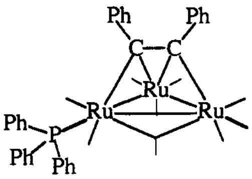

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trimetallic framework. The present work is also the first demonstration that the unsaturation inherent to the perpendicular mode is not a formalism but is effectively substantiated by chemical reactivity.

Acknowledgment. Financial support of this work by the CNRS is gratefully acknowledged.

Supplementary Material Available: A description of the experimental details for the X-ray structure analysis of complex **2** and tables of crystallographic data, refined atomic coordinates and hydrogen coordinates, anisotropic thermal parameters, interatomic distances, and bond angles (11 pages); a listing of observed and calculated structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

Laboratoire de Chimie de Coordination
du CNRS
associé à l'Université Paul Sabatier et à
L'Institut National Polytechnique
205, route de Narbonne
31077 Toulouse, France

Soa Rivomanana
Guy Lavigne*
Noël Lugan
Jean-Jacques Bonnet

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Articles

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Catalytic Oxidation of the (Hydroxymethyl)chromium(III) Ion by the Superoxochromium(III) Ion

Susannah L. Scott, Andreja Bakac,* and James H. Espenson*

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The superoxochromium(III) ion, CrO_2^{2+}, is an efficient catalyst for autoxidation of the (hydroxymethyl)chromium(III) ion, $CrCH_2OH^{2+}$, in aqueous solution. The reaction involves one-electron oxidation of $CrCH_2OH^{2+}$ by CrO_2^{2+}, $k = 137\ M^{-1}\ s^{-1}$, to yield Cr^{2+}, CH_2O, and the novel (hydroperoxo)chromium(III) ion, CrO_2H^{2+}. The Cr^{2+} produced reacts rapidly with O_2 to regenerate the catalyst, CrO_2^{2+}. When oxygen is depleted, the Cr^{2+} reacts instead with CrO_2^{2+} to produce the chromyl(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 molecular oxygen toward 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, 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] 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).

$$Cr^{2+} + O_2 \rightleftarrows CrO_2^{2+} \tag{1}$$

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

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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] On the basis of the kinetic and spectral evidence obtained in that early work, it was proposed that one-electron outer-sphere reduction of CrO_2^{2+} yields a long-lived (hydroperoxo)chromium(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 to us at that time (typically <40 μM).

In this paper, we report kinetic results for the autoxidation of $CrCH_2OH^{2+}$, consisting of an uncatalyzed path and a path catalyzed by CrO_2^{2+}. We present a mechanistic interepretation for the catalysis and conclusive evidence for the formation of CrO_2H^{2+} as a product at millimolar concentrations.

We also report 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. Also, the presence of alcohols in the reaction medium stabilizes CrO_2^{2+} toward spontaneous decomposition in aerated solutions.

Experimental Section

Dilute solutions (≤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 chromium(III) and $HCrO_4^-$ increase as the total concentration of chromium 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 used 0.1–1 M CH_3OH. Concentrations of CrO_2^{2+} were determined spectrophotometrically (λ_{max} 290 nm, ϵ 3.1 × 10^3 M^{-1} cm^{-1}; λ_{max} 245 nm, ϵ 7.4 × 10^3 M^{-1} cm^{-1}).[5,7]

The (hydroxymethyl)chromium ion, $CrCH_2OH^{2+}$, was prepared in solution[8] and standardized spectrophotometrically (λ_{max} 392 nm, ϵ 570 M^{-1} cm^{-1}; λ_{max} 282 nm, ϵ 2.4 × 10^3 M^{-1} cm^{-1}).[8,9] In several cases the complex was purified by ion exchange on Sephadex SP C-25. The behaviors of the purified and unpurified complexes were 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.

$[Co(NH_3)_5F](ClO_4)_2$ 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 and 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 added by syringe 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 Co.

