction mixture recorded immediately after the catalytic reaction (upper line) and 1.5 hours later (lower line); (b) Difference between the absorption spectrum of CrO_2H^{2+} and its decomposition products, obtained by subtraction of the spectra in (a). The initial concentrations of reagents were: 0.24 mM $CrCH_2OH^{2+}$, 0.020 mM CrO_2^{2+}, 0.16 M $HClO_4$, 0.45 mM O_2. Optical pathlength: 5 cm.

The sum of the concentrations of CrO_2^{2+} and CrO_2H^{2+}, 0.16 mM, is less than the amount of $CrCH_2OH^{2+}$ initially present, 0.23 mM. The missing Cr is present as Cr(III), ormed both by parallel acidolysis of $CrCH_2OH^{2+}$ and by decomposition of CrO_2H^{2+}, which appears to be complete in less than an hour. Since it takes ~10 min for the reaction of eq 7 to go to completion, some CrO_2H^{2+} decomposed before the addition of Ce(IV).

The presence of CrO_2^{2+} among the reaction products, and the established catalytic effect of this species on the reaction of $CrCH_2OH^{2+}$ with O_2, explain the appearance of the kinetic traces. As the uncatalyzed reaction of eq 7 produces more and more CrO_2^{2+}, the contribution from the catalytic pathway of eq 2 becomes increasingly important as the reaction nears completion.

In order to determine the rate constant for reaction 7 without complications from the catalytic path, experiments were conducted in the presence of Fe^{2+}, a good scavenger for CrO_2^{2+}.[5c] Under these conditions the $CrCH_2OH^{2+}$ disappears in two parallel processes, acidolysis[8,9] and reaction 7. All the CrO_2^{2+} produced in eq 7 is destroyed rapidly by Fe^{2+}. As expected, in the presence of a large excess of Fe^{2+} the disappearance of $CrCH_2OH^{2+}$ followed first-order kinetics cleanly according to the rate law of eq 8. The rate constants k_o were independent of the concentration of Fe^{2+} (1.0 - 100 mM), and yielded $k_o = 5.0 \pm 0.3$ L mol^{-1} s^{-1} in 0.10 M $HClO_4$, Figure I-5.

$$-d \ln[CrCH_2OH^{2+}]/dt = k_o = k_a + k_{O_2} [O_2] \qquad (8)$$

The reaction of $CrCH_2OH^{2+}$ with CrO_2^{2+} in the absence of O_2 is strikingly different from the reaction in oxygenated solutions. First, the removal of O_2 converts the catalytic system of eq 2 into a non-catalytic one. The stoichiometry of eq 9 was determined by

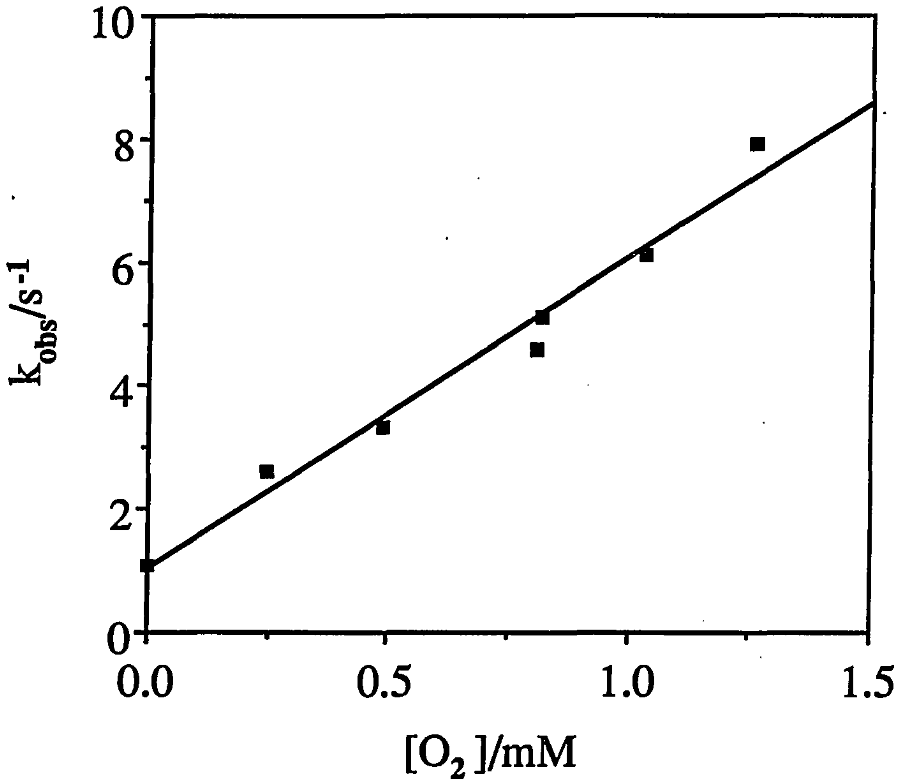

Figure I-5. Dependence of the pseudo-first-order rate constant for the reaction between $CrCH_2OH^{2+}$ and O_2 on the concentration of O_2. Experimental conditions: 0.055 mM $CrCH_2OH^{2+}$, 0.10 M $HClO_4$, 70 mM CH_3OH, 1 mM Fe^{2+}, 25.0 °C.

$$CrCH_2OH^{2+} + 2\,CrO_2^{2+} \rightarrow CH_2O + Cr(III)\ products \qquad (9)$$

spectrophotometric titration using CrO_2^{2+} as the titrant, as well as by formaldehyde analysis. Both types of experiments were conducted at low concentrations of CH_3OH (0 - 0.01 M). In the presence of ≥ 0.1 M CH_3OH, the stoichiometric ratio $\Delta[CrO_2^{2+}]/\Delta[CrCH_2OH^{2+}]$ was 4.0, and the yield of CH_2O was 3 moles per mole of $CrCH_2OH^{2+}$. Thus the reaction induces the oxidation of CH_3OH, eq 10.

$$CrCH_2OH^{2+} + 4\,CrO_2^{2+} + 2\,CH_3OH \rightarrow 3\,CH_2O + Cr(III)\ products \qquad (10)$$

The second effect is kinetic. Reaction 9 is much faster ($t_{1/2}$ = 1 - 2 s) in the absence of O_2 under conditions where $t_{1/2}$ = 25 - 30 s in its presence. The best way to illustrate the effect of the removal of O_2 is to conduct the catalytic reaction in the presence of a limiting amount of O_2. The kinetic trace, Figure I-1, starts out smoothly as expected for the reaction of eq 2. As soon as O_2 is depleted the absorbance drops abruptly, signalling that all the CrO_2^{2+} and an equivalent amount of $CrCH_2OH^{2+}$ have been consumed suddenly in reactions 9 or 10.

When the air-free reaction between CrO_2^{2+} and $CrCH_2OH^{2+}$ was conducted in the presence of 0.04 M $(NH_3)_5CoF^{2+}$, a good scavenger for Cr^{2+}, the disappearance of CrO_2^{2+} at 290 nm took place with a rate constant of 122 L mol^{-1} s^{-1}, a value close to that obtained in the catalytic system in the presence of O_2. Approximately 2 mM $Co(NH_3)_5F^{2+}$ is required to compete effectively with 0.15 mM CrO_2^{2+} for Cr^{2+}. Based on the known rate constant for the reaction between $Co(NH_3)_5F^{2+}$ and Cr^{2+}, $k = (9 \pm 1) \times 10^5$ L mol^{-1} s^{-1},[14] the rate constant for the reaction of CrO_2^{2+} with Cr^{2+} is estimated to be 2×10^7 L mol^{-1} s^{-1}.

DISCUSSION

Mechanistic Considerations

CrO_2^{2+} is quite an effective catalyst for the oxidation of $CrCH_2OH^{2+}$ by O_2. At 0.10 M ionic strength the rate constants for the catalyzed and uncatalyzed reactions are $k_2 = 137$ L mol^{-1} s^{-1} and $k_o = 5.0$ L mol^{-1} s^{-1}.

A straightforward mechanism for the catalyzed reaction that accommodates all the experimental observations is shown in eq 11 and 1.

$$CrCH_2OH^{2+} + CrO_2^{2+} \xrightarrow{k_2} Cr^{2+} + CH_2O + CrO_2H^{2+} \qquad (11)$$

The one-electron oxidation of $CrCH_2OH^{2+}$ by CrO_2^{2+} produces Cr^{2+} and CrO_2H^{2+}. The Cr^{2+} then reacts rapidly with O_2 ($k_1 = 1.6 \times 10^8$ L mol^{-1} s^{-1})[7] to regenerate the catalyst CrO_2^{2+}. It is quite reasonable that the reaction of eq 11 should produce Cr in the oxidation state 2+, given that reactions of $CrCH_2OH^{2+}$ with other oxidants, such as Cu^{2+},[8b] Fe^{3+},[8b] and VO_2^{+} [15] also yield Cr^{2+} as the initial product. Also, the quantitative formation of CH_2O and CrO_2H^{2+} confirms the overall stoichiometry of eq 11.

The exact mechanism of reaction 11 is more difficult to ascertain. Two possibilities seem particularly appealing. The first is an outer-sphere reaction, eq 12, which would yield CrO_2^{+} and $CrCH_2OH^{3+}$. In the rapid subsequent steps, eq 13 and 14, the reaction of CrO_2^{+} with H^{+} yields CrO_2H^{2+}, and $CrCH_2OH^{3+}$ undergoes a rapid intramolecular electron transfer producing Cr^{2+}, CH_2O and H^{+}.

$$CrO_2^{2+} + CrCH_2OH^{2+} \rightarrow CrO_2^{+} + CrCH_2OH^{2+} \quad (12)$$

$$CrO_2^{+} + H^{+} \rightleftharpoons CrO_2H^{2+} \quad (13)$$

$$CrCH_2OH^{2+} \rightarrow Cr^{2+} + CH_2O + H^{+} \quad (14)$$

The reduction potentials and self-exchange rate constants for the two reactants in eq 12 are not known, which rules out a possibility of estimating the expected rate constant for the process. However, both outer-sphere reduction of CrO_2^{2+} and outer-sphere oxidation of $CrCH_2OCH_3^{2+}$, the O-methylated analogue of $CrCH_2OH^{2+}$, have been demonstrated before. This, at least in principle, makes reaction 12 feasible. For example, outer-sphere reductants $Co(sep)^{2+}$, V^{2+}, and $Ru(NH_3)_6^{2+}$ reduce CrO_2^{2+} with rate constants in the range 10^5 - 10^6 L mol^{-1} s^{-1}.[5c] Similarly, $Ru(bpy)_3^{3+}$ ($E^o_{3+/2+} = 1.26$ V)[16] oxidizes $CrCH_2OCH_3^{2+}$ to $CrCH_2OCH_3^{3+}$ with a rate constant $k = 1.0 \times 10^7$ L mol^{-1} s^{-1}.[17] Subsequent rapid decomposition of $CrCH_2OCH_3^{3+}$ takes place in a reaction analogous to eq 14 to yield Cr^{2+}, CH_2O and CH_3OH.[17] The reduction potential of the $CrO_2^{2+/+}$ couple[18] is probably much lower than that of $Ru(bpy)_3^{3+/2+}$, and the lower reactivity of the former towards $CrCH_2OH^{2+}$ was to be expected.

Another feasible mechanism for reaction 2 is depicted below. The attack of CrO_2^{2+} at the alcoholic OH group of $CrCH_2OH^{2+}$ results in hydrogen transfer that yields CrO_2H^{2+}. The other products, CH_2O and Cr^{2+}, can be formed either concertedly, eq 15, or by a rapid subsequent decomposition of the transient $CrCH_2O^{2+}$.

$$CrCH_2OH^{2+} + CrO_2^{2+} \rightarrow [\,CrCH_2O \text{---} H \text{---} OOCr\,]^{4+}$$
$$\rightarrow Cr^{2+} + CH_2O + HO_2Cr^{2+} \quad (15)$$

The mechanism of eq 15 derives some support from the fact that replacement of $CrCH_2OH^{2+}$ in eq 2 by the O-methylated analogue, $CrCH_2OCH_3^{2+}$, results in a slow, kinetically ill-behaved reaction. The presence of the alcoholic OH group thus seems to be crucial mechanistically. If the outer-sphere mechanism of eq 12 were to hold, one would expect the two organochromium complexes to behave similarly, since both their reduction potentials and self-exchange rate constants should be comparable.

A hydrogen atom transfer mechanism involving the O-D bond is also consistent with a kinetic isotope effect $k_H/k_D > 1$ for $CrCD_2OD^{2+}$. The observed effect is, however, a composite of the solvent effect, arising from deuteration of H_2O coordinated to both reactants, and the possible genuine effect arising from hydrogen transfer. The value $k_H/k_D = 1.8$ is not sufficiently large to draw unequivocal mechanistic conclusions.

The rate constant for the direct autoxidation of $CrCH_2OH^{2+}$, $k_{O_2} = 5.0\ L\ mol^{-1}\ s^{-1}$, was determined in the presence of Fe^{2+} to scavenge any CrO_2^{2+} produced and thus eliminate a possible contribution from the catalytic pathway of eq 2. However, the rate constants obtained in the presence and absence of Fe^{2+} were comparable and only a hint of autocatalysis was obtained under the latter conditions. The yield of CrO_2^{2+} was < 25% of total chromium. All of these results indicate that the reaction proceeds by at least two pathways, only one of which produces Cr^{2+} that appears as CrO_2^{2+} in oxygen-containing solutions. This reaction might be an outer-sphere process, eq 16, yielding Cr^{2+}, CH_2O and $O_2^{\cdot}$. The latter would be converted rapidly to HO_2 which may either disproportionate[19] to O_2 and H_2O_2 or oxidize a second molecule of $CrCH_2OH^{2+}$.

$$CrCH_2OH^{2+} + O_2 \rightarrow Cr^{2+} + CH_2O + HO_2\cdot \qquad (16)$$

Most of the major chromium product, CrO_2H^{2+}, thus had to be formed by a route different from the CrO_2^{2+}-catalyzed route of eq 2. An interesting possibility is a direct attack by O_2 at the substitutionally labile[20] position trans to the CH_2OH group of the organochromium complex, eq 17, followed by the rapid protonation of CrO_2^+. Attack at the CH_2OH group that would yield HO_2 directly appears much less likely, since this would be an extremely unusual hydrogen atom abstraction by molecular oxygen.

$$O_2 + CrCH_2OH^{2+} \rightarrow [O_2CH_2OH^{2+}] \rightarrow O_2Cr^+ + CH_2O + H^+ \qquad (17)$$

It has been proposed before[5] that one-electron reduction of CrO_2^{2+} yields CrO_2H^{2+}. However, no direct evidence for this novel species has been obtained prior to this work. The full recovery of the CrO_2^{2+} spectrum upon oxidation of CrO_2H^{2+} with one equivalent of Ce(IV) leaves little doubt about the identity of this species.[21] The spectral features, Figure I-4, are as expected for an inorganic, weakly absorbing chromium(III) complex, and the molecule is probably best described as a hydroperoxochromium(III) species. The only uncertainty associated with this species seems to be the level of protonation in the acidity range studied, 0.10 - 1.0 M H^+. If one assumes that coordination to Cr^{3+} affects the acidity of H_2O_2 to the same extent that it does the acidity of H_2O (the pK_a of $Cr(H_2O)_6^{3+}$ is 4) and taking into account that the pK_a's of free H_2O (14) and H_2O_2 (11.9) differ by only two units, one might reasonably expect that both CrO_2H^{2+} and $Cr(H_2O_2)^{3+}$ coexist in acidic solutions. Such an expectation is corroborated by the fact that the acidity constants of $Fe(H_2O)_6^{3+}$, $pK_a = 3$, and $(H_2O)_5Fe(H_2O_2)^{3+}$, $pK_a = 1.2$ [22] differ by less than two pK units. Therefore the pK_a of $Cr(H_2O_2)^{3+}$ is probably in the range 1 - 3. However, for the sake of simplicity, the formula CrO_2H^{2+} is used to represent both forms of the hydroperoxo complex.

CrO_2H^{2+} is only the second example of an end-bonded hydroperoxometal complex that is long-lived in aqueous solution. The chemistry of the other one, $([14]aneN_4)CoO_2H^{2+}$,[3b,23] has been explored only marginally.

The effect of alcohols on the yields and lifetime of CrO_2^{2+}

The increased yields of CrO_2^{2+} in the reaction between Cr^{2+} and excess O_2 in the presence of even small amounts of an alcohol ([ROH] < 0.1 M) demonstrate that at least one reaction intermediate reacts with alcohols. Additional CrO_2^{2+} was formed even when the alcohol was added within a few seconds after the mixing of Cr^{2+} with excess O_2.

The reaction of Cr^{2+} with O_2 is known[5,7,24-27] to be a multistep process that involves several intermediates. Only the first one in the sequence, CrO_2^{2+}, has been identified directly in the autoxidation of Cr^{2+}.[7] Other proposed intermediates are CrO_2Cr^{4+}, $CrOCr^{4+}$, and CrO^{2+}. The first one has been prepared independently,[28] but has not been observed directly in the autoxidation process. The species proposed to be the $CrOCr^{4+}$ ion was in fact mischaracterized (see Chapter II). The last intermediate, CrO^{2+}, was proposed[5] to be an extremely short-lived transient that is rapidly reduced by Cr^{2+} to dimeric Cr(III). The same species is believed to be an intermediate in the reductions of Cr(VI) by a variety of organic reductants, including alcohols.[30] Neither CrO_2^{2+} nor CrO_2Cr^{4+} reacts with alcohols. Also, $HCrO_4^-$, which might be present in small concentrations,[5] is unreactive on these time scales.[30]

The reaction of Cr^{2+} with O_2 leads to formation of the surprisingly long-lived aquachromium(IV) ion, CrO^{2+} ($t_{1/2} \sim 45$ s at 25 °C, Chapter III).[31] The CrO^{2+} reacts with CH_3OH and other alcohols in a two-electron process which yields Cr^{2+} as the immediate product. In the presence of excess O_2, the Cr^{2+} is trapped and becomes CrO_2^{2+}. The effect of CH_3OH is therefore to convert CrO^{2+} into CrO_2^{2+}, Scheme I-1. A possible source of CrO^{2+} is the reaction of CrO_2^{2+} with Cr^{2+}, a reaction which has been proposed to be extremely fast.[5]

Scheme I-1. Mechanism of CrO_2^{2+} stabilization via CH_3OH trapping of CrO^{2+}

$$CrO_2^{2+} + Cr^{2+} \rightarrow n\ CrO^{2+} + \text{other Cr products} \qquad (18)$$

$$CrO^{2+} + CH_3OH \rightarrow Cr^{2+} + CH_2O + H_2O \qquad (19)$$

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \qquad (1)$$

The decomposition of CrO_2^{2+} was shown to involve rate-determining homolysis of the Cr-O bond to produce Cr^{2+} and O_2.[5] The Cr^{2+} either recombines with O_2 or reacts with CrO_2^{2+}; the latter process contributes to the net loss of CrO_2^{2+}. If the product of this reaction is CrO^{2+}, as proposed above, then CH_3OH will convert CrO^{2+} to Cr^{2+}, which again makes a choice between CrO_2^{2+} and O_2. Since the reaction with O_2 regenerates CrO_2^{2+}, the lifetime of CrO_2^{2+} increases in the presence of CH_3OH and O_2. The corollary is also observed: in the absence of O_2, the CH_3OH contributes to a decreased lifetime for CrO_2^{2+} by recycling CrO^{2+} into Cr^{2+}, which destroys additional CrO_2^{2+}.

