Chromium Complexes Derived from Molecular Oxygen

ANDREJA BAKAC* AND JAMES H. ESPENSON*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Molecular oxygen is a complex chemical reagent. Nowhere is this more clearly seen than when O_2 reacts with transition metal complexes. Water results from breaking the oxygen–oxygen bond and making four O–H bonds. This does not mesh well mechanistically with the electron-transfer oxidation of $ML_6{}^n$ to $ML_6{}^{n+1}$. If the metal ion does indeed react by electron transfer, then the oxygen reaction produces a succession of three unstable, reactive intermediates. They are in order the hydroperoxyl radical or the superoxide radical ion, hydrogen peroxide, and the hydroxyl radical. More often, however, the metal complexes bind various oxygen-containing entities—those mentioned above or their relatives.

We plan to emphasize the reaction of chromium(II) with oxygen, which is a complicated, multistep process with several intermediates. They are, without commitment as to the number of solvent molecules coordinated, $CrOO^{2+}$ (superoxo, hereafter $CrO_2{}^{2+}$), CrO^{2+} (oxo), $CrOOH^{2+}$ (hydroperoxo, hereafter CrO_2H^{2+}), and $CrOOCr^{4+}$ (μ-peroxo). Some mention will also be made of $CrOCr^{4+}$ (μ-oxo).

One can identify so many species in this system because chromium(III) is kinetically inert to ligand substitution. The conclusions drawn for chromium may then be extended, one hopes, to metal complexes that exchange or dissociate ligands rapidly. An Account at this time seems useful because oxygen chemistry is involved in many biological and industrial reactions. Also, the subject has now advanced to the point where

meaningful conclusions can be drawn concerning the intermediates and their reactions.

Historical Background. The aqueous O_2–Cr^{2+} reaction was first examined about eighty years ago.[1] This early work provided evidence for the intervention of two intermediates, both more highly oxidizing than chromium(VI). The product is mainly Cr(III), but variable concentrations of Cr(VI) are formed depending on the Cr^{2+} and O_2 concentrations and their ratio. Ion-exchange chromatography and oxygen-18 labeling were used to determine that the major chromium(III) product is the dimetallic species $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$, accompanied by a lesser amount of $[(H_2O)_5Cr(\mu\text{-}O)\text{-}Cr(OH_2)_5]^{4+}$.[2,3]

The superoxochromium(III) ion, $(H_2O)_5CrO_2{}^{2+}$, is the initial product of the 1:1 reaction between Cr^{2+} and O_2 in acidic, aqueous solution. Owing to the large equilibrium constant for its formation, solutions of $CrO_2{}^{2+}$ can be handled even under oxygen-free conditions. This presents a great advantage in mechanistic studies of its stoichiometric and catalytic reactions.

Resonance Raman spectroscopy revealed an O–O stretching vibration at 1165 cm^{-1}, which identified this as due to a superoxide ion, not peroxide. By comparison to complexes with known structures, we concluded that it is bound end-on.[4] For that reason we presume that five water molecules complete the coordination number of six invariably found for Cr(III). The magnetic moment of the closely related macrocyclic complex[4] $(H_2O)([14]aneN_4)CrO_2{}^{2+}$ shows the presence of four unpaired electrons, consistent with the constituents being Cr(III) and $O_2{}^{\bullet-}$. The UV spectrum of $(H_2O)_5$-

Dr. Andreja Bakac received her B.S. and Ph.D. degrees from the University of Zagreb, Croatia, under the supervision of Dr. Matko Orhanovic. She came to the Ames Laboratory at Iowa State University in 1976 and now holds the rank of Scientist.

Dr. James H. Espenson received his B.S. degree from Caltech and Ph.D. from the University of Wisconsin (with Edward L. King). After a postdoctoral year at Stanford University (with Henry Taube) he joined Iowa State University in 1963. He is currently Distinguished Professor of Chemistry.
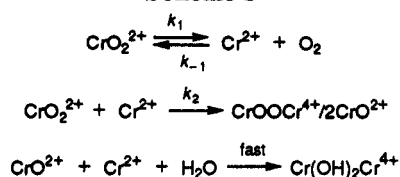
(1) Picard, J. *Ber.* 1913, *56*, 2477.
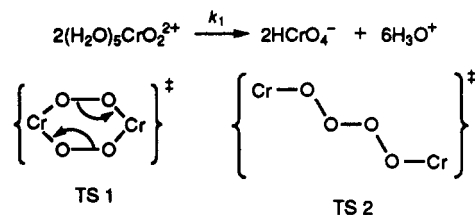(2) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* 1959, *81*, 3197.
(3) Kolaczkowski, R. W.; Plane, R. A. *Inorg. Chem.* 1964, *3*, 322.
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Scheme I