Inorganic products were identified and their concentrations determined spectrophotometrically. Oxidizing titer was evaluated by deaerating the product solution with argon and then adding an excess of solid sodium iodide. The absorbance at 350 nm due to triiodide (ϵ 2.5 × 10^4 M^{-1} cm^{-1})[11] was measured to determine the concentration of iodine in solution. Formaldehyde was determined by chromotropic acid analysis.[12]

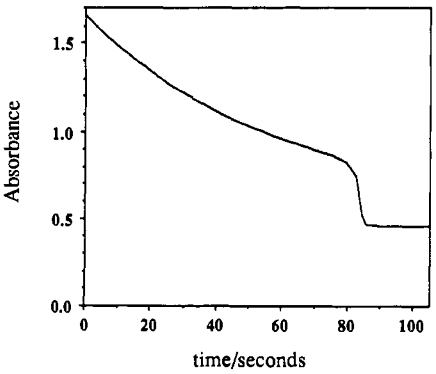

Figure 1. Kinetic trace at 290 nm for the reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} in the presence of a limiting amount of O_2. Experimental conditions: 0.10 mM CrO_2^{2+}, 0.42 mM $CrCH_2OH^{2+}$, 0.2 M CH_3OH, 0.10 M $HClO_4$, 0.34 mM O_2, optical path length 1 cm.

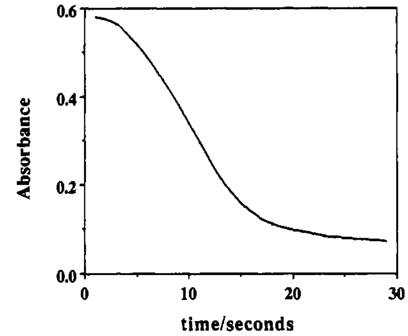

Figure 2. Kinetic trace at 290 nm for the reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} in the absence of O_2. Experimental conditions: 0.043 mM CrO_2^{2+}, 0.098 mM $CrCH_2OH^{2+}$, 0.02 M CH_3OH, 0.013 M $HClO_4$, optical path length 2 cm.

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 1). In the absence of O_2, the reaction was fast and autocatalytic (Figure 2).

Effect of CH_3OH on 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 $HClO_4$ (0.01–0.1 M) yielded CrO_2^{2+} quantitatively only at very low concentrations of Cr^{2+} (<40 μM). At higher concentrations, large amounts of Cr(III) and $HCrO_4^-$ (λ_{max} 345 nm, ϵ 1.44 × 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 ethanol and 2-propanol, 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 the alcohol than in those that did not.

Catalyzed Reaction of $CrCH_2OH^{2+}$ with O_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 (0.25–1.27 mM), a straightforward catalytic process takes place (eq 2). CrO_2^{2+} is recovered fully

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

at the end of the reaction, and CH_2O is produced quantitatively, i.e., $[CH_2O]_\infty \geq 0.9[CrCH_2OH^{2+}]_0$. 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

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

$$k_{obs} = k_0 + k_2[CrO_2^{2+}] \qquad (4)$$

$[O_2]$, $[H^+]$, and $[CH_3OH]$. k_2 increases with increasing ionic

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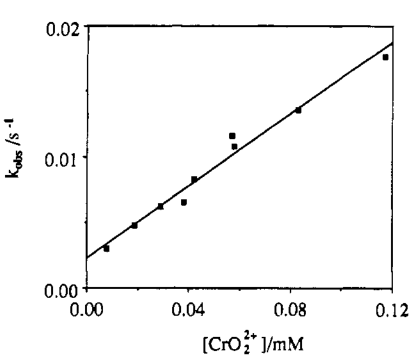

Figure 3. Dependence of the pseudo-first-order rate constant for the reaction between $CrCH_2OH^{2+}$ and CrO_2^{2+} on the concentration of CrO_2^{2+}. Experimental conditions: 0.42 mM $CrCH_2OH^{2+}$, 0.2 M CH_3OH, 0.10 M $HClO_4$, 0.3–1.2 mM O_2, 25.0 °C.

strength ($HClO_4$ + $LiClO_4$) at constant [$HClO_4$] = 0.10 M. The data in Figure 3 yield $k_2 = 137 \pm 5$ M^{-1} s^{-1} at $\mu = 0.10$ M. The intercept k_0 is a summation of terms corresponding to the known hydrolysis of $CrCH_2OH^{2+}$ [8,9] and direct autoxidation of $CrCH_2OH^{2+}$, discovered in this work and described subsequently. As seen in Figure 3, the k_0 term 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 $k_2 = 140$ M^{-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+}, $k_2 = 122$ M^{-1} s^{-1} for a primary isotope effect of $k_H/k_D = 1.1$. However, the value of k_2 for the reaction of $CrCD_2OD^{2+}$ in D_2O is 76 M^{-1} s^{-1}, therefore for O-deuteration, the kinetic isotope effect is 1.8.