At this stage of development[13] eq 18 implies only that the reaction of CrO_2^{2+} with Cr^{2+} yields some CrO^{2+}. The stoichiometry and the mechanism of the reaction have not been established,[13] although it is almost certain that this is not a simple outer-sphere electron transfer.

The anaerobic chain reaction

The reaction of $CrCH_2OH^{2+}$ with CrO_2^{2+} in the absence of O_2 is much faster than the first step in the catalytic autoxidation, eq 11. Thus a different catalytic reaction, or a chain reaction, sets in under air-free conditions. The scavenging effect of $(NH_3)_5CoF^{2+}$, which brings the rate constant down to that for reaction 11, strongly implicates Cr^{2+} as a crucial intermediate. The effect of CH_3OH on the overall stoichiometry requires at least one additional intermediate, which we believe to be CrO^{2+}. One plausible scheme in the absence of CH_3OH, Scheme I-2, consists of reaction 11 to form Cr^{2+}, reduction of CrO_2^{2+} to CrO^{2+}, eq 18, and oxidation of $CrCH_2OH^{2+}$, eq 21.

Scheme I-2. Mechanism of the airfree chain reaction between CrO_2^{2+} and $CrCH_2OH^{2+}$

chain initiation $\quad CrO_2^{2+} + CrCH_2OH^{2+} \rightarrow Cr^{2+} + CH_2O + CrO_2H^{2+} \qquad (11)$

chain propagation $\quad CrO_2^{2+} + Cr^{2+} \rightarrow n\,CrO^{2+} \qquad (18)$

$CrO^{2+} + CrCH_2OH^{2+} + H^+ \rightarrow Cr^{2+} + Cr^{3+} + CH_2O + H_2O \qquad (21)$

Although there is very little information about reaction 21, it is expected to yield Cr^{2+} irrespective of whether the reaction takes place by a one- or two-electron pathway.

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SECTION II

PREPARATION AND REACTIVITY OF THE AQUACHROMIUM(IV) ION. OXIDATION OF ALCOHOLS, ALDEHYDES AND CARBOXYLATES BY HYDRIDE TRANSFER

ABSTRACT

Four methods have been developed to prepare aquachromium(IV), which we believe to be an oxo ion, CrO^{2+}. It readily converts Ph_3P to Ph_3PO ($k = 2.1 \times 10^3$ L mol^{-1} s^{-1}) at 25°C in 85% CH_3CN/H_2O (0.10 M $HClO_4$). The reactions used to form CrO^{2+} are those between Cr^{2+} and (a) O_2, (b) anaerobic CrO_2^{2+}, (c) anaerobic $CrOOCr^{4+}$, and (d) anaerobic Tl(III). The CrO^{2+} has a half-life of 30 seconds in acidic solution at room temperature, and will oxidize alcohols, aldehydes and certain carboxylates as well as diethyl ether. The second-order rate constants (L mol^{-1} s^{-1}) in acidic solution ($\mu = 1.0$ M $HClO_4/LiClO_4$, 25 °C) are: CH_3OH, 52; CD_3OH, 15; C_2H_5OH, 88; C_2D_5OH, 41; $(CH_3)_2CHOH$, 12.0; $(CD_3)_2CDOH$, 4.6 ; $CH_2{=}CHCH_2OH$, 101 ; $CH_3(CH_2)_2CH_2OH$, 44; $(C_2H_5)(CH_3)CHOH$, 41; $(CH_3)_3CCH_2OH$, 39; $C_6H_5CH_2OH$, 56; $(C_6H_5)(CH_3)CHOH$, 30; $(C_6H_5)_2CHOH$, 10.5; p-$CH_3OC_6H_5CH_2OH$, 71; p-$CH_3C_6H_5CH_2OH$, 66; p-$CF_3C_6H_5CH_2OH$, 60; c-C_4H_7OH, 44; c-C_5H_9OH, 31; $HCHO{\cdot}H_2O$, 92; $(CH_3)_3CHO$, 37 ; HCO_2H, 11.6 ; HCO_2^-, 6.9×10^3; $HC_2O_4^-$, 2.2×10^3; $(C_2H_5)_2O$, 4.5. Activation parameters were also determined for selected reactions. In all but two of these reactions (cyclobutanol and pivaldehyde), Cr^{2+} is the immediate product as shown by trapping with O_2. Based on the kinetic and product analysis, the mechanism of oxidation by CrO^{2+} is proposed to be hydride transfer. The reactivity order for alcohols (1° > CH_3 > 2°), the small substituent effect for the benzyl alcohols and the similarity of all the rate constants regardless of the organic substrate are inconsistent with the formation of carbon-centered radicals. The reaction of $HCrO_4^-$ with $(CH_3)_2CHOH$ is also shown to involve CrO^{2+} and Cr^{2+} as intermediates. The latter reacts with $HCrO_4^-$ with a rate constant of 2×10^9 L mol^{-1} s^{-1} in 2.0 M $HClO_4$.

INTRODUCTION

The intermediate IV and V oxidation states of chromium proved elusive to coordination chemists for many years. Recently, complexes of Cr(V) with Schiff base[1] and carboxylate ligands[2] have been isolated in which the V oxidation state is stable enough to permit spectroscopic and even crystallographic characterization. The IV oxidation state is known as a diperoxo species[3] and with the tetraphenylporphyrin ligand[4]. Recently, electrochemical and kinetic evidence[5] for a Cr(IV) intermediate was obtained in the reduction of bis(2-ethyl-2-hydroxybutyrato)oxochromate(V). Without such ligand stabilization, i.e., as an aqua complex, Cr(IV) has generally been considered unstable and highly reactive, and therefore impossible to isolate.[6] Evidence to the contrary is presented in this chapter.

It has long been recognized that the one- and two-electron oxidations of various metal ions[7] and organic substrates[8] by H_2CrO_4 must proceed through hydrated Cr(IV) and (V) species. Evidence has been presented[9] for the intermediacy of Cr(V) in the oxidation of alcohols and carboxylates by H_2CrO_4, where the esr signal of a tetragonally-distorted d^1 species can be attributed to Cr(V). This Cr(V) species almost certainly contains coordinated alcoholate or carboxylate ligands. Hydrated Cr(IV) has not been observed directly, even though it has been invoked in many mechanisms[10] as a transient which reacts rapidly with other species in the reaction mixture. Also, the reaction of $Cr(H_2O)_6^{3+}$ with strong oxidants[11] involves these same intermediates.

In this work, the preparation of aqueous Cr(IV) in the absence of stabilizing ligands is described. This species was discovered during an investigation of the catalytic reactions of the superoxochromium(III) ion, CrO_2^{2+}.[12] (Throughout this work, coordinated water molecules are not shown.) Cr(IV) reacts with Ph_3P with a rate constant of $(2.1 \pm 0.2) \times 10^3\ M^{-1}s^{-1}$ in 85% CH_3CN/H_2O (0.10 M $HClO_4$) at 25 °C to give Ph_3PO and Cr^{2+}, which is trapped by O_2 to become CrO_2^{2+}. On this basis, and by analogy with the known $Cr^{IV}=O$ unit in porphyrin chemistry,[4] the $Cr(IV)_{(aq)}$ is assigned the formula CrO^{2+}. This Cr(IV) species is the same as the proposed intermediate in the reaction of H_2CrO_4 with alcohols, as demonstrated by O_2-trapping. The CrO^{2+} is stable enough (half-life 30 s in 1 M $HClO_4$) to use as a bulk reagent in mechanistic studies. The kinetics of the reactions of CrO^{2+} with various alcohols, aldehydes and carboxylates are described, and a hydride-transfer mechanism common to all these reactions is proposed. Although much of the literature on Cr(IV) reactions is based on the assumption that Cr(IV) is a one-electron oxidant,[13,14] we show that this is rarely the case. A two-electron path is not only thermodynamically viable, but unequivocally observed:

$$CrO^{2+} + RH_2 \rightarrow Cr^{2+} + R + H_2O \qquad (1)$$

EXPERIMENTAL SECTION

CrO^{2+} was usually prepared by syringe-injection of an air-free solution of Cr^{2+} (from Zn/Hg reduction of $Cr(H_2O)_6{}^{3+}$) into an acidic aqueous solution containing O_2. At very low Cr^{2+}:O_2 ratios, ca. 0.05:1, the adduct $CrO_2{}^{2+}$ is formed quantitatively.[15] The $CrO_2{}^{2+}$ was identified and quantified by its intense and characteristic uv spectrum: ε_{290nm}= 3100 $M^{-1}cm^{-1}$, ε_{245nm}= 7000 $M^{-1}cm^{-1}$.[16] At higher Cr^{2+}:O_2 ratios, for example 1:1, with efficient mixing in a stopped-flow jet, the CrO^{2+} is formed in ca. 30% yield (other products are nonoxidizing, low-absorbing Cr(III) species). At intermediate ratios, a mixture of CrO^{2+} and $CrO_2{}^{2+}$ is produced. The superoxo complex $CrO_2{}^{2+}$ is stable for at least half an hour at room temperature under O_2, and on this time scale does not react with any of the organic substrates studied here. In experiments where the product of the CrO^{2+} reaction is Cr^{2+}, it was necessary to work in the intermediate concentration regime (0.15 Cr^{2+}/O_2). Under these conditions, the Cr^{2+} product is trapped efficiently by oxygen, thus avoiding the autocatalytic consumption of $CrO_2{}^{2+}$ by Cr^{2+}, eq 1 and 2:[12]

$$CrO_2{}^{2+} + 2\,Cr^{2+} + 2\,H^+ \rightarrow CrO^{2+} + Cr(OH)_2Cr^{4+} \qquad (2)$$

In much of this work, CrO^{2+} was prepared by injection of Cr^{2+} into O_2-saturated aqueous $HClO_4$ (0.02 - 1.0 M), as described above. In some cases it was prepared by mixing of Cr^{2+} and O_2 solutions in the stopped-flow apparatus, with one of the solutions containing the desired organic substrate. CrO^{2+} is also made by three other reactions, eq 2-4, all anaerobic.[17]

$$CrOOCr^{4+} + Cr^{2+} + H_2O \rightarrow CrO^{2+} + Cr(OH)_2Cr^{4+} \qquad (3)$$

$$TlOH^{2+} + Cr^{2+} \rightarrow Tl^+ + CrO^{2+} + H^+ \qquad (4)$$

Enough experiments were done with these other sources of CrO^{2+} that we are confident the same oxochromium ion results from each, by virtue of identical reaction kinetics.

The ultraviolet spectrum of CrO^{2+} was obtained by mixing 0.26 mM O_2 and 0.3 mM Cr^{2+} in a Durrum stopped-flow apparatus equipped with a rapid-scan lamp. Extinction coefficients were obtained by adding $ABTS^{2-}$ (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonate))[18] and measuring the amount of the intensely-colored radical anion $ABTS^{-\cdot}$ formed (λ 417 nm, $\varepsilon = 3.47 \times 10^4\ M^{-1}cm^{-1}$; λ 645 nm, $\varepsilon = 1.35 \times 10^4\ M^{-1}cm^{-1}$).

Reactions of CrO^{2+} were monitored in three ways. Occasionally, the weak absorption of CrO^{2+} (λ 260 nm, $\varepsilon = (5 \pm 1) \times 10^3\ M^{-1}\ cm^{-1}$) itself was used. Some reactions were conducted by adding $ABTS^{2-}$ simultaneously with the substrate. The formation of $ABTS^{-\cdot}$ concurrent with substrate oxidation provided a convenient kinetic probe. Many reactions were conducted in O_2-saturated solutions. In these cases, the product Cr^{2+} is rapidly converted to CrO_2^{2+}, and the rate of CrO^{2+} consumption is equal to the rate of CrO_2^{2+} production. Rate constants from the three methods agreed.

In a typical experiment, 0.2 mM Cr^{2+} was injected into O_2-saturated acidic solution (pH maintained by $HClO_4$, ionic strength by $LiClO_4$) containing at least a ten-fold excess of the appropriate organic substrate. Results were identical when the organic substrate was added after the Cr^{2+}, or when the two solutions were mixed in a Durrum stopped-flow spectrophotometer. The absorbance changes due to buildup of CrO_2^{2+} as CrO^{2+} reacted with the substrate were monitored either at the 290 or 245 nm maximum of CrO_2^{2+}. Temperature was controlled at 25.0 ± 0.2°C by means of a thermostated cell-holder connected to a circulating water bath. All data were fit to a pseudo-first-order equation, since the rate of CrO_2^{2+} formation from the rapid[16] reaction between Cr^{2+} and O_2 is governed by the rate of reaction 1. Thus $d[CrO_2^{2+}]/dt = k_1[CrO^{2+}][RH_2]$, and with $[RH_2]_0 >> [CrO^{2+}]_0$, first-order kinetics are obeyed.

In contrast, the kinetic data in the presence of $ABTS^{2-}$ fit a biexponential rate law, since $ABTS^{2-}$ reacts with both CrO_2^{2+} and CrO^{2+}. The CrO_2^{2+} is inevitably formed in experiments with all but the highest Cr^{2+}:O_2 ratios. That is, reactions 5 and 6 occur simultaneously, such that the buildup of $ABTS^{-\cdot}$ follows the rate law given in eq 7:

$$CrO^{2+} + ABTS^{2-} + H^+ \rightarrow CrOH^{2+} + ABTS^{-\cdot} \quad (5)$$

$$CrO_2^{2+} + ABTS^{2-} + H^+ \rightarrow CrO_2H^{2+} + ABTS^{-\cdot} \quad (6)$$

$$d[ABTS^{-\cdot}]/dt = k_5[ABTS^{2-}]\,[CrO^{2+}] + k_6\,[ABTS^{2-}][CrO_2^{2+}] \quad (7)$$

Data were analyzed to determine k_5 and k_6, and the k_6 value agrees with that evaluated independently by mixing $ABTS^{2-}$ with a pure sample of CrO_2^{2+}.

The dissolved O_2 concentration was calculated using the known solubility of oxygen in water at 25°C under O_2 and air atmospheres.[19] Thallium(III) sulfate, CrO_3, $NaHCO_2$, $NaHC_2O_4$, diammonium 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonate), and the various alcohols, aldehydes, and ethers were purchased from commercial sources and used as received. Solutions of HCHO were obtained by dissolving paraformaldehyde in warm 1 M $HClO_4$, and were standardized by chromotropic acid analysis.[20] $CrOOCr^{4+}$ was prepared by a literature method[21] and was standardized spectrophotometrically (ε_{634nm}= 404 $M^{-1}cm^{-1}$). Organic products were determined on an HP 5730A gas chromatograph equipped with a VZ-10 column.

Unless stated otherwise, the kinetic data were determined at 25.0 °C and 1.0 M ionic strength ($HClO_4$ + $LiClO_4$).

RESULTS

Formation of CrO^{2+}

The reaction of Cr^{2+} with O_2 produces $CrO_2{}^{2+}$ quantitatively only in the presence of a large (≥20-fold) excess of O_2. When O_2 is not in large excess, another short-lived oxidizing Cr species is formed which decays to nonoxidizing Cr products. This short-lived species is identified (see Discussion) as oxochromium(IV) or CrO^{2+}. The reactions cited in eq 2 - 4 also yield CrO^{2+}.

That the same species was produced in all three reactions was shown by conducting any one of the several reactions described subsequently with CrO^{2+} from an alternate source. This species is a fairly strong oxidant, as shown in subsequent work.

Spectrum of CrO^{2+}

Stopped-flow mixing of 0.3 mM $Cr^{2+}{}_{(aq)}$ and 0.26 mM O_2 produces ~ 0.045 mM CrO^{2+}. The difference spectrum, shown in Figure II-1 relative to the absorbance after CrO^{2+} has decomposed, has a peak at 260 nm ($\varepsilon = (5 \pm 1) \times 10^3$ L mol^{-1} cm^{-1}) and a well-defined shoulder at 300 nm.

Reaction of CH_3OH with CrO^{2+}

The immediate addition of millimolar quantities of CH_3OH to O_2-saturated solutions containing 0.1 mM of CrO^{2+} causes the spectrum of $CrO_2{}^{2+}$ to intensify, Figure II-2. The rate of formation of $CrO_2{}^{2+}$ follows first-order kinetics, and the pseudo-first-order rate constants vary linearly with the concentration of CH_3OH at a given ionic strength, as shown in Figure II-3. The plot has a nonzero intercept, 0.033 s^{-1} at μ= 1.0 M,

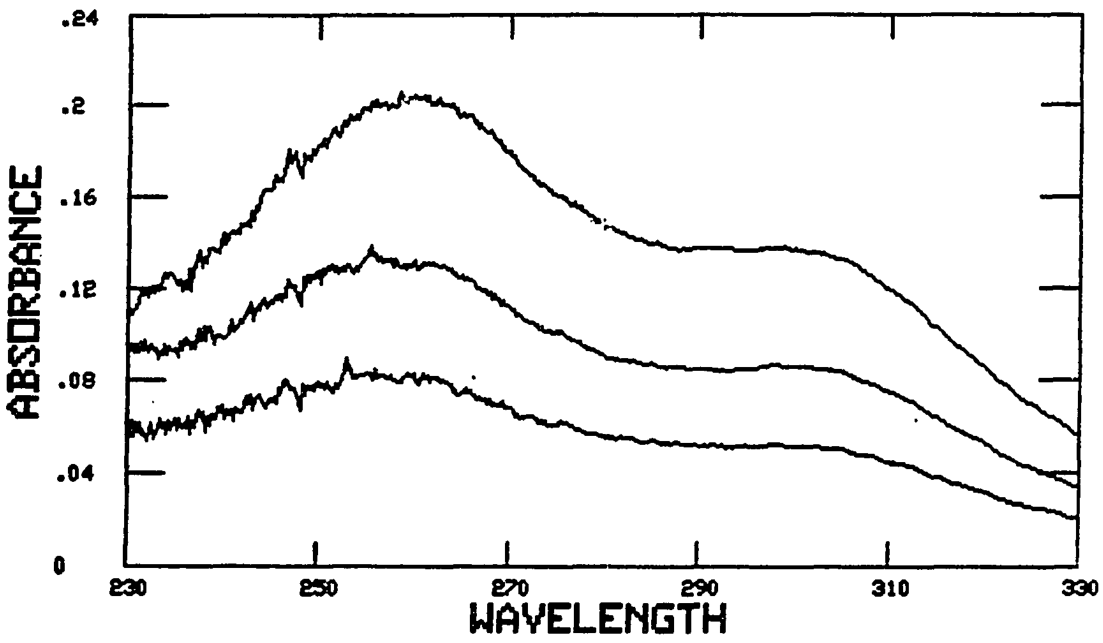


Figure II-1. Difference spectra of CrO^{2+} formed by stopped-flow mixing of 0.3 mM Cr^{2+} and 0.26 mM O_2 in 1.0 M $HClO_4$. Time interval between spectra is 20 s. Spectra were obtained by difference from the spectrum at 60 s. The yield of CrO^{2+} is 15 % based on total Cr. Optical pathlength 2cm.