$$CrO_2^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{2+} + O_2$$

$$CrO_2^{2+} + Cr^{2+} \xrightarrow{k_2} CrOOCr^{4+}/2CrO^{2+}$$

$$CrO^{2+} + Cr^{2+} + H_2O \xrightarrow{fast} Cr(OH)_2Cr^{4+}$$

Scheme II

$$2(H_2O)_5CrO_2^{2+} \xrightarrow{k_1} 2HCrO_4^- + 6H_3O^+$$

$$\left[\begin{array}{c} Cr \cdots O \cdots O \\ \\ O \cdots O \end{array} Cr \right]^{\ddagger} \qquad \left[\begin{array}{c} Cr-O \\ O-O \\ O-Cr \end{array} \right]^{\ddagger}$$

TS 1   TS 2

CrO_2^{2+} shows two intense absorptions at 290 nm (ϵ 3.1 $\times 10^3$ L mol^{-1} cm^{-1}) and 245 nm (7.0 $\times 10^3$ L mol^{-1} cm^{-1}). The 245-nm band is like that of $O_2^{•-}$; its existence is further evidence for the valence assignment given; it was used for the resonance excitation in the Raman experiment. The 290-nm band appears to have ligand-to-metal charge-transfer character; irradiation at this wavelength decomposes the complex by photohomolysis to Cr^{2+} and O_2.

The rate constant for CrO_2^{2+} formation in the reaction of Cr^{2+} and O_2, see Scheme I, is $k_{-1} = 1.6 \times 10^8$ L mol^{-1} s^{-1} at 25 °C, determined by pulse radiolysis[5,6] and flash photolysis. Because of certain side reactions, the maximum concentration of CrO_2^{2+} formed when the two reagents are mixed in water at pH 0–2 is ca. 10^{-4} M. With 0.01–0.1 M methanol or other alcohol added, however, concentrations of CrO_2^{2+} of $\sim 10^{-3}$ M can be realized. The effect of methanol will be discussed later. The best yields are obtained when O_2 is in large excess; the complex cannot tolerate Cr^{2+}, with which it reacts.

The decomposition of $(H_2O)_5CrO_2^{2+}$, which takes place over a few hours, occurs by two parallel pathways.[7] One sequence starts with the homolysis of the complex (Scheme I); the other, with a bimolecular reaction between two superoxo complexes (Scheme II). The first pathway yields $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$, the second $HCrO_4^-$. We suggest two possible transition states, TS 1 and TS 2, for the chromate-forming path.

By these two pathways, the rate of loss of CrO_2^{2+} is[7]

$$-\frac{d[CrO_2^{2+}]}{dt} = \frac{2k_1[CrO_2^{2+}]}{1 + k_{-1}[O_2]/k_2[CrO_2^{2+}]} + 2k_3[CrO_2^{2+}]^2 \tag{1}$$

Experiments over a wide range of $[CrO_2^{2+}]$ and $[O_2]$, including some in the absence of O_2 and others with $p(O_2) > 1$ atm, were used to verify this form.[7] The rate constants at 25 °C are $k_1 = 2.5 \times 10^{-4}$ s^{-1}, $k_3 = 6.0$ L mol^{-1} s^{-1}, and $k_2 \simeq 8 \times 10^8$ L mol^{-1} s^{-1}; k_{-1} was fixed at the independently-determined value.

The first step of Scheme I produces Cr^{2+}, which either regenerates CrO_2^{2+} (k_{-1}) or reacts with CrO_2^{2+} (k_2). Not all of the stepwise details of the CrO_2^{2+}–Cr^{2+} reaction, with its CrO^{2+} intermediate, are known; the reactants are ultimately consumed in a 1:3 ratio, as in eq 2. The reaction occurs so rapidly that it imposes a limit on the

$$CrO_2^{2+} + 3Cr^{2+} + 2H_2O \rightarrow 2Cr(OH)_2Cr^{4+} \tag{2}$$
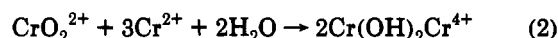
yield of CrO_2^{2+} since O_2 and CrO_2^{2+} compete for Cr^{2+}. In aqueous alcohols, on the other hand, the intermediate CrO^{2+} is converted to CrO_2^{2+} when O_2 is present, by a reaction presented subsequently. Addition of an alcohol thus enhances the yield and increases the lifetime of CrO_2^{2+} in the presence of O_2.[8]