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 nonlinear.

The (Hydroperoxo)chromium(III) Ion. The identification of the chromium product as CrO_2H^{2+} is based on the following evidence. After completion of reaction 2, iodometric analysis of spent solutions confirmed the presence of 2 oxidizing equiv/mol 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^+, 50 mM I^-) is complete in a few seconds. The product is thus clearly not free H_2O_2, whose reaction with iodide was measured under identical conditions and required several hours for completion.

The most convincing evidence for this reaction being an *intact* one-electron reduction product of CrO_2^{2+} comes from its reaction with Ce(IV). When 1 equiv 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. Some decay of CrO_2H^{2+} takes place on the time scale of the experiment; see later.

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

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+}.

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

After reaction 2 is complete, the absorbance in the visible range decreases with a simultaneous loss of the oxidizing titer of the solution. We assign this process to the decomposition of CrO_2H^{2+}. The final spectrum is that of Cr^{3+}, although we cannot rule out the presence of some other low-absorbing chromium products. Figure 4 shows the spectrum measured immediately after completion of reaction 2, the final spectrum obtained 1.5 h later, and a difference spectrum of CrO_2H^{2+}. A complete study of the decomposition and reactivity of CrO_2H^{2+} will be reported elsewhere.[13]

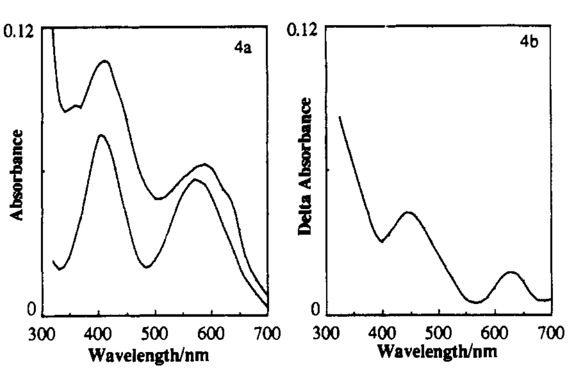

Figure 4. (a) Spectra of the reaction mixture recorded immediately after the catalytic reaction (upper line) and 1.5 h later (lower line). (b) Difference between the absorption spectra of CrO_2H^{2+} and its decomposition products, obtained by subtraction of the spectra in (a). The initial concentrations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

Uncatalyzed Reaction of $CrCH_2OH^{2+}$ with O_2. Air-free solutions of $CrCH_2OH^{2+}$ slowly decompose by acid-dependent acidolysis to yield Cr^{3+} and CH_3OH.[8,9] The decomposition of $CrCH_2OH^{2+}$ is strongly accelerated by O_2 and yields formaldehyde. At 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 1×10^{-3} and 8×10^{-3} s^{-1}. The reaction in the presence of O_2 appears to have a minor autocatalytic component, and the rate constant evaluated at the very 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+} (≤0.06 mM) 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.

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

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 chromium is present as Cr(III), formed both by parallel acidolysis of $CrCH_2OH^{2+}$ and by decomposition of CrO_2H^{2+}, which appears to be complete in less than 1 h. Since it requires ~10 min for the completion of reaction 7, 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, $CrCH_2OH^{2+}$ 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_0 were independent of the concentration of Fe^{2+} (1.0–100 mM) and yielded $k_{O_2} = 5.0 \pm 0.3$ M^{-1} s^{-1} in 0.10 M $HClO_4$ (Figure 5).

$$-d \ln [CrCH_2OH^{2+}]/dt = k_0 = k_a + k_{O_2}[O_2] \qquad (8)$$

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.

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[13] Scott, S. L.; Bakac, A.; Espenson, J. H. Work in progress.