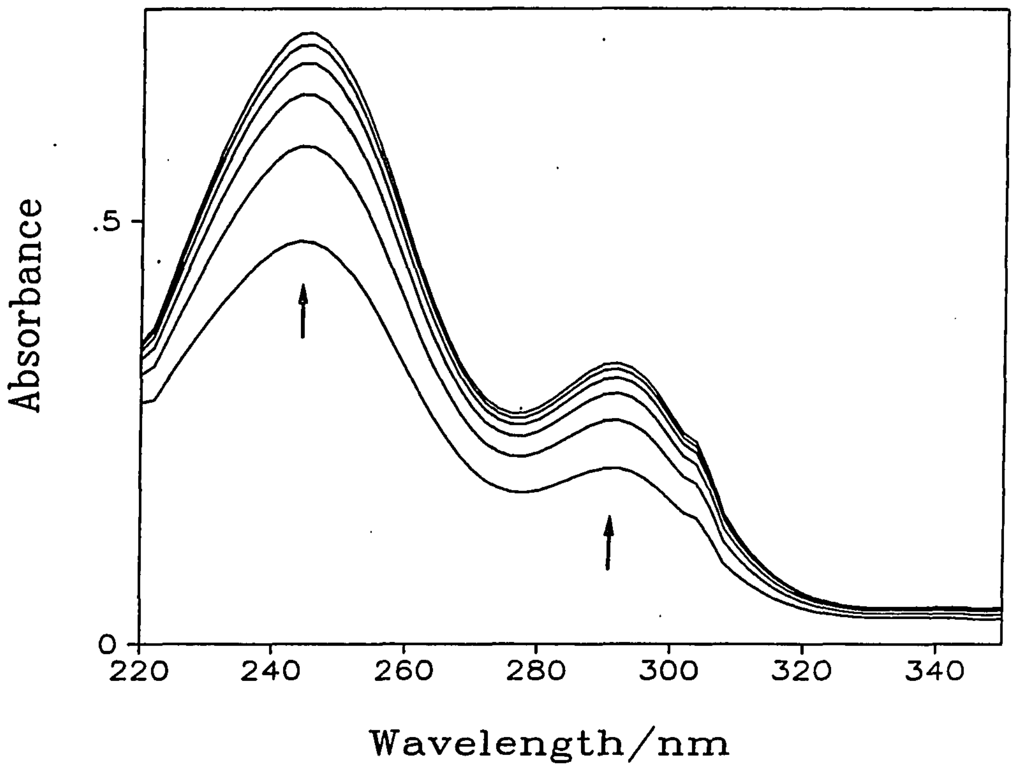


Figure II-2. Formation of CrO_2^{2+} (λ_{max} 290, 245 nm) from the reaction between 1 mM CH_3OH, 1.26 mM O_2 and 0.1 mM CrO^{2+}, in 0.10 M $HClO_4$. Spectra were recorded at 10 s intervals in a 1 cm cell.

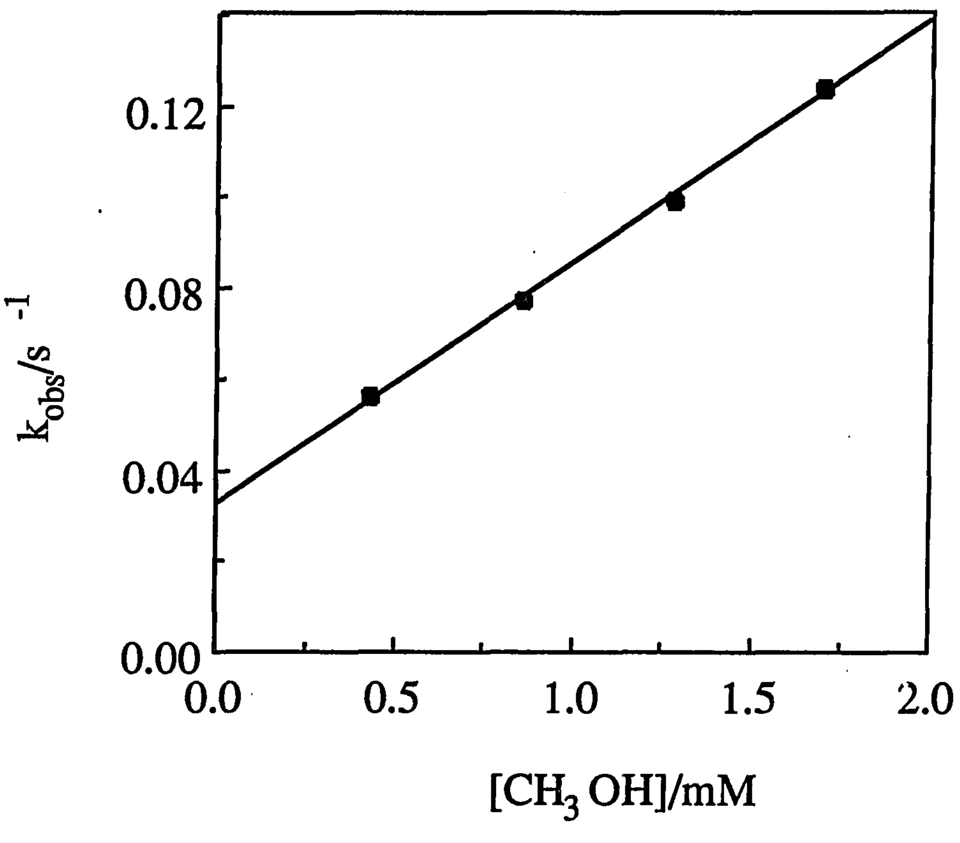


Figure II-3. Dependence of the pseudo-first-order rate constants for the oxidation of CH_3OH by CrO^{2+} on the concentration of CH_3OH. Conditions: 1.26 mM O_2, 0.10 M $HClO_4$, 0.90 M $LiClO_4$, 25.0 °C.

which appears repeatedly throughout this work and is not a characteristic of CH_3OH in particular. The slope of the plot gives $k_8 = 52.2 \pm 1.4$ L mol^{-1} s^{-1} as the rate constant for the reaction between CrO^{2+} and CH_3OH, eq 8, followed by eq 9:

$$CrO^{2+} + CH_3OH \rightarrow Cr^{2+} + HCHO + H_2O \qquad (8)$$

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \qquad (9)$$

The rate constant decreases to 15.1 ± 1.7 L mol^{-1} s^{-1} upon deuteration of the carbon-hydrogen bonds, eq 10, for an isotope effect $k_H/k_D = 3.46$.

$$CrO^{2+} + CD_3OH \rightarrow Cr^{2+} + DCDO + H_2O \qquad (10)$$

The rate constant for oxidation of CH_3OH is independent of $[O_2]$, provided O_2 is in excess, and of $[H^+]$ in the range 0.01 - 1.0 M, but decreases significantly with decreasing ionic strength. In H_2O at $\mu = 0.10$ M, the rate constant is $k_8 = 22.7 \pm 0.6$ L mol^{-1} s^{-1}. Rate constants were also determined for oxidation of CH_3OD in D_2O and CH_3OH in 6.3 M CH_3CN at 0.10 M ionic strength, with values of 23.8 ± 1.6 and 22.6 ± 1.6 L mol^{-1} s^{-1} respectively.

HCHO was identified as the organic product by chromotropic acid analysis. Quantitation was difficult under kinetic conditions in the presence of O_2, because the inorganic product CrO_2^{2+} eventually oxidizes CH_3OH during its decomposition (by homolysis[15] to form Cr^{2+} followed by reactions 2 and 8, which form a catalytic cycle). CrO^{2+} is the only intermediate in the decomposition reaction which oxidizes CH_3OH on these time scales. The yield of HCHO was determined by analyzing an aged solution of pure CrO_2^{2+} to which CH_3OH was added. The yield of HCHO was found to be 430 %

based on the initial concentration of CrO_2^{2+}, implying induced oxidation of CH_3OH by O_2, eq 11.

$$O_2 + 2\ CH_3OH \xrightarrow{CrO_2^{2+}} 2\ HCHO + 2\ H_2O \qquad (11)$$

Stopped-flow mixing of 0.3 mM Cr^{2+} with 1.2 mM O_2 in the presence of 0.06 - 0.6 M CH_3OH gives rise to first-order absorbance increases at 290 nm, identical to the traces obtained by syringe transfer of reagents. When the O_2 concentration was lowered to 0.26 mM, a biphasic trace appeared, Figure II-4. The formation of CrO_2^{2+} from the reaction of CrO^{2+} with CH_3OH begins as before, but O_2 is quickly consumed. The Cr^{2+} product then reacts with the CrO_2^{2+}, causing the absorbance to decrease autocatalytically.

The reaction of CrO^{2+} with CH_3OH can also be studied in the visible region at 417 or 610 nm in the presence of the kinetic probe $ABTS^{2-}$ and excess O_2. Both CrO^{2+} and CrO_2^{2+} are formed in the stopped-flow mixing of Cr^{2+} and O_2, with or without CH_3OH, and both species oxidize $ABTS^{2-}$ at an appreciable rate, as in eq 5 and 6. The biphasic formation of $ABTS^{-\cdot}$ in the absence of CH_3OH gave $k_5 = (7.9 \pm 0.6) \times 10^4$ L mol^{-1} s^{-1} and $k_6 = (1.36 \pm 0.11) \times 10^3$ L mol^{-1} s^{-1} at 25°C in 0.10 M H^+. The product of reaction 6, the hydroperoxo species CrO_2H^{2+}, has been prepared independently (see Chapter I)[12] and does not oxidize $ABTS^{2-}$ under these conditions.

When the reaction was conducted in the presence of CH_3OH, the rate constant for the faster phase of $ABTS^{-\cdot}$ formation increased, while the magnitude of the associated absorbance change decreased. The rate constant for the reaction of CrO^{2+} with CH_3OH was then obtained from the faster phase by use of the expression $-d[CrO^{2+}]/dt = (k_5 [ABTS^{2-}] + k_8 [CH_3OH]) [CrO^{2+}]$, yielding $k_8 = 22.4 \pm 2.9$ L mol^{-1} s^{-1} at 0.1 M H^+,

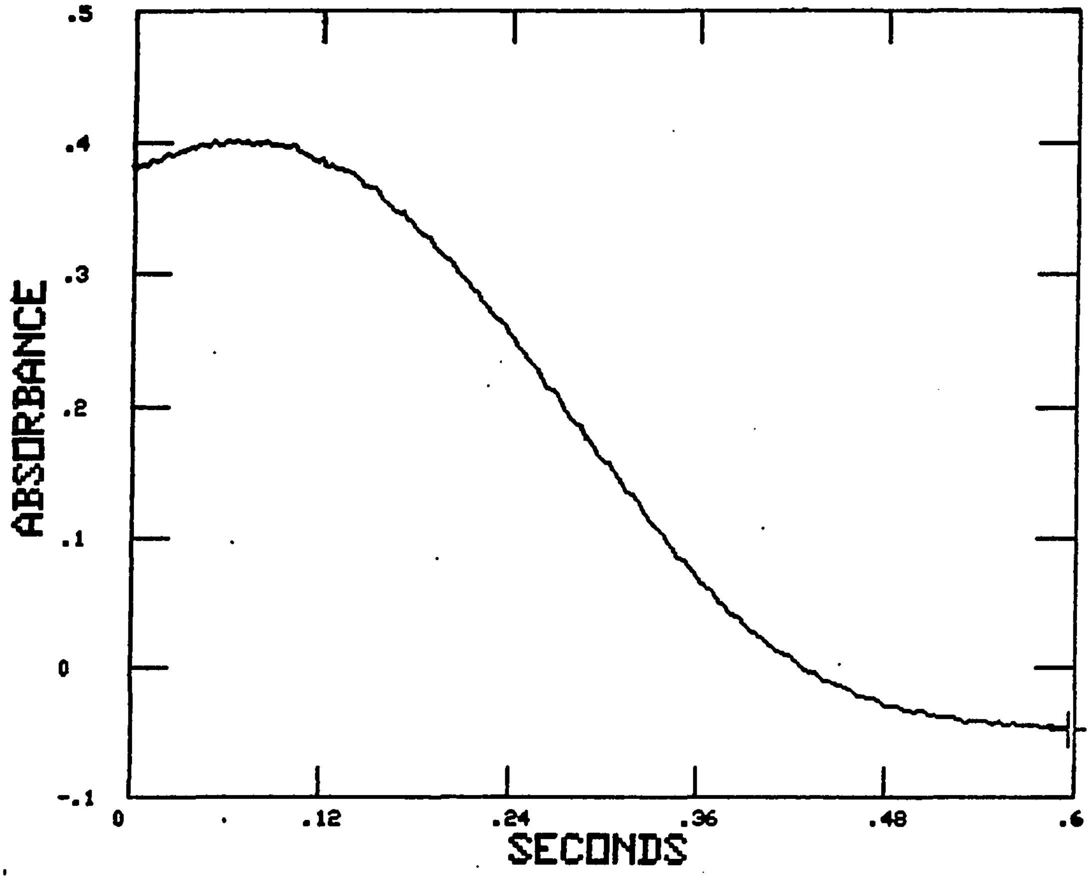


Figure II-4. Kinetic trace showing the reaction of CrO^{2+} with 0.19 M CH_3OH in the presence of an insufficient excess of O_2. The mixture of CrO^{2+} and CrO_2^{2+} was generated by stopped-flow mixing of 0.08 mM Cr^{2+} with 0.13 mM O_2. The Cr^{2+} product from the reaction of CrO^{2+} with CH_3OH consumes CrO_2^{2+} autocatalytically. $[HClO_4] = 0.10$ M; T = 25 °C; optical pathlength = 2 cm.

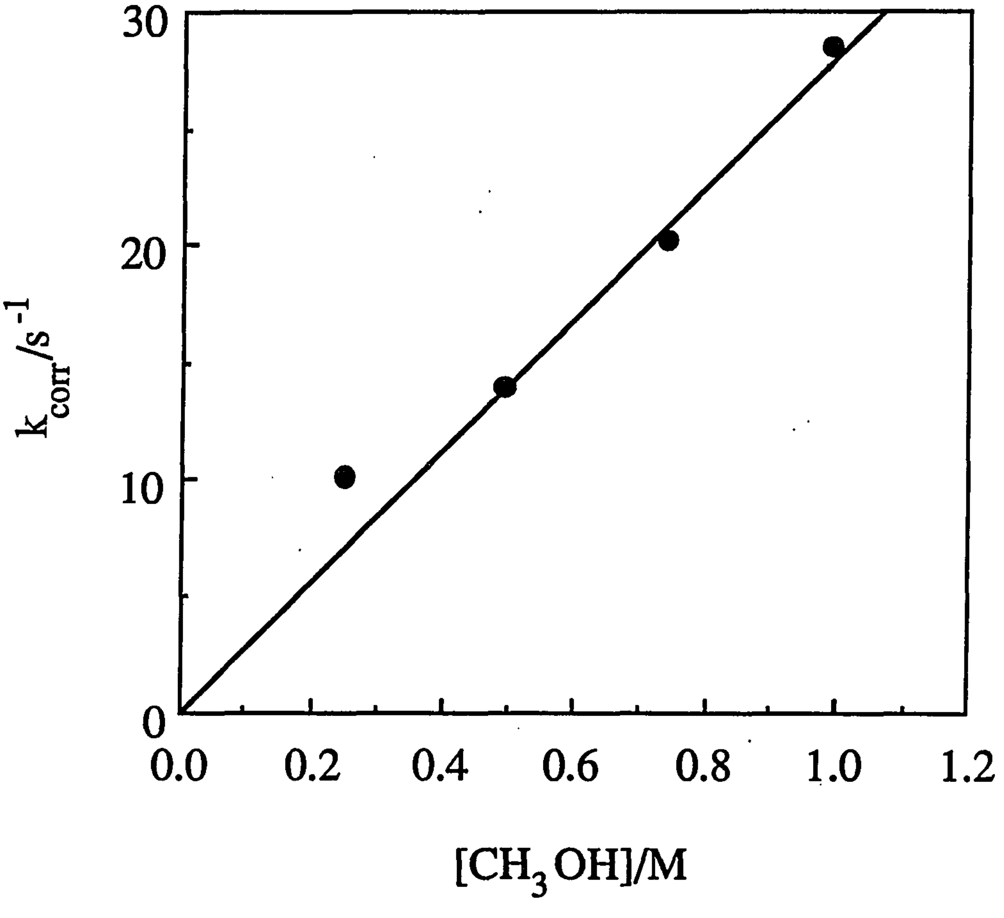


Figure II-5. Dependence of the corrected rate constant, $k_{corr} = k_{obs} - k_5[ABTS^{2-}]$ on the concentration of CH_3OH. $ABTS^{2-}$ is a kinetic probe for the reaction between CrO^{2+} and CH_3OH. $[HClO_4] = 0.10$ M, 25 °C. Slope = 28 L mol^{-1} s^{-1}.

Figure II-5. This compares well with the value 22.7 L mol^{-1} s^{-1} determined directly from the rate of CrO_2^{2+} formation.

Reactions of other alcohols

For every alcohol shown in Table II-1 except cyclobutanol, the reaction produced CrO_2^{2+} when conducted in the presence of O_2. The pseudo-first-order rate constants were derived in the same way as for CH_3OH by following the formation of CrO_2^{2+} in the presence of at least a ten-fold excess of the alcohol. The first-order rate constants were plotted against alcohol concentration. In each case, a significant nonzero intercept of 0.01 - 0.03 s^{-1} appears in these plots. Significant isotope effects were found for CH_3CH_2OH ($k_H/k_D = 2.13$) and $(CH_3)_2CHOH$ ($k_H/k_D = 2.61$) upon deuterium substitution in all the carbon-hydrogen bonds. The ionic strength dependence of the first-order rate constants is shown for $(CH_3)_2CHOH$ in Figure II-6. Activation parameters were determined for the reactions of CH_3OH, CD_3OH and $(CH_3)_2CHOH$ from the temperature dependence of the rate constants (listed in Table II-2 and shown for $(CH_3)_2CHOH$ in Figure II-7) and are listed in Table II-3.

The formation of CrO_2^{2+} is taken as evidence that Cr^{2+} is the immediate product of the reaction of CrO^{2+} with these alcohols. In the oxidation of neopentyl alcohol, the product solution was analyzed for HCHO, a product of the cleavage of the hydroxyneopentyl radical, eq 12. No HCHO was found.

$$(CH_3)_3C\dot{C}HOH \quad \rightarrow \quad (CH_3)_3C\cdot \quad + \quad HCHO \qquad (12)$$

The yield of the inorganic product CrO_2^{2+} does not depend on the ionic strength in the range 0.10 M - 1.0 M.

Table II-1. Bimolecular rate constants for the oxidation of alcohols by CrO^{2+} [a]

Alcohol	**k / L mol^{-1} s^{-1}**	**Alcohol**	**k / L mol^{-1} s^{-1}**
CH_3OH	52.2 ± 1.4	$C_6H_5CH_2OH$	56.0 ± 3.6
CD_3OH	15.1 ± 1.7	$C_6H_5CH(OH)CH_3$	29.6 ± 5.6
CH_3CH_2OH	88.4 ± 4.4	$(C_6H_5)_2CHOH$	10.5 ± 0.8
CD_3CD_2OH	41.5 ± 4.2	$(4\text{-}CH_3O)C_6H_5CH_2OH$	71.2 ± 3.6
$(CH_3)_2CHOH$	12.0 ± 0.4	$(4\text{-}CH_3)C_6H_5CH_2OH$	65.6 ± 3.8
$(CD_3)_2CDOH$	4.6 ± 0.2	$(4\text{-}CF_3)C_6H_5CH_2OH$	60.1 ± 1.7
$CH_2{=}CHCH_2OH$	100.7 ± 6.6	cyclobutanol	44.1 ± 1.2
$CH_3(CH_2)_2CH_2OH$	43.8 ± 3.9	cyclopentanol	30.6 ± 0.6
$CH_3CH_2CH(OH)CH_3$	41.4 ± 0.7	$(CH_3)_3CCH_2OH$	39.0 ± 3.3

[a] All rate constants were measured at 25 °C in O_2-saturated aqueous 0.10 M $HClO_4$/0.90 M $LiClO_4$ or 1.0 M $HClO_4$. In each case, CrO^{2+} was generated by the reaction of Cr^{2+} with O_2, and for all but cyclobutanol, the reaction of CrO^{2+} with ROH was monitored using the increase in absorbance at 290 nm due to CrO_2^{2+} formation. For cyclobutanol, the loss of absorbance at 270 nm due to CrO^{2+} was monitored.

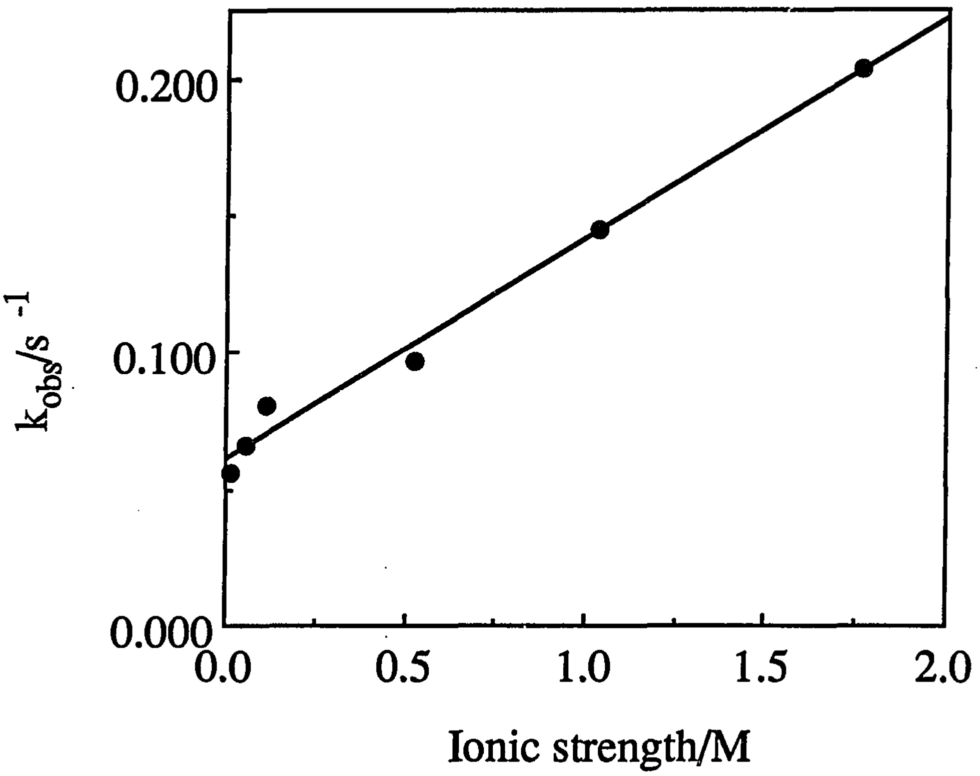


Figure II-6. Ionic strength dependence of the observed rate constant for the oxidation of 9 mM $(CH_3)_2CHOH$ by CrO^{2+} at 25 °C. Since there is no dependence of the rate constant on $[H^+]$, the ionic strength was varied either by varying $[HClO_4]$ or $[LiClO_4]$.

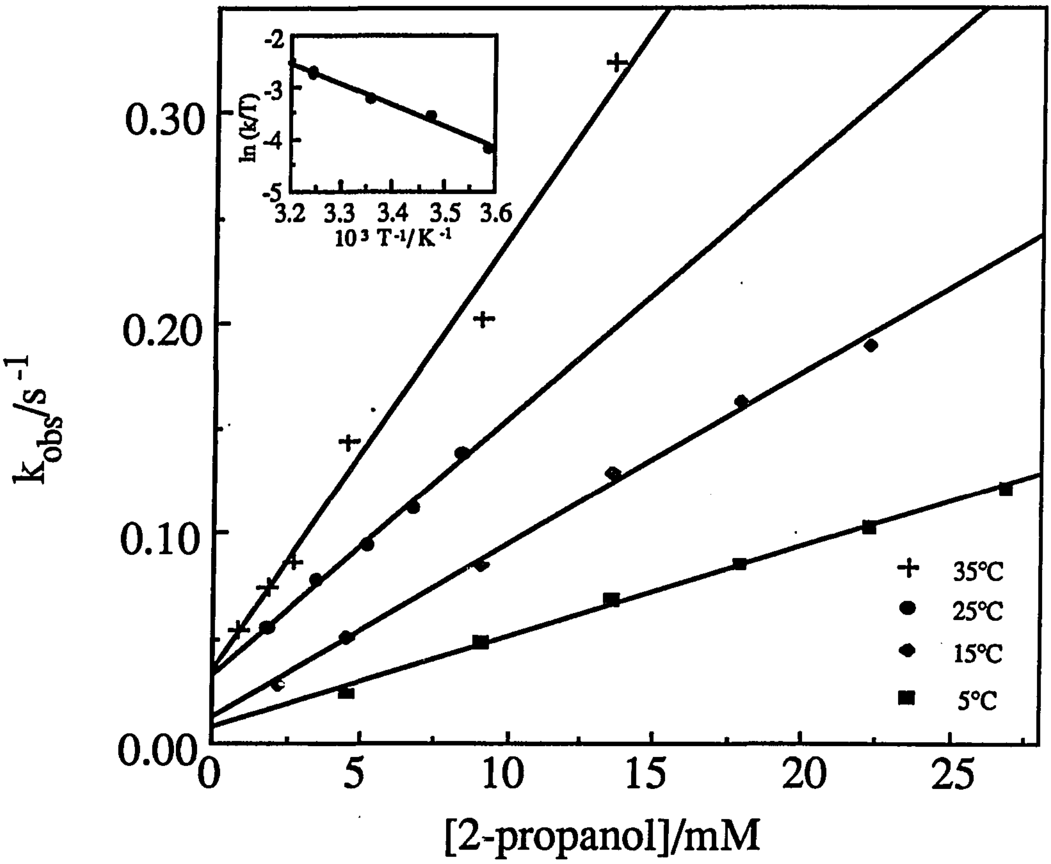


Figure II-7. Dependence of the bimolecular rate constant for the oxidation of $(CH_3)_2CHOH$ by CrO^{2+} on temperature. All measurements were made in a 1 cm spectrophotometer cell containing 0.10 M $HClO_4$/0.90 M $LiClO_4$ saturated with O_2. The inset shows a plot of ln(k/T) versus temperature, with slope $\Delta H^\ddagger/R = 4007\ K^{-1}$ and intercept $(\Delta S^\ddagger/R)+\ln(R/Nh) = 10.277$.

Table II-2. Rate constants for the oxidation of selected substrates by CrO^{2+} at various temperatures

Substrate	Rate Constant /L mol^{-1} s^{-1}			
	T = 5.3 °C	T = 14.7 °C	T = 25.0 °C	T = 35.2 °C
CH_3OH	18.7	31.6	53.2	
CD_3OH	3.7	6.5	15.9	19.0
HCHO	29.0	44.0	96.7	184
cyclobutanol		21.8	44.1	88.6

Reaction of cyclobutanol

This reaction is unlike the reactions with all the other alcohols studied here in that it does not give rise to CrO_2^{2+} in the presence of excess O_2. Also, the reaction is not autocatalytic in the presence of a limiting amount of O_2. The reaction is characterized by an absorbance decrease in the ultraviolet region, corresponding to the loss of CrO^{2+}. First-order kinetic traces were obtained at 270 nm where CrO^{2+} absorbs significantly. The pseudo-first-order rate constants are linearly dependent on the concentration of cyclobutanol, giving a bimolecular rate constant of 44.1 ± 1.2 L mol^{-1} s^{-1} in 1.0 M H^+ at 25°C. The rate constant is independent of $[H^+]$ and ionic strength in the range 0.10 - 1.0 M. Activation parameters for the oxidation of cyclobutanol by CrO^{2+} are given in Table II-3.

Table II-3. Activation parameters for the oxidation of organic substrates by hydride transfer

Oxidant	Substrate	Activation $\Delta H^{\ddagger}$/kJ mol^{-1}	Parameters $\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	Ref
CrO^{2+}	CH_3OH	34± 6	- 99 ± 20	this work
	CD_3OH	38 ± 7	-95 ± 21	this work
	$(CH_3)_2CHOH$	33 ± 3	-112 ± 14	this work
	cyclobutanol	46 ± 1	-61 ± 2	this work
$Ru(bpy)_2pyO^{2+}$	CH_3OH	58 ± 8	-109 ± 25	33a
	CD_3OH	71 ± 8	- 88 ± 20	33a
	CH_3CH_2OH	38 ± 3	-167 ± 8	33a
	$C_6H_5CH_2OH$	24 ± 1	-159 ± 4	33a
	$C_6H_5CD_2OH$	23±3	-192 ± 8	33a
$Ru(trpy)(bpy)O^{2+}$	$(CH_3)_2CHOH$	38 ± 4	-142 ± 17	33b
Ph_3C+	CH_3CH_2OH	70	-92	34
	$(CH_3)_2CHOH$	60	-109	34

Reactions of HCHO and pivaldehyde

The reaction of 0.1 mM CrO^{2+} with millimolar aqueous HCHO in the presence of O_2 also yields CrO_2^{2+}. The pseudo-first-order rate constants are linearly dependent on the concentration of HCHO, with an intercept of 0.029 s^{-1} and a slope of 91.7 ± 2.9 L mol^{-1} s^{-1} in 0.10 M H^+ (μ = 1.0 M). The bimolecular rate constant is acid-independent in the range 0.10 - 1.0 M. Activation parameters are $\Delta H^‡$ = 46.8 ± 1.7 kJ/mol and $\Delta S^‡$ = -50.0 ± 1.9 J/K·mol. The formation of CrO_2^{2+} from CrO^{2+} and 0.6 mM HCHO is not observed in the presence of 1 - 10 mM Mn^{2+}, a scavenger for CrO^{2+}.[10] Under these conditions an absorbance decrease rather than an increase was recorded at 290 nm. The reaction mixture containing Mn^{2+} developed an intense yellow color and an insoluble precipitate of MnO_2 regardless of whether HCHO was present or not.

The reaction of CrO^{2+} with pivaldehyde, $(CH_3)_3CCHO$, does not yield CrO_2^{2+}. The reaction was studied by monitoring the loss of CrO^{2+} at 260 nm. The second-order rate constant is 37.1 ± 6.4 L mol^{-1} s^{-1} at 25°C and is acid-independent. CH_4, isobutane and isobutene were identified as the major organic products by gas-phase chromatography. The other expected organic product, acetone, was not determined.

Reactions of HCO_2H and $H_2C_2O_4$

These reactions give CrO_2^{2+} as the inorganic product in the presence of O_2, regardless of the order of mixing of reagents. At a 1:1 Cr^{2+}:O_2 ratio, the formation of CrO_2^{2+} is followed by an autocatalytic decrease in absorbance, similar to that reported above for the alcohol reactions. When O_2 is in large excess over Cr^{2+}, the increase in absorbance at 290 nm is pseudo-first-order for all concentrations of excess HCO_2H and for $[H_2C_2O_4] < 0.025$ M. At higher $H_2C_2O_4$ concentrations, mixed-first- and second-order traces were obtained. Therefore, kinetic analyses were performed only at lower $H_2C_2O_4$

concentrations. The bimolecular rate constants for both reactions are inversely acid-dependent. The rate law was resolved into acid-independent and acid-dependent terms using the known acid-base equilibria between the carboxylic acids H_2A and their conjugate bases HA^-:

$$k_{obs} = k'[H_2A] + k''[HA^-] + k_d = \frac{k'[H^+] + k''K_a}{K_a + [H^+]}[A]_{total} + k_d \qquad (13)$$

where $K_a = [HA^-][H^+]/[H_2A]$ and $k_d = 0.022\ s^{-1}$ is the intercept of the plot of k_{obs} versus total carboxylic acid concentration. For HCO_2H, $pK_a = 3.53$[22] leads to simplification of the rate law, since $[H^+] >> K_a$. Thus,

$$k_{obs} - k_d = \left(k' + \frac{k''K_a}{[H^+]}\right)[A]_{total} \qquad (14)$$

A plot of $(k_{obs} - k_d)/[A]_{total}$ versus $[H^+]^{-1}$ is linear with slope $k''K_a = 2.03 \pm 0.10\ s^{-1}$, giving $k'' = (6.68 \pm 0.33) \times 10^3\ M^{-1}s^{-1}$ as the bimolecular rate constant for the reaction of HCO_2^- with CrO^{2+}. The intercept yields $k' = 11.6 \pm 1.1\ L\ mol^{-1}\ s^{-1}$.

For $H_2C_2O_4$, $pK_{a1} = 1.04$[22], so the assumption made in eq 14 is not valid. Therefore, the acid-dependent rate constants k_{obs} were fitted to the complete rate law of eq 13 using a non-linear least-squares fitting routine and allowing k', k'', and K_a to vary. The fitting routine reproduced the literature value for $K_a = 0.093$ and gave a negligible value for k'. With the k' term assumed to be zero, the rate law simplifies to eq 15:

$$k_{obs} - k_d = \frac{k''K_a}{K_a + [H^+]}[A]_{total} \qquad (15)$$

A least-squares fit to equation 15 gave k" = $(2.23 \pm 0.25) \times 10^3$ L mol^{-1} s^{-1} as the bimolecular rate constant for the oxidation of $HC_2O_4^-$ by CrO^{2+}.

Reaction of $(CH_3CH_2)_2O$

CrO_2^{2+} is formed from CrO^{2+} by its reaction with $(CH_3CH_2)_2O$ in the presence of O_2. The pseudo-first-order rate constants vary linearly with the concentration of $(CH_3CH_2)_2O$, which is the excess reagent. The bimolecular rate constant is 4.45 ± 0.28 L mol^{-1} s^{-1} in 0.10 M H^+ at 25°C. Tetrahydrofuran does not react with CrO^{2+} under these conditions.

Formation of air-free CrO^{2+} from CrO_2^{2+} or CrO_2Cr^{4+}

Stopped-flow mixing of 0.050 mM argon-saturated CrO_2^{2+} with a solution containing 0.025 mM Cr^{2+} and 0.3 - 2 mM $ABTS^{2-}$ in 0.10 M H^+ causes a biphasic formation of $ABTS^{-\cdot}$ at 417 nm. The rate constant for the fast phase is $(8.4 \pm 1.2) \times 10^4$ $M^{-1}s^{-1}$, in agreement with the rate constant for reaction 5 reported above in the presence of O_2, 7.9×10^4 L mol^{-1} s^{-1}. When CH_3OH was also present, the rate constant of the fast phase was higher due to reaction 8, however, the absorbance change was smaller because reaction 8 does not contribute to the absorbance increase, and because some of the Cr^{2+} product reduces $ABTS^{-\cdot}$. The slow phase is the reaction of $ABTS^{2-}$ with residual CrO_2^{2+}, and its rate is not affected by the addition of CH_3OH.