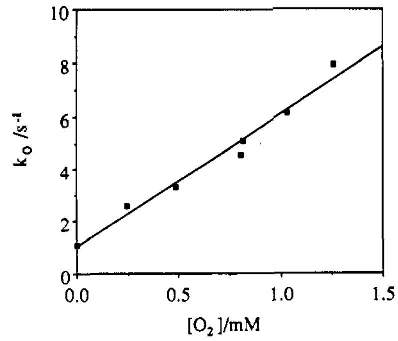

Figure 5. Dependence of the pseudo-first-order rate constant for the reaction between $CrCH_2OH^{2+}$ and O_2 on the concentration of O_2. Experimental conditions: 0.055 mM $CrCH_2OH^{2+}$, 0.10 M $HClO_4$, 70 mM CH_3OH, 1 mM Fe^{2+}, 25.0 °C.

First, the removal of O_2 converts the catalytic system of eq 2 into a noncatalytic one. The stoichiometry of eq 9 was determined

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

by spectrophotometric titration using CrO_2^{2+} as the titrant and by formaldehyde analysis. Both types of experiments were conducted at low concentrations of CH_3OH (0–0.01 M). In the presence of $\geq$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 mol/mol of $CrCH_2OH^{2+}$. Thus the reaction induces the oxidation of methanol (eq 10).

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

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 1) begins smoothly, as expected for the reaction of eq 2. As soon as O_2 is depleted, the absorbance drops abruptly, signaling that all the CrO_2^{2+} and an equivalent amount of $CrCH_2OH^{2+}$ have been consumed suddenly in reaction 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+},[14] the disappearance of CrO_2^{2+} at 290 nm occurred with a rate constant of 122 $M^{-1}\,s^{-1}$, a value close to that obtained in the catalytic system in the presence of O_2.

Discussion

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 $M^{-1}\,s^{-1}$ and k_{O_2} = 5.0 $M^{-1}\,s^{-1}$.

A straightforward mechanism for the catalyzed reaction that accommodates all the experimental observations is shown in eqs 11 and 1. The one-electron oxidation of $CrCH_2OH^{2+}$ by CrO_2^{2+}

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

produces Cr^{2+} and CrO_2H^{2+}. Cr^{2+} then reacts rapidly[7] with O_2 (k_1 = 1.6 × 10^8 $M^{-1}\,s^{-1}$) to regenerate the catalyst, CrO_2^{2+}. It is quite reasonable that the reaction of eq 11 should produce chromium 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, eqs 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^+.

$$CrO_2^{2+} + CrCH_2OH^{2+} \rightarrow CrO_2^{+} + CrCH_2OH^{3+} \quad (12)$$

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

$$CrCH_2OH^{3+} \rightarrow Cr^{2+} + CH_2O + H^+ \quad (14)$$

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 $M^{-1}\,s^{-1}$.[5c] Similarly, $Ru(bpy)_3^{3+}$ ($E°_{3+/2+}$ = 1.26 V)[16] oxidizes $CrCH_2OCH_3^{2+}$ to $CrCH_2OCH_3^{3+}$ with a rate constant k = 1.0 × 10^7 $M^{-1}\,s^{-1}$.[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 toward $CrCH_2OH^{2+}$ was to be expected.

Another feasible mechanism for reaction 2 is depicted in eq 15. The attack of CrO_2^{2+} at the alcohol OH group of $CrCH_2OH^{2+}$

$$CrCH_2OH^{2+} + CrO_2^{2+} \rightarrow [Cr{-}CH_2{-}O\cdots H\cdots O{-}O{-}Cr]^{4+} \rightarrow Cr^{2+} + CH_2O + HO_2Cr^{2+} \quad (15)$$

results in hydrogen transfer that yields CrO_2H^{2+}. The other products, CH_2O and Cr^{2+}, can be formed either in a concerted manner (eq 15) or by a rapid subsequent decomposition of the transient $CrCH_2O^{2+}$.

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 alcohol 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 of $k_H/k_D > 1$ for $CrCD_2OD^{2+}$. The observed effect is, however, a composite of the solvent effect, the 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 $M^{-1}\,s^{-1}$, 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,

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

and O_2^-. The latter would be converted rapidly to HO_2 and disproportionate[19] to O_2 and H_2O_2, or it might oxidize a second molecule or $CrCH_2OH^{2+}$.