Mixing of 0.0275 mM air-free $CrOOCr^{4+}$ and 0.275 - 2.06 mM $ABTS^{2-}$ in 0.10 M H^+ was done at 25 °C in the stopped-flow apparatus. The rate of formation of $ABTS^{-\cdot}$ was recorded at 417 nm and fitted to a first-order kinetic equation. The pseudo-first-order rate constants were plotted against the $[ABTS^{2-}]$, giving a straight line with slope k = 802 ± 47 L mol^{-1} s^{-1} and negligible intercept. When the $ABTS^{2-}$ solution contained Cr^{2+}, a biphasic absorbance increase was observed. The rate constant for the slower phase corresponds to the reaction of the remaining $CrOOCr^{4+}$ with $ABTS^{2-}$, while the rate constant measured for the faster phase, 7.1×10^4 $M^{-1}s^{-1}$, corresponds to the reaction between $ABTS^{2-}$ and CrO^{2+} formed in mixing time. The total absorbance change in the presence of Cr^{2+} is only 35% of the absorbance change in the absence of Cr^{2+}, due to consumption of some CrO^{2+} by Cr^{2+} during mixing time, eq 16.

$$CrO^{2+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} \qquad (16)$$

Formation of CrO^{2+} from Cr^{2+} and $TlOH^{2+}$

A solution of 0.22 mM $TlOH^{2+}$ in 0.10 M H^+ was saturated with argon, then 0.22 mM Cr^{2+} was injected. Then an equal volume of O_2-saturated 0.10 M $HClO_4$ containing 0.37 - 2.34 mM CH_3OH was quickly mixed with the CrO^{2+}-containing solution. The increase in absorbance at λ290 nm yielded $k_8 = 29.3 \pm 0.8$ L mol^{-1} s^{-1}, in agreement with the values determined by other CrO^{2+}-generating methods at 0.10 M ionic strength. At the end of the reaction, the uv spectrum shows clearly the 290 nm peak of CrO_2^{2+}, produced in ca. 15% yield based on initial $[Cr^{2+}]$. The low yield is again attributed to the loss of CrO^{2+} in reaction 16, which competes effectively with reaction 4 ($k_4 = 2 \times 10^6$ L mol^{-1} s^{-1}).[23] A blank experiment, in which all components except CH_3OH were mixed as described above, showed no formation of CrO_2^{2+}. $TlOH^{2+}$ does not oxidize CH_3OH under these conditions.

Intermediacy of CrO^{2+} in the reaction of $HCrO_4^-$ with $(CH_3)_2CHOH$

An O_2-saturated solution containing 0.069 mM $HCrO_4^-$ in 2.0 M $HClO_4$ was allowed to react with 0.21 M $(CH_3)_2CHOH$. The peak in the visible spectrum at 345 nm due to $HCrO_4^-$ decreased in intensity over a period of five minutes, while new peaks at 290 and 245 nm grew in, Figure II-8. The final spectrum was that of CrO_2^{2+}. The percent yield of CrO_2^{2+} depends on the initial concentration of $HCrO_4^-$, as shown in Table II-4, and approaches 100% as the concentration of $HCrO_4^-$ is lowered.

Table II-4. Yield of CrO_2^{2+} from the oxidation of 2-propanol by $HCrO_4^-$ [a]

$[HCrO_4^-]$/mM	Yield of CrO_2^{2+}/mM[b]	% Yield of CrO_2^{2+}
0.364	0.099 (0.091)	28
0.069	0.042 (0.042)	64
0.042	0.032 (0.030)	76
0.016	0.013 (0.014)	81

[a] Concentrations of $HCrO_4^-$ and CrO_2^{2+} were determined spectrophotometrically. Solutions contained 2 M $HClO_4$, 1.26 mM O_2 and 0.23 M 2-propanol at 25 °C.

[b] Values in parentheses are predicted yields from numerical integration using the program KINSIM. Rate constants used in the simulation were: $k_{29} = 2 \times 10^9$ L mol^{-1} s^{-1}; $k_9 = 1.6 \times 10^8$ L mol^{-1} s^{-1}; $k_{-9} = 2.5 \times 10^{-4}$ L mol^{-1} s^{-1}; $k_{17} = 8 \times 10^8$ L mol^{-1} s^{-1}.

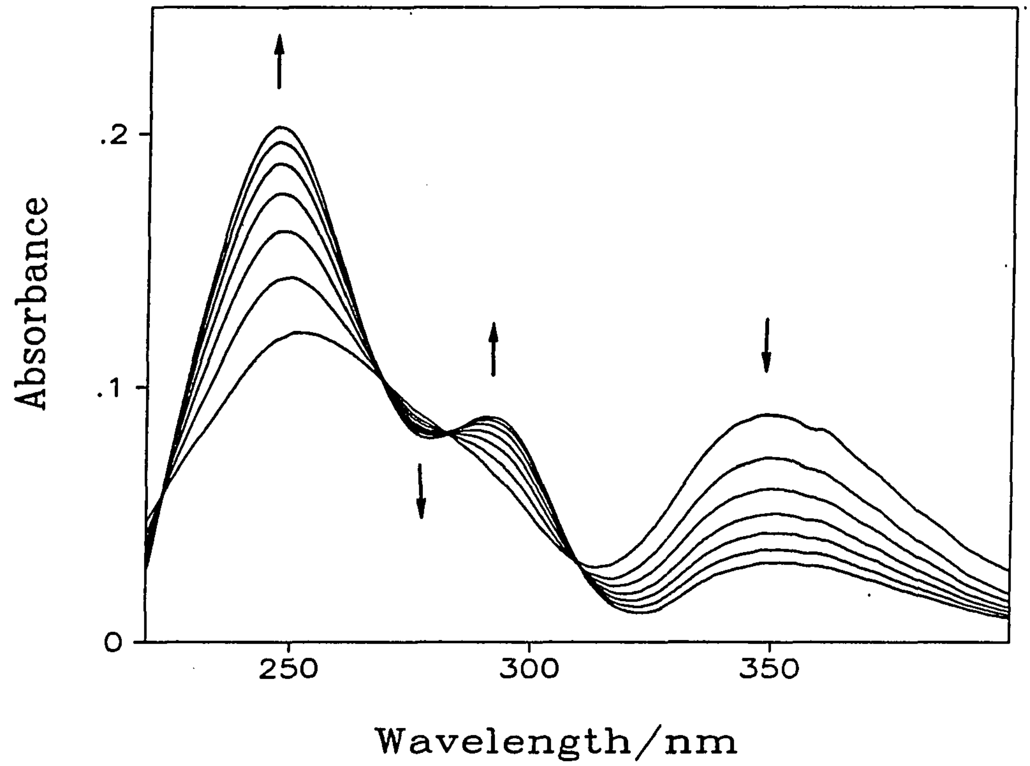


Figure II-8. Formation of CrO_2^{2+} (λ_{max} 290, 245 nm) during the oxidation of 0.21 M $(CH_3)_2CHOH$ by 0.069 mM $HCrO_4^-$ (λ_{max} 345, 255 nm). The solution contained 2.0 M $HClO_4$ and 1.26 mM O_2. Spectra were recorded at 4 min intervals in a 1 cm cell.

DISCUSSION

Reaction of Cr^{2+} with O_2

This is a complex, multistep reaction. The first step was identified by pulse radiolysis[16] as formation of a 1:1 adduct between O_2 and Cr^{2+}. The adduct, CrO_2^{2+}, was described as a superoxochromium(III) because of its electronic spectrum, its kinetic stability and its thermodynamic stability constant.[15] Subsequent steps in the reduction of O_2 by Cr^{2+} are not well-established, because they are extremely rapid. For example, the reaction of CrO_2^{2+} with Cr^{2+} is too rapid for conventional stopped-flow mixing, although an estimate of the rate constant (1×10^7 L mol^{-1} s^{-1}) was obtained by competition with $Co(NH_3)_5F^{2+}$ (see Chapter I). The ultimate product of the Cr^{2+}+ O_2 reaction is known to be $Cr(OH)_2Cr^{4+}$,[24] formed when Cr^{2+} enters the coordination sphere of Cr(IV) and is then oxidized. After electron transfer, both metal centers become Cr(III), in which the coordination spheres are frozen. Therefore the bis-µ-hydroxy dimer is produced, rather than $Cr(H_2O)_6^{3+}$. One proposal[15] for the complete mechanism is shown in Scheme II-1, although as a result of this work, certain features of it must now be revised.

Scheme II-1. Mechanism of oxidation of Cr^{2+} by O_2

$$Cr^{2+} + O_2 \rightleftharpoons CrO_2^{2+} \tag{9}$$

$$CrO_2^{2+} + Cr^{2+} \rightarrow CrOOCr^{4+} \tag{17}$$

$$CrOOCr^{4+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} + CrO^{2+} \tag{3}$$

$$CrO^{2+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} \tag{16}$$

Both $CrOOCr^{4+}$ and CrO^{2+} are proposed intermediates in the oxidation of Cr^{2+} by O_2, and both are now known in other reactions as well. Since k_{17} is very large, reaction

17 competes with 9 when the concentrations of CrO_2^{2+} and O_2 are comparable. However, no real evidence has ever been found in this or in previous work for the intermediacy of $CrOOCr^{4+}$. Therefore, (a) $CrOOCr^{4+}$ is not stable enough to be observed or isolated, or (b) $CrOOCr^{4+}$ reacts with Cr^{2+} much more rapidly than CrO_2^{2+} does, or (c) $CrOOCr^{4+}$ is not formed. The first option is ruled out by the independent preparation[21] of $CrOOCr^{4+}$ by the reaction of CrO_3 and H_2O_2, which demonstrated that the $CrOOCr^{4+}$ is stable for several minutes at room temperature. It also has a characteristic and fairly intense uv-visible spectrum. The second option seems unlikely because the $Cr^{2+} + CrO_2^{2+}$ reaction is already very rapid, and the reduction of $CrOOCr^{4+}$ by Cr^{2+} could not be significantly faster. In fact, it may be much slower if the sluggishness of the reaction between Cr^{2+} and H_2O_2 is any guide.[25] The last option seems the most likely then.

The formation of the other intermediate, CrO^{2+}, may be direct, as in

$$CrO_2^{2+} + Cr^{2+} \rightarrow 2\, CrO^{2+} \qquad (18)$$

or indirect, via some other intermediate, for example Cr^VO^{3+},

$$CrO_2^{2+} + Cr^{2+} + H^+ \rightarrow CrO^{3+} + CrOH^{2+} \qquad (19)$$

$$CrO^{3+} + Cr^{2+} \rightarrow CrO^{2+} + Cr^{3+} \qquad (20)$$

The observation that the CrO^{2+} generated independently by the reaction of Cr^{2+} with CrO_2^{2+} *in the absence of oxygen* reacts with $ABTS^{2-}$ with essentially the same rate constant as the intermediate in the reaction of Cr^{2+} with O_2 supports the contention that the same reaction in both systems gives rise to CrO^{2+}. The CrO^{2+} so formed oxidizes alcohols, aldehydes and some carboxylates, as shown in this work. Aged solutions of initially pure CrO_2^{2+} which contain CH_3OH were also found to contain HCHO, even though CrO_2^{2+} does not react with CH_3OH directly. This observation is easily accounted for by reactions 18 or 19 - 20, since homolysis of CrO_2^{2+} generates the Cr^{2+} needed to produce CrO^{2+}.

The assertion that the oxidant in these reactions contains Cr in the unusual +4 oxidation state, and that this species undergoes two-electron reduction to Cr^{2+}, results from the following reasoning. Consider the possible oxidizing Cr species which could be present in the reaction mixture:

(a) Cr^{VI} would be present as $HCrO_4^-$ under these concentration and pH conditions. It can be detected spectrophotometrically by its absorption maximum at λ 345 nm ($\varepsilon = 1.4 \times 10^3$ M^{-1} cm^{-1}), and it was not observed. Although $HCrO_4^-$ is known to oxidize alcohols, the reaction is very slow at pH 1. The intermediate studied here is certainly a more facile oxidant than $HCrO_4^-$.

(b) Aqueous Cr^V is believed to oxidize alcohols by a two electron path and/or disproportionate.[9] If it reacts directly with the alcohol, the products must be Cr(III) and a ketone/aldehyde. No combination of these products can possibly give rise to CrO_2^{2+}. If Cr^V disproportionates, one product must be $HCrO_4^-$, which was not observed.

(c) Cr^{IV} is believed to be a strong oxidant that reacts with a variety of alcohols and other organic substrates. These reactions have traditionally been written as one-electron hydrogen-atom abstractions[26] because of the kinetic isotope effects and the stability of the Cr(III) product. However, if Cr^{3+} and a carbon-centered radical are the immediate products of the reaction, then Cr^{3+} must be reduced to Cr^{2+} by the radical in order to form the ultimate product, CrO_2^{2+}. While it is thermodynamically possible for a hydroxyalkyl radical to reduce $Cr(H_2O)_6^{3+}$,

$$Cr(H_2O)_6^{3+} + e^- \rightarrow Cr^{2+}_{(aq)} \qquad E^\circ = -0.416\ V \qquad (21)$$

$$CH_2O + H^+ + e^- \rightarrow \cdot CH_2OH \qquad E^\circ = -0.83\ V^{27} \qquad (22)$$

this reaction has been shown not to occur[28] because of the reluctance of $Cr(H_2O)_6^{3+}$ to undergo outer-sphere electron transfer and the substitutional inertness of $Cr(H_2O)_6^{3+}$, which prohibits an inner-sphere path. The conclusion is that the only possible way to obtain Cr^{2+}, and consequently CrO_2^{2+}, is by a two-electron reduction of a Cr(IV) species.

Mechanism of reaction of CrO^{2+} with alcohols

The rate constants for the reaction of CrO^{2+} with various alcohols are remarkable in their uniformity. The reactivity of alcohols towards one-electron oxidants such as Ce(IV) varies widely according to the ease of formation of the corresponding hydroxyalkyl radicals: the range of second-order rate constants spans several orders of magnitude.[29] For the reactions studied here, not only is the range of rate constants relatively small, but the reactivity order is unconventional. CH_3OH is invariably more difficult to oxidize than $(CH_3)_2CHOH$ by a one-electron (hydrogen-atom-abstraction) path: DH°_{298} (R-H) = 95.9 ± 1.5 kcal/mol for CH_3OH, 90.7 ± 1.1 kcal/mol for $(CH_3)_2CHOH$.[30] However, the thermodynamic properties of the two-electron oxidations are very similar: ΔH°_f(ketone) - ΔH°_f(alcohol) = 17.0 kcal/mol for CH_3OH and 16.75 kcal/mol for $(CH_3)_2CHOH$.[31] Also, the formation of the diphenylhydroxymethyl radical is thermodynamically more favorable than the formation of the phenylhydroxymethyl radical because of the additional benzylic stabilization, yet benzyl alcohol reacts with CrO^{2+} faster than does diphenylmethanol. The lack of a significant para substituent effect in the oxidation of substituted benzyl alcohols also implies that benzyl radicals are not formed in the oxidation process. Hammett ρ values for processes involving these radicals are generally large and negative, for example -2.0

with Ce(IV) as the oxidant.[14] Therefore the oxidation of these alcohols by CrO^{2+} does not proceed by alkyl radical formation.

Instead, the reactions with alcohols may take place by a concerted, two-electron hydride transfer mechanism:

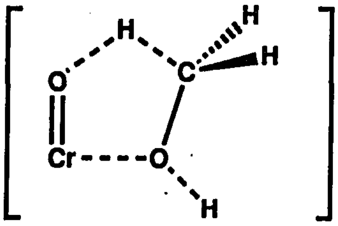
$$CrO^{2+} + R_2CHOH \rightarrow [CrO\cdots\cdots H\cdots\cdots CR_2OH]^{2+} \rightarrow CrOH^{+} + R_2CO + H^{+} \qquad (23)$$

Although this mechanism has not received much attention in the literature, it would seem to be thermodynamically preferable to the previously-proposed hydrogen-atom transfer reaction, eq 24.

$$CrO^{2+} + CH_3OH \rightarrow CrOH^{2+} + \cdot CH_2OH \qquad (24)$$

The additional energy required to form $CrOH^{+}$ rather than $CrOH^{2+}$ is more than compensated by the formation of the stable aldehyde (or ketone) instead of the highly-energetic hydroxyalkyl radical. The standard potential for the Cr(IV)/Cr(III) couple is unknown, although estimates as high as 2.0 V have been made.[32] However, the difference of free energies $\Delta G°_{23} - \Delta G°_{24}$ does not depend on this potential. Taking into account the protonation states of the chromium products, $CrOH^{+}$ and $CrOH^{2+}$, the free energy difference is estimated as -28 kJ/mol. Therefore the hydride transfer path is more favorable than the hydrogen-atom transfer path by 28 kJ/mol. This difference is not so large, however, as to preclude the hydrogen-atom transfer path when an especially stable alkyl radical is formed. Other possible mechanisms are proton-coupled electron transfer via the hydroxyl group, ruled out on the basis of the absence of a solvent isotope effect, and outer-sphere electron transfer which is unlikely because of the high energies of the protonation states of both products (CrO^+ and $ROH^{\cdot}$) which would result.

The moderate primary isotope effects (CH_3OH/CD_3OH, 3.46; C_2H_5OH/C_2D_5OH, 2.13; C_3H_7OH/C_3D_7OH, 2.61) support the direct involvement of the carbon-hydrogen bond in the rate-determining step. The effects are not as large as for the $Ru(bpy)(py)O^{2+}$ oxidation of alcohols,[33] which range from $k_H/k_D = 9$ for CH_3OH/CD_3OH to 50 for $C_6H_5CH_2OH/C_6H_5CD_2OH$ and for oxidation by RuO_4 ($k_H/k_D = 4.6 \pm 0.2$ with 2-propanol-2-D)[34] which are all claimed to proceed by hydride mechanisms. Isotope effects are smaller for the known hydride transfers between Ph_3C^+ and $(CH_3)_2CHOH$ (k_H/k_D=1.84) or HCO_2^- (k_H/k_D=2.5).[35] Quantum mechanical tunneling has been invoked to explain the largest primary isotope effects. However, even the magnitude of the more normal isotope effects depends strongly on the geometry of the transition state, being greatest when the C-H-O system is linear . Since the RuN_5O^{2+} complexes are substitutionally inert, and there is little likelihood of coordination-sphere expansion, the transition-state for hydride abstraction is probably linear. However, MO analysis[36] has shown that the activation energy for hydride transfer from methanol to the oxo ligand of RuN_5O^{2+} would be substantially lowered by prior coordination of the substrate to the metal via the hydroxylic oxygen. Such an intermediate in the CrO^{2+} reaction with CH_3OH would have the following structure:



Formation of a side-on hydrogen bond rather than a linear hydrogen bond minimizes the repulsion between the C-H bond and the oxo lone pair. The cyclic intermediate would certainly exhibit smaller isotope effects than would a linear transition state. Since Cr(IV) is substitutionally labile,[11] it is plausible that alcohols, aldehydes and carboxylic acids coordinate to CrO^{2+} before being oxidized. Analogous esters have been identified in the reactions between $HCrO_4^-$ and alcohols in nonaqueous solvents.[8] Prior coordination may explain why alcohols that are sterically hindered react more slowly (e.g. $(CH_3)_2CHOH$ vs CH_3CH_2OH, and $(C_6H_5)_2CHOH$ vs $C_6H_5CH_2OH$).

The intercepts in all the plots of k_{obs} versus [ROH] are small, reproducible and do not depend in any apparent way on the nature of the alcohol. This feature, a CrO^{2+}-consuming process with a first-order rate constant of ca. 0.030 s^{-1} in 1.0 M $HClO_4$ and 0.015 s^{-1} in 0.10 M $HClO_4$, represents the spontaneous decomposition of CrO^{2+}. If alcohol addition to the CrO^{2+}-containing solution was delayed by a few minutes, no CrO_2^{2+} was formed. Both observations are easily explained if CrO^{2+} decomposes on this time scale. The products and mechanism of this side-reaction have not yet been explored.

Activation parameters

Values are shown in Table II-3 for the oxidations of CH_3OH, CD_3OH, $(CH_3)_2CHOH$ and cyclobutanol by CrO^{2+}. Parameters for other reactions known to be hydride transfers are also shown in Table II-3 for comparison. Hydride transfers are generally characterized by positive values of $\Delta H^\ddagger$ and large negative values of $\Delta S^\ddagger$. The latter have been attributed to the strict orientational requirements for hydride transfer. In the CrO^{2+} system, collinearity is not required, but formation of a complex between CrO^{2+} and ROH and achievement of the cyclic transition state would certainly contribute to a large negative value of $\Delta S^\ddagger$.

Mechanism of reaction of $HCrO_4^-$ with alcohols and Cr^{2+}

The currently accepted mechanism[26] for the oxidation of alcohols by $HCrO_4^-$ involves Cr(IV), but not Cr^{2+}, as in Scheme II-2.

Scheme II-2. Literature mechanism for oxidation of alcohols by acid chromate

$$HCrO_4^- + R_2CHOH \rightarrow Cr^{IV} + R_2CO + 2H^+ \tag{25}$$

$$Cr^{IV} + R_2CHOH \rightarrow Cr^{3+} + R_2COH + H^+ \tag{26}$$

$$HCrO_4^- + R_2COH \rightarrow Cr^{V} + R_2CO + H^+ \tag{27}$$

$$2\,Cr^{V} \rightarrow HCrO_4^- + Cr^{IV} \tag{28}$$

However, CrO_2^{2+} formation during the oxidation of $(CH_3)_2CHOH$ by $HCrO_4^-$ requires the intermediacy of Cr^{2+}. The variation in the yield of CrO_2^{2+} can reasonably be ascribed to a competition between $HCrO_4^-$ and O_2 for Cr^{2+}, as in eq 29 and 9.

$$Cr^{2+} + HCrO_4^- \rightarrow Cr^{3+} + Cr^{V} \tag{29}$$

The rate constant k_{29} is too large to measure using conventional stopped-flow techniques.[6] Using the known value of $k_9 = 1.6 \times 10^8$ L mol^{-1} s^{-1},[15] the rate constant k_{29} was derived from the yields of CrO_2^{2+} in Table II-4 by eq 31:[37]

$$\frac{k_{29}}{k_9} = \frac{[O_2]\ \ln\left([HCrO_4^-]_0 / [CrO_2^{2+}]_\infty\right)}{[CrO_2^{2+}]_\infty} \tag{30}$$

The derived value for k_{29} is (2.0 ± 0.6) x 10^9 L $mol^{-1}s^{-1}$ in 2.0 M $HClO_4$. The yields of CrO_2^{2+} are well-predicted by kinetic simulation using this value for k_{29} (see Table II-4). Because the yield of CrO_2^{2+} approaches 100% as the concentration of $HCrO_4^-$ decreases, oxidation of CrO^{2+} by $HCrO_4^-$, can be ruled out. This reaction has been proposed in the literature[10] even though it is thermodynamically uphill. The possible disproportionation[10,38] of CrO^{2+} also does not seem important in the presence of a large excess of alcohol.

The two-electron reaction of CrO^{2+} with aliphatic alcohols is incorporated into Scheme II-3, which we believe should supersede the model in Scheme II-2.

Scheme II-3. Revised mechanism for oxidation of alcohols by acid chromate

$$HCrO_4^- + R_2CHOH + 3\,H^+ \rightarrow CrO^{2+} + R_2CO + 3\,H_2O \qquad (25)$$

$$CrO^{2+} + R_2CHOH \rightarrow Cr^{2+} + R_2CO + H_2O \qquad (31)$$

$$HCrO_4^- + Cr^{2+} \rightarrow Cr^V + Cr^{3+} \qquad (29)$$

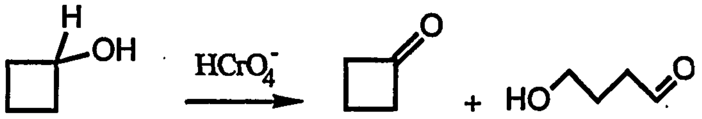
$$2\,Cr^V \rightarrow HCrO_4^- + CrO^{2+} \qquad (28)$$

The precise formula of the Cr^V intermediate is unknown. Scheme II-3 does not contradict previous observations (no polymerization of acrylonitrile and no kinetic effect of O_2),[39] because radicals are not produced and Cr^{2+} reacts with $HCrO_4^-$ even more rapidly than it does with O_2.

Oxidation of 1,2-diarylethanols and cyclobutanol

The presence of organic oxidative cleavage products when $HCrO_4^-$ oxidizes a 1,2-diaryl- or 1,2-arylalkylethanol,[14] eq 32, or cyclobutanol,[40] eq 33, has been interpreted as evidence for a one-electron oxidation by CrO^{2+}.

$$\mathrm{ArCH(OH)CH_2Ar'} \xrightarrow{\mathrm{HCrO_4^-}} \mathrm{ArCHOAr'} + (\mathrm{ArCHO} + \mathrm{Ar'CH_2OH}) \quad (32)$$



(33)

Oxidative cleavage is characteristic of one-electron oxidants such as Ce(IV).[40] In previous work on Cr(IV) oxidations,[39] cyclobutanol was the only alcohol studied which did not show a primary isotope effect, leading the authors to conclude that C-C bond cleavage is rate-determining. In the present study, cyclobutanol again behaves differently from all the other alcohols, because its reaction with CrO^{2+} does not yield Cr^{2+}. Also, the activation parameters for the cyclobutanol reaction are different, with larger $\Delta H^{\ddagger}$ and smaller $\Delta S^{\ddagger}$ compared to the values in other alcohol reactions, Table II-3.

In order to reconcile these observations with the proposed mechanism in eq 23, let us consider two alternatives. Oxidative cleavage may result from a two-electron process; such reactions have been documented[41] but only when especially stable organic cations are formed. Two-electron oxidative cleavage of cyclobutanol would be unprecedented. Alternately, the CrO^{2+} may be capable of either one-electron or two-electron oxidation, depending on the organic reactant. For simple primary and secondary alcohols, and even benzylic alcohols, formation of Cr^{2+} instead of Cr^{3+} is less expensive than production of alkyl radicals, and is favored by the stability of the aldehyde or ketone products. If the product ketone would be highly strained, as in the case of cyclobutanone, or if oxidative cleavage would lead to a stabilized alkyl radical, then Cr^{3+} and a hydroxyalkyl radical are formed instead. The change in mechanism is signalled by a change in the measured activation parameters, since hydrogen-atom transfer reactions usually have larger $\Delta H^\ddagger$ and smaller $\Delta S^\ddagger$ values than do hydride transfer reactions.[31] Therefore cleavage of cyclobutanol by a given oxidant does not indicate that all reactions of that oxidant are one-electron processes, as was previously suggested.[40] However, in the case of CrO^{2+} oxidations, the presence or absence of the CrO_2^{2+} product is definitive in determining the mechanism.

Oxidation of $(CH_3CH_2)_2O$

A unique property of hydride-abstracting reagents is the ability to oxidize ethers. While one-electron (hydrogen-atom abstraction) oxidation of an ether is very difficult compared to one-electron oxidation of a similar alcohol, hydride abstraction is feasible from both alcohols and ethers.[42] The oxidation of di-isopropyl ether by MnO_4^- proceeds by hydride abstraction at almost the same rate as the oxidation of isopropyl alcohol.[43] We have found that CrO^{2+} oxidizes $(CH_3CH_2)_2O$ twenty times more slowly than CH_3CH_2OH, but only 2.7 times more slowly than $(CH_3)_2CHOH$.

Mechanism of reaction of CrO^{2+} with aldehydes

The oxidation of simple aldehydes by H_2CrO_4[44] and Cr(IV)[45] has already been studied in some detail: the $HCrO_4^-$ oxidation of HCHO induces the oxidation of Mn^{2+} with an induction factor (ratio of moles of Mn^{2+} oxidized to moles of aldehyde oxidized) of 0.5, implying that Cr(IV) is a reactive intermediate. The fate of Cr(IV) may have been oxidation by H_2CrO_4, one-electron oxidation of HCHO yielding Cr^{3+}, or two-electron oxidation of

HCHO to yield Cr^{2+}. No evidence was then available to distinguish between these alternatives. In the more recent study,[45] the reaction of $HCrO_4^-$ with VO^{2+} was used to generate Cr(IV) *in situ*. Addition of an aldehyde to the reaction mixture decreases the yield of VO_2^+ without affecting the rate of loss of $HCrO_4^-$, which led the authors to conclude that the aldehyde reacts only with Cr(IV) and not with Cr(V). Based on the relative reactivity of various aldehydes, it was shown that aldehydes react exclusively in their hydrated forms. Since HCHO is essentially completely hydrated in aqueous solution, ($K = 1.8 \times 10^3$),[46] the rate constant measured in this work, 91.7 L mol^{-1} s^{-1}, is the rate constant for the reaction between CrO^{2+} and $CH_2(OH)_2$. The mechanism of oxidation is hydride abstraction based on the observation of the inorganic product CrO_2^{2+}. The organic product is inferred to be HCOOH.

The reaction of pivaldehyde with CrO^{2+} in the presence of O_2 does not yield CrO_2^{2+} but does give large amounts of radical cleavage products. A one-electron oxidation by hydrogen-atom abstraction, followed by elimination of CO from the pivaloyl radical, was suggested by Roček and Ng because of a substantial primary kinetic isotope effect. The proposed reactions, which are in accord with out observations that Cr^{3+} and radical cleavage products are formed, is shown in reactions 34 - 35.

$$CrO^{2+} + (CH_3)_3CCHO \rightarrow CrOH^{2+} + (CH_3)_3\dot{C}CO \tag{34}$$

$$(CH_3)_3\dot{C}CO \rightarrow (CH_3)_3C\cdot + CO \tag{35}$$

The fate of the t-butyl radical depends on the O_2 concentration.[47] At low or zero $[O_2]$, the radical disproportionates to isobutane and isobutene. In oxygenated solutions the t-butyl peroxyl radical is formed, which then decomposes bimolecularly to the t-butoxyl radical.

This radical fragments to acetone and methyl radical, and the latter abstracts a hydrogen atom from pivaldehyde to become methane.

Mechanism of reaction of CrO^{2+} with HCO_2H and $H_2C_2O_4$

The formation of CrO_2^{2+} in both of these reactions implies a two-electron, hydride-transfer mechanism. The inverse acid-dependence is consistent with direct formation of CO_2 from HCO_2^- and $HC_2O_4^-$, as in eq 36 and 37.

$$CrO^{2+} + HCO_2^- \rightarrow CrOH^+ + CO_2 \quad (36)$$

$$CrO^{2+} + HC_2O_4^- \rightarrow CrOH^+ + 2\,CO_2 \quad (37)$$

The rate constants k_{36} and k_{37} are much larger than the rate constants for oxidation of HCO_2H and $H_2C_2O_4$, because the product, CO_2, is formed directly from HCO_2^- and $HC_2O_4^-$ in the correct protonation state. The second-order kinetic term observed at high $[H_2C_2O_4]$ may be due to association of $H_2C_2O_4$ in solution; such interactions have been previously noted.[48]

Summary

CrO^{2+} is a versatile oxidant with a half-life of ca. 30 seconds in 1.0 M $HClO_4$ at 25 °C. It oxidizes alcohols, aldehydes and carboxylates by a two-electron mechanism in all cases except for cyclobutanol, where cleavage of the strained four-membered ring is favored, and pivaldehyde, where elimination of CO from the pivaloyl radical is preferred.

The rate constants for all the alcohol and aldehyde reactions studied here are very similar, and the reactivity trends are inconsistent with the formation of alkyl radicals. The rate of oxidation of R_2CHOH to R_2CO depends slightly on the steric bulk of R, which suggests that prior coordination of the alcohol to CrO^{2+} may be required before hydride transfer occurs.

APPENDIX: REACTION OF CrO^{2+} WITH PPh_3

The CrO^{2+} formed by syringe injection or stopped-flow mixing of Cr^{2+} and O_2 reacts readily with 0.01 - 0.04 M PPh_3. The stoichiometry of the reaction is 1:1, based on the absorbance change at 260 nm, where $\Delta\varepsilon = 1.3 \times 10^4\ M^{-1}\ cm^{-1}$ for the conversion of PPh_3 to $O{=}PPh_3$.

$$Cr{=}O^{2+}_{(aq)} + PPh_3 \rightarrow Cr^{2+}_{(aq)} + O{=}PPh_3 \qquad (38)$$

In the presence of excess PPh_3, the uv region is completely obscured, and the reaction was more conveniently studied using the reaction of CrO^{2+} with $ABTS^{2-}$ as a kinetic probe. The formation of $ABTS^{-\cdot}$ occurs by the rate law of eq 39.

$$-d[CrO^{2+}]/dt = (k_5\ [ABTS^{2-}] + k_{38}\ [PPh_3])\ [CrO^{2+}] \qquad (39)$$

The rate constant k_{38} varies linearly with $[PPh_3]$, with a value $k_{38} = (2.1 \pm 0.2) \times 10^3\ L\ mol^{-1}\ s^{-1}$ in 0.10 M $HClO_4$ / 85% CH_3CN at room temperature. Under the experimental conditions, reaction 38 is complete in less than 0.2 seconds, therefore the decomposition of CrO^{2+} does not contribute to the kinetics. The simplest mechanism for a two-electron oxidation of PPh_3 is an oxo transfer from CrO^{2+}. Other metal-oxo species, including a Cr^V oxo complex,[1] are known to transfer oxygen to PPh_3. The stoichiometry of the reaction of PPh_3 with aquachromium(IV) supports its formulation as an oxo ion.

While pure CrO_2^{2+} does not react with PPh_3, CrO_2^{2+} contaminated with CrO^{2+} does. When 0.2 mM Cr^{2+} was injected into a solution containing 1.3 mM O_2 and 1.3 mM

PPh_3, all of the PPh_3 was converted to $O{=}PPh_3$. The reaction is approximately first-order with a half-life of 8 minutes at 25 °C in 85% CH_3CN/0.10 M $HClO_4$. Since CrO^{2+} does not live long enough to be the bulk oxidant on this timescale, the autoxidation of PPh_3 must be catalyzed by CrO_2^{2+}. A proposal for the catalytic chain is shown in Scheme II-4.

Scheme II-4. Mechanism for the CrO_2^{2+}-catalyzed autoxidation of PPh_3

$$Cr^{2+} + O_2 \rightleftharpoons CrO_2^{2+} \tag{9}$$

$$CrO_2^{2+} + Cr^{2+} \rightarrow CrO^{2+} + \text{(other Cr products)} \tag{2}$$

$$Cr{=}O^{2+}{}_{(aq)} + PPh_3 \rightarrow Cr^{2+}{}_{(aq)} + O{=}PPh_3 \tag{38}$$

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SECTION III

REVERSIBLE REDUCTION OF A DICHROMIUM-SEMIQUINONE COMPLEX PREVIOUSLY MISIDENTIFIED AS THE μ-OXO DIMETALLIC ION, $CrOCr^{4+}$

ABSTRACT

The complex described in the literature as the μ-oxo complex, $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$, is shown to be a dichromium(III) semiquinone complex, $(H_2O)_5CrOC_6H_4OCr(H_2O)_5{}^{5+}$. It is prepared by the reaction of 1,4-benzoquinone with Cr^{2+} in acidic, aqueous solution. The reaction also yields $Cr(H_2O)_6{}^{3+}$ and a dichromium(III) hydroquinone complex of 4+ charge. The semiquinone complex is reversibly reduced by outer-sphere electron transfer to the dichromium(III) hydroquinone complex, $(H_2O)_5CrOC_6H_4OCr(H_2O)_5{}^{4+}$. Any of Cr^{2+}, $Ru(NH_3)_6{}^{2+}$, or V^{2+} accomplishes this reduction. The hydroquinone complex is reoxidized by Fe^{3+}, 1,4-benzoquinone, Br_2 or Ce(IV) to the semiquinone complex. Cyclic voltammograms obtained with either the hydroquinone complex or the semiquinone complex are identical, and correspond to a reversible, one-electron process. The standard reduction potential of the semiquinone complex is +0.61 V (NHE). The semiquinone complex decomposes, over a period of hours, by aquation of Cr(III) followed by disproportionation of the organic ligand, yielding hydroquinone, benzoquinone and $Cr(H_2O)_6{}^{3+}$. A literature report of the quinone oxidation of ethanol catalyzed by Cr^{3+} can now be interpreted correctly in terms of the reversible formation of the coordinated semiquinone radical complex.

INTRODUCTION

The preceding work in this manuscript on the various intermediates formed during the reaction of $Cr(H_2O)_6^{2+}$ with O_2 inspired an investigation of the involvement of $(H_2O)_5CrOCr(H_2O)_5^{4+}$, hereafter $CrOCr^{4+}$. This species is a natural candidate for the product of the reaction between the recently-prepared $CrO^{2+}{}_{(aq)}$[1] and Cr^{2+}. However, $CrOCr^{4+}$ has not been observed in this reaction or in any other reactions of Cr^{2+} with O_2.[2] It was reported as one of several major products during a mechanistically ill-defined reaction between Cr^{2+} and 1,4-benzoquinone in aqueous perchloric acid, and as the product of oxidation of a dichromium(III) hydroquinone complex.[3] This product is unusual in that has an intense visible spectrum with several narrow peaks. Moreover it is a good but irreversible oxidizing agent, with E° given as + 0.54 V(NHE).[4] Neither of these properties is characteristic of inorganic Cr(III) species and thuspecial electronic interactions within a linear Cr-O-Cr unit were invoked. The so-called $CrOCr^{4+}$ ion was also claimed to decompose irreversibly to Cr^{3+} in a reaction catalysed by H^+ or by reductants such as Cr^{2+}.[4,5]

In this work, the intense and narrow visible bands actually belong to a complex containing the coordinated semiquinone radical, whose correct formula is $CrOC_6H_4OCr^{5+}$, presumably with water molecules in all the remaining coordination positions. Evidence is presented here to support this formulation. The reduction of the semiquinone complex yields the dichromium(III) hydroquinone complex, and is fully reversible. Coordination of semiquinone to two Cr(III) ions greatly stabilizes the semiquinone radical, which would otherwise disproportionate very rapidly in acidic solution. A proposed mechanism for the eventual disproportionation, limited by the low rate of aquation of bound Cr^{3+}, is given.