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(18) The potential for the couple $([14]aneN_4)CoO_2^{2+/+}$ has been estimated[3c] as 0.3 ± 0.1 V. The potential of the $CrO_2^{2+/+}$ couple is probably not very different, given that the rate constants for the oxidation of the three reductants by CrO_2^{2+} [5c] and $([14]aneN_4)CoO_2^{2+}$ [3c] are remarkably similar.

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Most of the major chromium product, CrO_2H^{2+}, thus had to be formed by a route different from the CrO_2^{2+}-catalyzed reaction 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 in effect by a hydrogen atom abstraction by molecular oxygen.

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

It has been proposed previously[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 1 equiv of Ce(IV) leaves little doubt about the identity of this species.[21] The spectral features (Figure 4) are as expected for an inorganic, weakly absorbing chromium(III) complex, and the molecule is probably best described as a (hydroperoxo)chromium(III) species. The only uncertainty associated with this species seems to be the level of protonation in the acidity range studied, 0.1-1 M H^+. Assuming that coordination of 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 2 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 $Fe(H_2O)_6^{3+}$ ($\rightleftarrows Fe(H_2O)_5OH^{2+} + H^+$; pK_a 3) and $(H_2O)_5Fe(H_2O_2)^{3+}$ ($\rightleftarrows (H_2O)_5FeO_2H^{2+} + H^+$; pK_a 1.2)[22] differ by less than 2 pK units. We can thus assume with some confidence that the pK_a of $Cr(H_2O_2)^{3+}$ is 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.

To our knowledge CrO_2H^{2+} is only the second example of an end-bonded (hydroperoxo)metal complex that is long-lived in aqueous solution. The chemistry of the other example, $([14]\text{aneN}_4)CoO_2H^{2+}$,[3b,23] has been explored only marginally.

Effect of Alcohols on 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) show clearly that at least one reaction intermediate reacts with alcohols. Even more surprising was the finding that additional CrO_2^{2+} was found 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+} and 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 two have been prepared independently,[28,29] but they *have not* been observed directly in the autoxidation process. The last, 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]

None of the long-lived oxidizing species (CrO_2^{2+}, CrO_2Cr^{4+}, and $CrOCr^{4+}$) react with alcohols. Also, $HCrO_4^-$, which might be present in small concentrations,[5] is unreactive on these time scales.[30]

We have recently reported that the reaction of Cr^{2+} with O_2 leads to formation of the surprisingly long-lived oxochromium(IV) ion, CrO^{2+} ($t_{1/2}$ ~40 s at 25 °C).[31] CrO^{2+} reacts with methanol and other alcohols in a two-electron process which yields Cr^{2+} as the immediate product. In the presence of excess O_2, Cr^{2+} is trapped and becomes CrO_2^{2+}. The effect of methanol is therefore to convert CrO^{2+} into CrO_2^{2+} (Scheme I). 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

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

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

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

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] 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, 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. We favor the initial formation of an oxygen-bridged intermediate (or transition state), as proposed previously.[5,24] The intermediate then either cleaves spontaneously or reacts with additional Cr^{2+} [5] to yield CrO^{2+}. If the former path should operate, the intermediate CrO_2Cr^{4+} produced in reaction 18 would have to be an isomer of the known species of the same formula,[28] since the latter does not yield CrO^{2+} nor does it react with alcohols.

Although the oxochromium(IV) ion, CrO^{2+}, has until now been an elusive species, the long-lived 4+ oxidation state is not unknown in chromium chemistry. The reaction of $(TPP)Cr^{III}$ (TPP = dianion of tetraphenylporphyrin) with O_2 in toluene has been reported[32] to yield a stable chromyl complex that has been characterized crystallographically. Alternative routes to this and other chromyl porphyrin complexes have since been reported.[33-35] Other stable chromium(IV) compounds include tetraalkoxides, tetraalkyls, and tetrakis(dialkylamides).[36] Also, diperoxochromium(IV) complexes are quite stable in aqueous solution[37] and a transient chelated chromium(IV) has recently been observed.[38]

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, occurs under air-free conditions. The scavenging effect of $(NH_3)_5CoF^{2+}$, which lowers the rate constant to the value of that

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for reaction 11, strongly implicates Cr^{2+} as a crucial intermediate. The effect of methanol 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 II)