The new level of understanding of the spectra and redox properties of the hydroquinone- and semiquinone-bridged dichromium complexes permits a reinterpretation of some early results on the Cr^{3+}-catalyzed quinone oxidation of ethanol.

EXPERIMENTAL SECTION

Because the literature assignments of the two chromium complexes in this study will be disputed in this chapter, the original labels will be used to describe their preparation and reactivity. Complex I is the species described by Holwerda and Petersen[3] as a dichromium(III) hydroquinone complex, although with a structure different from the one propose here. Complex II is identical to the proposed $CrOCr^{4+}$ ion, for which an entirely different composition has been found. Both Complex I and Complex II were prepared by a slight modification of the literature procedure.[3] Yields of both complexes were found to be much higher when a 2:1 rather than a 1:1 mole ratio of Cr^{2+}: 1,4-benzoquinone was used. 1,4-Benzoquinone (65 mg; 0.6 mmol) was dissolved in 2 mL CH_3CN and diluted to 100 mL with 0.1 M aqueous $HClO_4$. This solution was thoroughly deaerated with argon, then 1.2 mmol Cr^{2+} was added dropwise by syringe. The solution containing the products was loaded onto a column of ice-cooled Sephadex SP C-25 cation-exchange resin. The column was rinsed repeatedly with 0.1 M $HClO_4$ to remove uncoordinated benzoquinone and hydroquinone, which were retained by the resin more strongly than expected for uncharged species. Because this procedure took some two hours, the Complexes I and II decomposed slightly on the column, liberating more free hydroquinone as well as Cr^{3+}. Therefore, to obtain samples of highest purity both complexes were eluted with 0.10 M $HClO_4$/0.90 M $LiClO_4$ and then re-ion-exchanged. Complex I eluted as a dense dark green band followed by a diffuse yellow-green band of Complex II. Complex II was used immediately, since it decomposes completely within a few hours. Complex I was frozen and used over the course of the next three days. To obtain fresh samples of Complex II, Complex I was oxidized with Br_2 and then ion-exchanged again to remove any uncoordinated quinone species and Cr^{3+}.

Solutions of $Ru(NH_3)_6^{2+}$, Cr^{2+} and V^{2+} were prepared by reducing air-free, acidic aqueous $[Ru(NH_3)_6]Cl_3$, $Cr(ClO_4)_3$ and $VO(ClO_4)_2$, respectively, over Zn/Hg. $Fe(ClO_4)_3$

was prepared by dissolving $FeCl_3{\cdot}6H_2O$ in conc. $HClO_4$ and evaporating HCl until the solution gave a negative test for Cl^- with $AgNO_3$. Total chromium was analyzed by the basic H_2O_2 method.[6] Hydroquinone and benzoquinone were quantified spectrophotometrically (λ 290 nm, ε 2.3×10^3 M^{-1} cm^{-1} and λ 248 nm, ε 2.14×10^4 M^{-1} cm^{-1}, respectively).[7,8] Br_2 was standardized spectrophotometrically (λ 392 nm, ε 175 M^{-1} cm^{-1}).[9]

Electronic spectral measurements, spectrophotometric titrations and kinetic runs were performed on a Shimadzu UV-3101PC Scanning Spectrophotometer equipped with a thermostatted cell-holder. First-order rate constants were obtained from the slopes of plots of log $(A-A_\infty)$ versus time. Cyclic voltammetry was performed on a BAS-100 Electrochemical Analyzer with a freshly-polished glassy carbon working electrode and a Ag/AgCl reference electrode containing saturated NaCl.

RESULTS

Composition

The composition of Complex I was established by analysis of a decomposed sample for hydroquinone and total Cr. The solution contained 3.6 mM hydroquinone and 7.6 mM total Cr, confirming the original assignment of a 1:2 hydroquinone-chromium complex.[3] Extinction coefficients were determined from the spectrum of the solution, Figure 1a, immediately after ion-exchange, and are given in Table III-1. The values are slightly higher than those given in the previous work.[3] Doubly-ion-exchanged Complex II was analyzed for total Cr, and the resulting extinction coefficients are also shown in Table III-1. The very high extinction coefficients in the visible region and the sharpness of the bands (Figure 1b) are unique. They set Complex II apart from almost every other known chromium(III) complex.

Reversible redox chemistry

A sample of 0.19 mM Complex I, Figure 1a, was oxidized with one equivalent of Fe^{3+}. The spectrum of Complex II developed over several minutes, Figure 1b. Its concentration was also 0.19 mM, based on the independently-determined extinction coefficients. The solution of Complex II was deaerated with argon and an equal concentration of Cr^{2+} was added. The spectrum of 0.19 mM Complex I was recovered quantitatively, Figure 1c. The addition of Fe^{3+} followed by Cr^{2+} was repeated several times and the same reversible spectral changes were observed, eq 1-2.

$$\text{Complex I} + Fe^{3+} \rightarrow \text{Complex II} + Fe^{2+} \qquad (1)$$

$$\text{Complex II} + Cr^{2+} \rightarrow \text{Complex I} + Cr^{3+} \qquad (2)$$

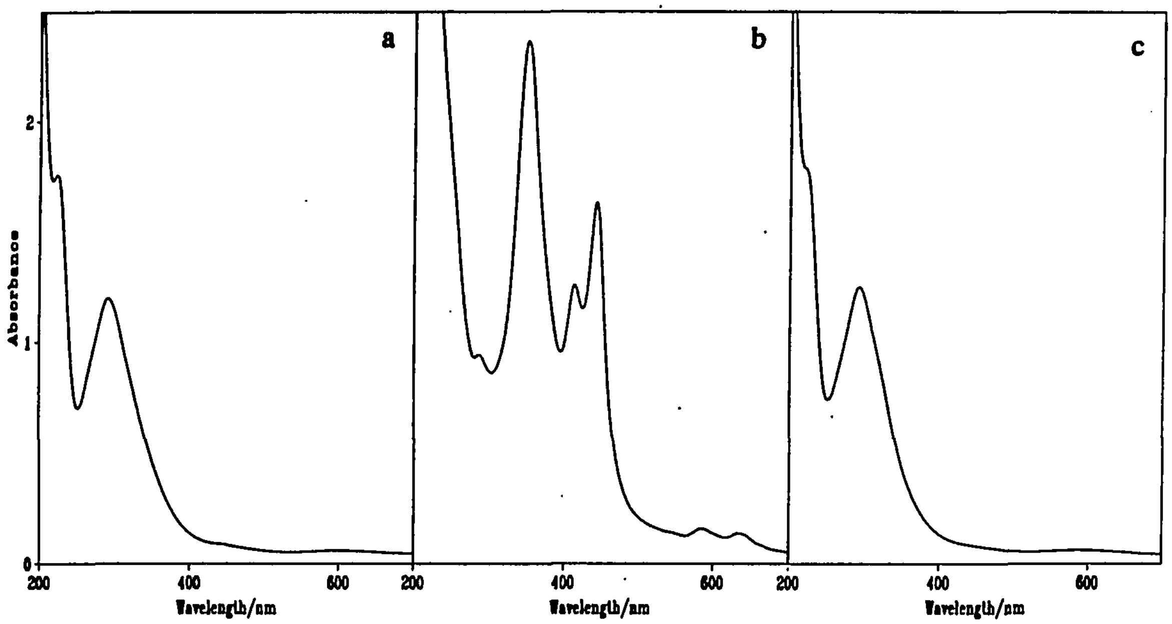


Figure III-1. Reversible spectral changes upon oxidation of Complex I and reduction of Complex II: (a) spectrum of 0.19 mM Complex I in 0.10 M $HClO_4$/0.90 M $LiClO_4$, in a 1 cm cell; (b) spectrum of Complex II obtained by adding Fe^{3+} to the solution of Complex I; (c) spectrum of Complex I obtained by adding Cr^{2+} to the deaerated solution of Complex II.

Table III-1. Spectral bands and extinction coefficients for free quinones and quinone complexes, $CrQCr^{4+}$ and $CrQCr^{5+}$

Chromophore	λ_{max} / nm	$\varepsilon / M^{-1}cm^{-1}$ [a]	Reference
1,4-benzoquinone	248	2.14×10^4	8
hydroquinone	290	2.3×10^3	7
	221	4.4×10^3	
semiquinone radical anion	458	9.4×10^3	10
	428	7.5×10^3	
	406	4.7×10^3	
	325	2.5×10^4	
$CrQCr^{4+}$ (complex I)	599	2.4×10^2	this work
	292	6.50×10^3	
	224	1.00×10^4	
$CrQCr^{5+}$ (complex II)	634	4.6×10^2	this work
	585	5.5×10^2	
	443	7.52×10^3	
	413	5.84×10^3	
	350	1.19×10^4	
	226	9.32×10^3	

[a] For Complexes I and II, extinction coefficients are given per mole of complex, i.e., per two moles of chromium.

The yield of Complex II from a solution of Complex I decreases as the time delay between addition of Cr^{2+} (to form Complex I) and the addition of Fe^{3+} increases. After 2 hours, only 73% of Complex II was obtained. Based on the rate constant for the decomposition of Complex I (see below), a yield of 75% is predicted.

Qualitatively, the same spectral changes were observed using Br_2, Ce(IV) or 1,4-benzoquinone as the oxidant and either $Ru(NH_3)_6^{2+}$ or V^{2+} as the reductant. However, the Br_2 and Ce(IV) oxidations produce Complex II quantitatively only when Complex I is in excess, because of overoxidation (see below). Fe^{2+} does not reduce Complex II.

To establish the stoichiometry of the reversible redox reaction, two spectrophotometric titrations were carried out. The addition of 0.036 mM Br_2 to a solution containing 0.236 mM Complex I resulted in the formation of 0.068 mM Complex II. Continued addition of Br_2 did not lead to 100% yield of complex II, but did cause formation of a peak at 248 nm attributed to free benzoquinone. However, the stoichiometry of the reaction when Br_2 is not in excess is clearly 1 Br_2 : 2 Complex I, contrary to the original assignment of 1 Br_2: 1 Complex I.[3] Doubly-ion-exchanged Complex II was titrated with Cr^{2+}, and a clean endpoint was observed at 0.90 Cr^{2+} : 1 Complex II, Figure III-2. This result to be identical within the experimental error to a 1:1 endpoint since Complex II is not completely stable on the timescale required for these manipulations.

Electrochemistry

Cyclic voltammetry was performed separately on samples of pure Complexes I and II. Both complexes show identical quasi-reversible cathodic and anodic waves, Figure 3. The peak positions and intensity ratios are given in Table II. The average position of the cathodic and anodic peaks yields a reduction potential of 0.61 V (NHE) in 0.10 M $HClO_4$/0.90 M $LiClO_4$.

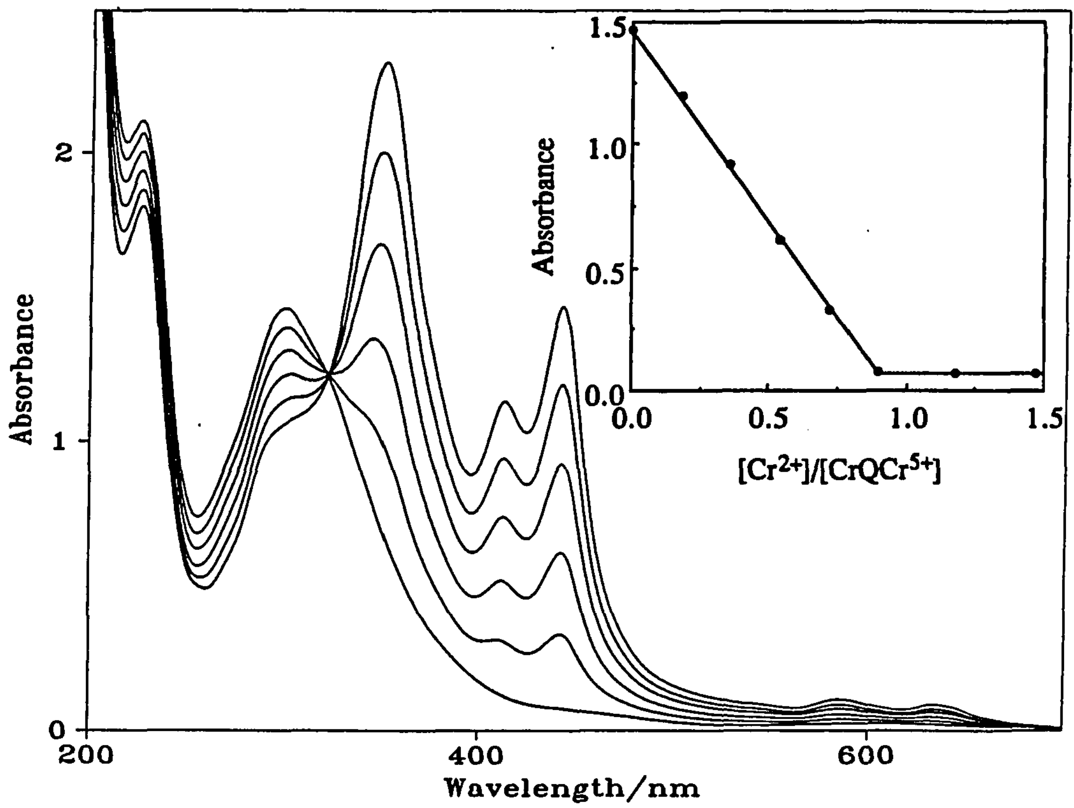


Figure III-2. Spectrophotometric titration of airfree 0.195 mM Complex II with Cr^{2+} in 0.10 M $HClO_4$/0.90 M $LiClO_4$. Optical pathlength 1 cm.

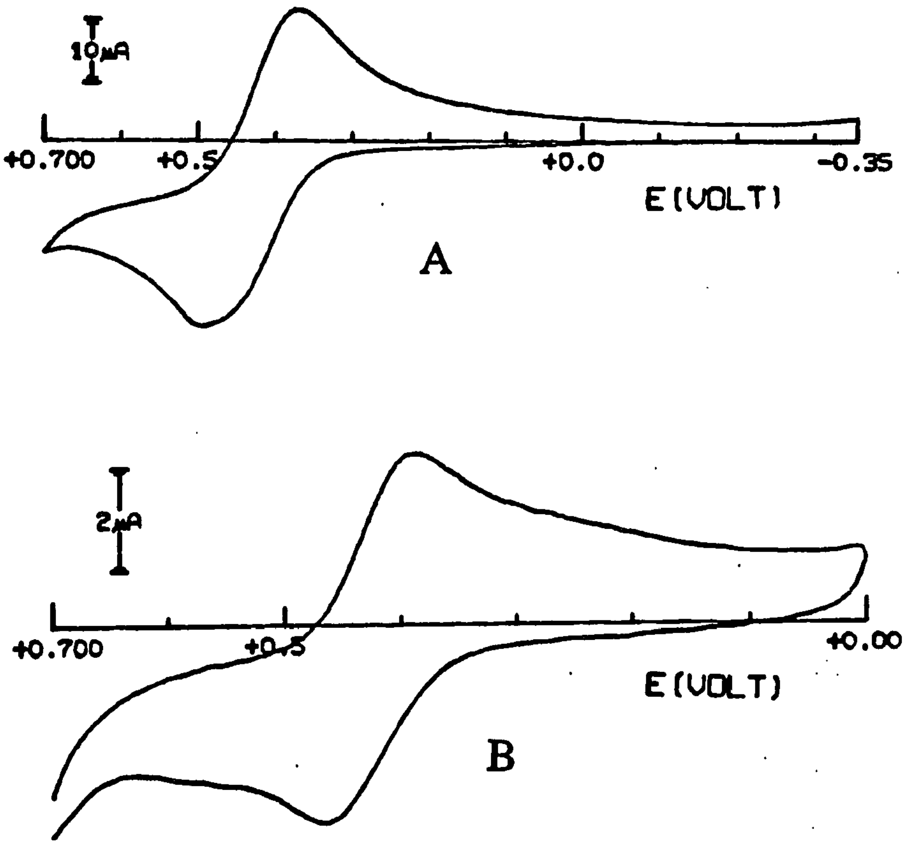


Figure III-3. Cyclic voltammograms of (a) Complex I, and (b) Complex II, in 0.10 M $HClO_4$/0.90 M $LiClO_4$ at a glassy carbon working electrode and a Ag/AgCl reference electrode. Both complexes were purified by ion-exchange.

Table III-2. Electrochemical data for $CrQCr^{4+}$ and $CrQCr^{5+}$ [a]

Complex	$E_{p,c}$ / mV [b]	$E_{p,a}$ / mV [b]	$I_{p,c}/I_{p,a}$
$CrQCr^{4+}$ (complex I)	678	791	0.961
$CrQCr^{5+}$ (complex II)	692	768	0.974

[a] Obtained at a glassy carbon working electrode versus a Ag/AgCl reference electrode. Solutions contained 0.10 M $HClO_4$/ 0.90 M $LiClO_4$ and air. Sweep rate 50 mV/s.

[b] All potentials are given relative to the standard hydrogen electrode.

Kinetics

The kinetics of reduction of Complex II with Cr^{2+} and $Ru(NH_3)_6^{2+}$ have already been reported.[4] A few of these experiments were repeated and essentially the same results were obtained: $k_{Cr} = 1.8 \times 10^4$ L mol^{-1} s^{-1} and k_{Ru} too fast to measure by stopped-flow. The kinetics of oxidation of Complex I have not been examined, so a study of the reaction between Complex I and Fe^{3+} was undertaken. In the presence of a pseudo-first-order excess of Fe^{3+}, an exponential increase in absorbance at 443 and 350 nm was recorded. When aged samples of Complex I were used, a biphasic absorbance increase was observed. The rate constant for the slower phase, 28 L mol^{-1} s^{-1}, is similar to that observed for the oxidation of free hydroquinone by Fe^{3+}.[8] The rate constant for the faster phase, which is the direct reaction between Fe^{3+} and Complex I, is linearly dependent on the concentration of excess Fe^{3+}, with a slope of 1.5×10^2 L mol^{-1} s^{-1} in 0.10 M $HClO_4$/0.90 M $LiClO_4$ at 25.0 °C.

The kinetics of the decomposition of doubly-ion-exchanged Complexes I and II were studied by following the loss of absorbance at 290 and 443 nm, respectively, in 0.10 M $HClO_4$/0.90 M $LiClO_4$ at 25 °C. Both processes were first-order. The rate constant for decomposition of Complex I is 3.9×10^{-5} s^{-1} and for Complex II is 2.4×10^{-4} s^{-1}. The latter number agrees with the previously-determined value for Complex II at this pH.[5] The acid-dependence found in previous work was therefore not investigated further.

Decomposition products

The spectrum of a solution of decomposed Complex I contains two very weak bands in the visible region at 574 and 406 nm and two intense peaks in the uv at 288 and 221 nm. The positions and intensities of the visible peaks are consistent with Cr^{3+} as the sole inorganic product. The positions and intensities of the uv peaks match exactly those for hydroquinone.

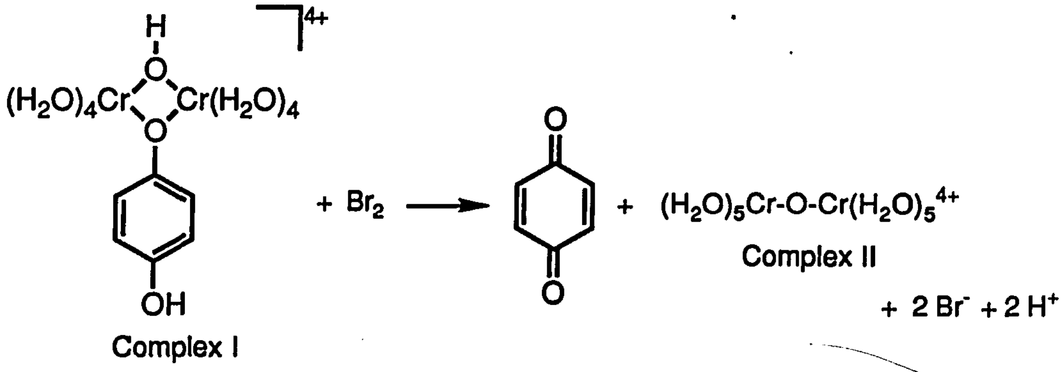
The spectrum of a solution containing decomposed Complex II has all the peaks described above and an additional peak at 248 nm, the maximum for 1,4-benzoquinone. Evidence that this peak is actually due to 1,4-benzoquinone was obtained by addition of Cr^{2+} to the nearly colorless decomposed solution. The yellow-green color and the characteristic intense spectrum of Complex II reappeared immediately, as in the reaction of Cr^{2+} with authentic 1,4-benzoquinone. The total amount of quinone (0.20 mM hydroquinone + 0.10 mM benzoquinone) found in the decomposed solution is essentially equal to the initial amount of Complex II, 0.29 mM, originally present. Only slightly more benzoquinone was found in a more rapidly decomposed solution of Complex II in 1.0 M $HClO_4$. Because the amount of Complex II was calculated from extinction coefficients which are based on analysis of total chromium, the analysis of the decomposed solution confirms the stoichiometry of Complex II as a 2:1 complex of chromium and a quinone species.

DISCUSSION

The nature of Complexes I and II

The previous finding that Complex I is a 2:1 complex of Cr and hydroquinone has been confirmed by these experiments, and its ion-exchange behavior indicates that its charge is +4. However, the findings regarding the nature of Complex II are significantly different from the previous study. In that work, the oxidation of Complex I to II was reported to be irreversible with liberation of free p-benzoquinone into solution.[3] The authors also claimed that Complex II contains no coordinated quinone. On the basis of a similarity with the spectrum of the basic rhodo ion, $(NH_3)_5CrOCr(NH_3)_5^{4+}$, the formula $(H_2O)_5CrOCr(H_2O)_5^{4+}$ was assigned to Complex II. The latter was claimed to decompose to Cr^{3+} in a reaction catalyzed by Cr^{2+} and $Ru(NH_3)_6^{2+}$. The proposed reactions are shown in Scheme I, eq 3-6.[3,4]

Scheme III-1. Proposed formation and catalyzed aquation of $CrOCr^{4+}$



(3)

$$(H_2O)_5CrOCr(H_2O)_5^{4+} + C_{red} \rightarrow (H_2O)_5CrOCr(H_2O)_5^{3+} + C_{ox} \qquad (4)$$

$$(H_2O)_5CrOCr(H_2O)_5^{3+} + H_2O + 2\,H^+ \rightarrow Cr(H_2O)_6^{2+} + Cr(H_2O)_6^{3+} \qquad (5)$$

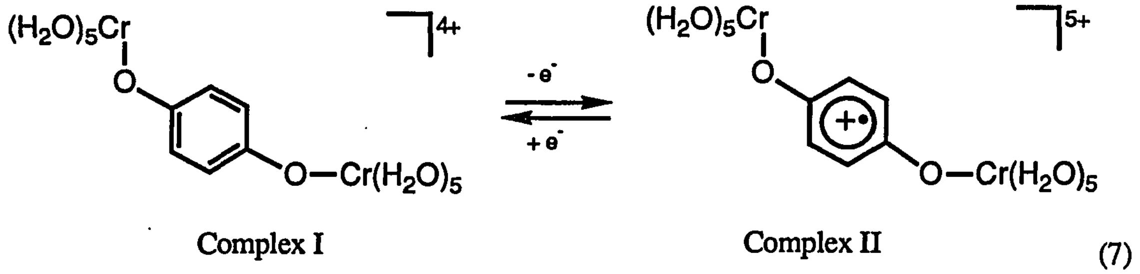
$$Cr(H_2O)_6^{2+} + C_{ox} \rightarrow Cr(H_2O)_6^{3+} + C_{red} \qquad (6)$$

In Scheme I, C_{red} and C_{ox} are the reduced and oxidized forms of the catalyst which is supposed to catalyze the hydrolysis of Complex II to Cr^{3+}. For example, C_{red} may be either Cr^{2+} or $Ru(NH_3)_6^{2+}$. The products of the reaction of Cr^{2+} with Complex II were subjected to ion-exchange. A blue 3+ species was identified as Cr^{3+} and a green 4+ species was presumed to be $Cr(OH)_2Cr^{4+}$ resulting from aerobic oxidation of the Cr^{2+} catalyst during workup. As reported above and discussed later, this green 4+ species is actually Complex I, and the reaction of Complex II with C_{red} is actually a stoichiometric (not catalytic) reduction to Complex I. The latter is more stable towards hydrolysis than Complex II and is not further reduced by Cr^{2+}.

The results obtained here require an interpretation different from the above proposal for the nature of Complex II. It is an intact one-electron-oxidized product from the hydroquinone Complex I, as demonstrated by the complete reversibility of the chemical reactions and by the peak-to-peak separations observed in the cyclic voltammograms. The quinone ligand must still be coordinated, and in fact the spectrum of Complex II resembles that of the unbound semiquinone radical anion, whose spectral characteristics are given in Table III-1.[10] The intensities of the peaks of Complex II, Table III-1, are also comparable to those of the semiquinone radical anion. In contrast, the visible spectrum of the basic rhodo ion, $(NH_3)_5CrOCr(NH_3)_5^{4+}$, while intense, is considerably weaker, with an extinction coefficient of 650 L^{-1} mol Cr^{-1} cm^{-1} at 325 nm.[11] Analogs of the basic rhodo ion with the ammine ligands replaced by aromatic ligands such as tris(2-pyridylmethyl)amine or bipyridyl have higher extinction coefficients, but none of these complexes can be reduced.[12] The only electrochemical features they possess are reversible oxidation waves. Therefore the extent of similarity between Complex II and known μ-oxo bridged dichromium(III) species is small.

The mechanism of reduction of Complex II by Cr^{2+} and $Ru(NH_3)_6^{2+}$ was convincingly argued to be outer-sphere.[4] Although Cr^{2+} ($E^\circ_{3+/2+} = -0.41$ V) is a much better reductant than $Ru(NH_3)_6^{2+}$ ($E°_{3+/2+} = +0.06$ V), the rate constant for Cr^{2+} reduction is approximately one order of magnitude smaller than for $Ru(NH_3)_6^{2+}$ reduction. This reactivity order is not observed when Cr^{2+} can react by an inner-sphere mechanism, but it is quite common when the reaction is perforce outer-sphere, because the self-exchange rate constant for the Cr^{2+}/Cr^{3+} couple is so low, $\leq 2 \times 10^{-5}$ L mol^{-1} s^{-1}.[13] If the proposed structure for Complex I, eq 3, were correct, then reversibly-formed Complex II must also have both Cr(III) ions coordinated to the same oxygen atom of semiquinone, leaving most of the radical character of the semiquinone on the uncoordinated oxygen. It is difficult to believe that Cr^{2+} would ignore such an opportunity for an inner-sphere pathway and instead choose to react by an outer-sphere mechanism. It is more probable that Complexes I and II contain quinone coordinated at both oxygens, as in Scheme II.

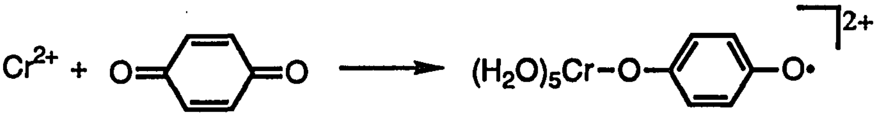
Scheme III-2. Structure and reversible oxidation of a dichromium(III) hydroquinone complex



(7)

This structural type was previously proposed for the product of the reaction between $Co(CN)_5^{3-}$ and 1,4-benzoquinone, $(NC)_5CoOC_6H_4OCo(CN)_5^{6-}$,[14] as well as for the product of reaction of Cr^{2+} with various substituted quinones.[15] Moreover, if we consider the stepwise process by which Complex I is formed, starting with a 1:1 reaction of Cr^{2+} and 1,4-

benzoquinone,[2b] the first intermediate would be the mononuclear semiquinone radical complex shown in eq 8.



(8)

The rate constant for this reaction was determined by pulse radiolysis to be 3.2 x 10^8 L mol^{-1} s^{-1}.[16] The product of eq 8 seems more likely to react with a second Cr^{2+} at the uncoordinated oxygen radical to yield the Complex I shown in Scheme II than at the oxygen coordinated to Cr to yield the structure in Scheme I. Finally, Complex II is formed in the reaction between Cr^{2+} and 1,4-benzoquinone by the *in situ* oxidation of Complex I by benzoquinone. The feasibility of this reaction was tested independently, showing and an ion-exchanged sample of Complex I was converted to Complex II when benzoquinone was added.

Reduction of Complex II does not lead to rapid aquation to $Cr(H_2O)_6^{3+}$, as previously suggested. The Cr^{3+} product is formed directly from the Cr^{2+} reactant and the green 4+ product is Complex I, eq 2. Although the colors and ion-exchange properties of Complex I and the $Cr(OH)_2Cr^{4+}$ ion are very similar, the product spectrum is clearly not that of $Cr(OH)_2Cr^{4+}$. Therefore Complex I must have the formula $CrOC_6H_4OCr^{4+}$, or simply $CrQCr^{4+}$, and Complex II must be $CrOC_6H_4OCr^{5+}$, or $CrQCr^{5+}$. The reversible oxidation of aqua[15] and azamacrocyclic[17] chromium-hydroquinone complexes has been previously noted.

Redox chemistry

The one-electron reduction potential of free hydroquinone E°($HQ\cdot/H_2Q$) is 1.04 V at pH 0.[18] This potential is strongly pH-dependent because of the difference in protonation levels and the acidity constants of both species ($pK_1 = 9.85$, $pK_2 = 11.4$ for H_2Q and $pK = 4.1$ for

HQ·).[8,18] At pH 14, where both hydroquinone and semiquinone are fully deprotonated, the lower potential $E(Q^{\cdot -}/Q^{2-}) = 0.023$ V[19] reflects the increasing ease of oxidation of hydroquinone once the proton barrier is removed. Then by comparison, hydroquinone coordinated as Q^{2-} is much more difficult to oxidize than free Q^{2-}, given that $(CrQCr^{5+}/CrQCr^{4+}) = 0.61$ V. This is true not only for $CrQCr^{4+}$, but also for $(NC)_5CoOC_6H_4OCo(CN)_5{}^{6-}$, where no oxidation wave for the hydroquinone complex was observed at potentials up to +1.1 V.[14] The increased stability of coordinated hydroquinone in $(NC)_5CoOC_6H_4OCo(CN)_5{}^{6-}$ towards oxidation was attributed to both a coordination effect, since binding to cobalt(III) increases the electronegativity of the oxygen atoms, and interaction of the π levels of the ligand with the π^* levels of the $Co(CN)_5$ groups, which effectively stabilizes the ligand HOMO.

Quinone oxidation of ethanol catalyzed by chromic ion

The reactions and spectral changes observed during the quinone oxidation of ethanol catalyzed by Cr^{3+}[15] are now understandable in terms of the chemistry proposed here. A green species, G, was observed but not correctly identified in the reaction of Cr^{2+} with 2,5-dihydroxy-1,4-benzoquinone, H_2Q'. G has the distinctive spectrum of a semiquinone radical complex.

$$2\,Cr^{2+} + (Q')^{2-} \rightarrow CrQ'Cr^{2+} \xrightarrow{(Q')^{2-}} \underset{G}{CrQ'Cr^{3+}} \qquad (9)$$

G is also formed when Cr^{3+} and H_2Q' are combined in ethanol solvent. In this reaction, ethanol is oxidized to acetaldehyde simultaneously with formation of G, eq 10-11. Oxygen slowly oxidizes G, eq 12, to a red species, R, which is probably a chromium-quinone complex. R then oxidizes more ethanol, creating a catalytic cycle.

$$2\,\mathrm{Cr^{3+}} + \mathrm{(Q')^{2-}} \rightarrow \mathrm{CrQ'Cr^{4+}} \tag{10}$$

$$2\,\mathrm{CrQ'Cr^{4+}} + \mathrm{CH_3CH_2OH} \rightarrow 2\,\mathrm{CrQ'Cr^{3+}} + \mathrm{CH_3CHO} + 2\,\mathrm{H^+} \tag{11}$$

$$\underset{\mathrm{G}}{4\,\mathrm{CrQ'Cr^{3+}}} + \mathrm{O_2} + 4\,\mathrm{H^+} \rightarrow \underset{\mathrm{R}}{4\,\mathrm{CrQ'Cr^{4+}}} + 2\,\mathrm{H_2O} \tag{12}$$

Coordinative stabilization of radicals

Coordination of radicals to metal ions sometimes leads to impressive stabilization of the radical species. The reaction of Cr^{2+} with various substituted pyrazines leads to long-lived complexes of Cr(III) with the pyrazine radical anion, whose reducing ability is much lower than that of the unbound radical anion.[20] Reaction of O_2 with Cr^{2+} gives CrO_2^{2+}, a stable superoxochromium(III) ion whose uv spectrum resembles that of the free superoxide radical.[2] Coordination of the semiquinone radical to Cr(III) greatly enhances the stability of the radical towards disproportionation. Whereas free semiquinone disproportionates by a second-order process at nearly the diffusion-controlled rate ($k_d = 1.1 \times 10^9$ L mol^{-1} s^{-1} for $HQ\cdot + HQ\cdot$, and $k_d = 1 \times 10^8$ L mol^{-1} s^{-1} for $Q^{-\cdot} + Q^{-\cdot}$),[21] the dichromium(III) semiquinone complex, $CrQCr^{5+}$, decomposes in a slow first-order process which is acid-catalyzed.[5] Rate-limiting acidolysis, a common process in substitutionally-inert Cr(III) complexes with organic ligands, was suggested as the first step. The products of acidolysis would be Cr^{3+} and the mononuclear semiquinone-Cr(III) complex shown in eq 8. The mononuclear complex may disproportionate, eq 13, or release quinone by internal electron-transfer, eq 14. The latter reaction is analogous to the decomposition reactions of the Cr(III)-pyrazine radical complexes.[20]

$$2\,\mathrm{CrQH}^{3+} \rightarrow \mathrm{CrQ}^{3+} + \mathrm{CrQH}^{2+} + \mathrm{H}^{+} \rightarrow 2\,\mathrm{Cr}^{3+} + \mathrm{Q} + \mathrm{H_2Q} \qquad (13)$$

$$\mathrm{CrQH}^{3+} \rightleftharpoons \mathrm{Cr}^{2+} + \mathrm{Q} + \mathrm{H}^{+} \qquad (14)$$

The Cr^{2+} product of eq 14 may react with quinone by an inner-sphere mechanism, regenerating the mononuclear semiquinone complex, or by an outer-sphere electron transfer, yielding Cr^{3+} and free semiquinone radical anion. In either case, the product ratio of hydroquinone: benzoquinone is expected to be 1:1. However, spectral analysis of the product solution showed more hydroquinone than benzoquinone. A blank experiment revealed that the 248 nm peak of 1,4-benzoquinone in 0.10 M $HClO_4$ decreases in intensity by 30% in 24 hours, with concurrent formation of peaks at 221 and 290 nm. The positions and intensities of these peaks (probably due to 1,2,4-trihydroxybenzene)[22] are very similar to those of hydroquinone. This spontaneous decomposition of benzoquinone can account for most, but not all, of the "missing" benzoquinone among the products of decomposition of $CrQCr^{5+}$. Coordination to Cr(III) apparently enhances the rate of spontaneous decomposition of benzoquinone in aqueous solution.

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GENERAL SUMMARY

The superoxochromium(III) ion, CrO_2^{2+}, is an efficient catalyst for the autoxidation of $CrCH_2OH^{2+}$. In the presence of sufficient O_2 to trap the Cr^{2+} product, $CrCH_2OH^{2+}$ is converted quantitatively into CrO_2H^{2+}. The latter species is an end-bonded hydroperoxochromium(III) ion, characterized for the first time in this work. In the absence of O_2, a stoichiometric chain reaction occurs, in which CrO_2^{2+}, $CrCH_2OH^{2+}$ and also free CH_3OH are consumed. The oxidation of CH_3OH is attributed to a chromium(IV) intermediate, CrO^{2+}. This process results in stabilization of CrO_2^{2+} under aerobic conditions, and much higher concentrations of CrO_2^{2+} are now accessible because of it.

Formation of bulk quantities of CrO^{2+} was accomplished both aerobically and anaerobically. CrO^{2+} oxidizes PPh_3 to $O{=}PPh_3$ by oxo transfer in a reaction with a 1:1 stoichiometry. The reaction of CrO^{2+} with various alcohols, aldehydes and carboxylates was studied using the formation of CrO_2^{2+} as a spectroscopic probe. Most are two-electron reactions, with no evidence for formation of alkyl radicals. The generally-accepted mechanism for $HCrO_4^-$ oxidation of alcohols was revised in light of this direct evidence for one of the intermediate steps.

The "$CrOCr^{4+}$" ion was shown to be a semiquinone radical-bridged dichromium ion, $CrQCr^{5+}$. This species undergoes reversible electrochemical and chemical reduction. Coordination to chromium stabilizes the semiquinone radical, and no direct disproportionation of the complex was observed. Instead, the complex decomposes by rate-limiting aquation to Cr^{3+} and a mononuclear chromium(III)-semiquinone complex.

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