Scheme II

chain initiation

$$CrO_2^{2+} + CrCH_2OH^{2+} \rightarrow Cr^{2+} + CH_2O + H_2O \quad (11)$$

chain propagation

$$CrO_2^{2+} + Cr^{2+} \rightarrow nCrO^{2+} \quad (18)$$

$$CrO^{2+} + CrCH_2OH^{2+} \xrightarrow{H^+} Cr^{2+} + Cr^{3+} + CH_2O + H_2O \quad (20)$$

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 20). Although we have very little information on reaction 20, we expect it to yield Cr^{2+}, irrespective of whether the reaction takes place by a one- or two-electron pathway. A complete study of the air-free reaction between CrO_2^{2+} and $CrCH_2OH^{2+}$ and of reactions 18 and 20 is in progress.[13]

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Registry No. CrO_2^{2+}, 115185-67-6; $CrCH_2OH^{2+}$, 32108-95-5; $CrCD_2OD^{2+}$, 136358-09-3; CrO_2H^{2+}, 136358-10-6; CH_2O, 50-00-0.

Contribution from the Department of Medicinal Chemistry, Hiroshima University, School of Medicine, Kasumi, Minami-ku, Hiroshima 734, Japan, Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

The First Gold(III) Macrocyclic Polyamine Complexes and Application to Selective Gold(III) Uptake

Eiichi Kimura,*,†,‡ Yasuhisa Kurogi,† and Toshikazu Takahashi†

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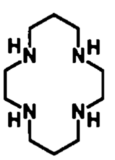
The hitherto unreported gold(III) macrocyclic polyamine complexes **12**, **14**, **18**, **19**, **23**, and **24** with cyclam (1,4,8,11-tetraazacyclotetradecane, **1**), phenol-pendant cyclam **2**, pyridyl-pendant cyclam **3**, monooxocyclam **4**, phenol-pendant monooxocyclam **5**, and pyridyl-pendant monooxocyclam **6** have been synthesized and characterized. Dissociation of a proton from one of the secondary amines in the "Au^{III}-in" cyclam complexes **12**, **14**, and **18** readily occurs with pK_a values of 5.0–5.4 at 25 °C and $I = 0.1$ ($NaClO_4$). Although monooxocyclam **4** does not accommodate Au(III), the donor-pendant monoxocyclams **5** and **6** enclose Au(III) with concomitant dissociation of an amide proton to yield **23** and **24**, respectively. As anticipated for the diamagnetic d^8 complexes, the pendant donors only weakly interact from an axial site. The extraordinary acidity of Au(III) over other common metal ions in interaction with cyclam can be utilized for selective uptake of Au(III) with lipophilic cyclam derivatives **9** and **10**.

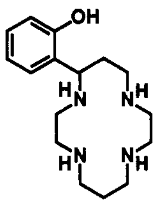
Introduction

Although cyclam (1,4,8,11-tetraazacyclotetradecane, **1**) has been widely used to sequester metal ions,[1] its complex with Au(III) is unknown. This is very puzzling in the light of the well-documentable Au(III) ability to form square-planar tetraamine (e.g. tetraamine, bis(ethylenediamine)) complexes.[2-4]



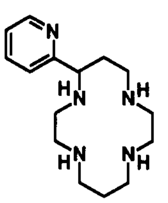
1

Cyclam



2

Phenol-pendant cyclam



3

Pyridyl-pendant cyclam

We now have isolated the Au(III)–cyclam complex **12**. Its characterization has disclosed a rigid N_4 square planarity and strong acidity of Au(III). This encouraged us to study more about the Au(III) complexation with phenol-pendant cyclam **2**,[5-11] pyridyl-pendant cyclam **3**,[12-14] and the corresponding monooxocyclams **4–6**,[15-18] which were extremely useful in defining the acidic and coordinating properties of Cu^{II},[7,10,14,16] Ni^{II},[6-10,12-14,16,17] or Zn^{II}.[7,11,18] We were also interested in how the Au(III) acidity is reflected in the smaller macrocyclic ring **7**. As the Au(III) interaction mode with macrocyclic tetraamines was disclosed, an application of cyclam derivatives **9–11** for Au(III) uptake has been investigated. The results have proved the macrocyclic polyamines

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‡ Institute for Molecular Science.

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