The path that forms chromate(VI) ions becomes more prevalent at high $[O_2]$ and high $[CrO_2^{2+}]$, as indicated by eq 1.[7] Although CrO_2^{2+} and $HCrO_4^-$ are in one sense at the same formal oxidation state of chromium, as indicated by the equation $(H_2O)_5CrO_2^{2+} \rightarrow HCrO_4^- + 3H_3O^+$, this equation is of no mechanistic significance since the rate of $HCrO_4^-$ formation is proportional to $[CrO_2^{2+}]^2$. The transformation suggested by the transition state TS 1 in Scheme II would require the subsequent expulsion of coordinated H_2O and H_3O^+, which should not pose a significant barrier. The alternative version of the transition state, TS 2, resembles that for the decomposition of alkylperoxyl radicals.[9] This is clearly an attractive possibility since CrO_2^{2+} can be considered an inorganic analogue of $RO_2^•$. We are unable to choose between the two transition states, and the matter is currently under examination with, in part, the use of oxygen-18 labeling.

The thermodynamic stability of $(H_2O)_5CrO_2^{2+}$ in a *homolytic* sense is measured by the equilibrium constant for eq 3. The kinetic formulation in Scheme I identifies this to be k_{-1}/k_1; its value is 6×10^{11} L mol^{-1} at 25 °C.

$$Cr(H_2O)_6^{2+} + O_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} (H_2O)_5CrO_2^{2+} + H_2O \tag{3}$$
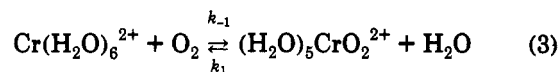
From this and the known electrode potentials for the couples $O_2/O_2^{•-}$ (–0.16 V vs NHE with 1 M O_2 as standard state) and Cr^{3+}/Cr^{2+} (–0.42 V) we have calculated the equilibrium constant for the *heterolytic* process. This gives for eq 4 an equilibrium constant of $K_4 = 3 \times 10^7$ L mol^{-1}.

$$Cr(H_2O)_6^{3+} + O_2^{•-} \rightleftharpoons (H_2O)_5CrO_2^{2+} + H_2O \tag{4}$$
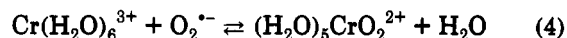
These are thermodynamic formulations, and the relative equilibrium constants do not, of course, determine the reaction pathway. Although the heterolytic decomposition of CrO_2^{2+} is the more favorable thermodynamically, no evidence for it has been obtained. Likewise, a reaction between chromium(III) and superoxide ions has never been observed.

What is special about reaction 4 is the magnitude of the binding constant for superoxide ions compared to those for other anions. The affinity of $Cr(H_2O)_6^{3+}$ for superoxide ion ($K_4 = 10^{7.2}$) greatly exceeds that for fluoride ($K = 10^{4.4}$)[10] and acetate ions ($K = 10^{4.7}$).[11] With respect to the binding of protons, however, the three acids have comparable pK_a's: 4.7 (HO$_2^•$), 3.2 (HF), and 4.7 (HOAc). As expected, OH$^-$ binds to Cr^{3+} more

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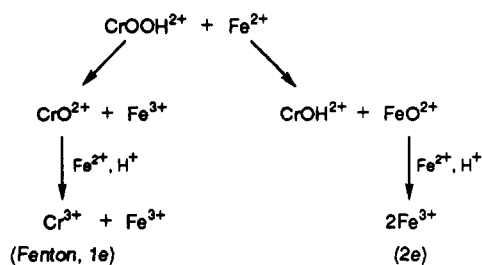
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Scheme III

$$CrOOH^{2+} + Fe^{2+}$$

$$CrO^{2+} + Fe^{3+} \qquad CrOH^{2+} + FeO^{2+}$$

$$\downarrow Fe^{2+}, H^+ \qquad\qquad \downarrow Fe^{2+}, H^+$$

$$Cr^{3+} + Fe^{3+} \qquad\qquad 2Fe^{3+}$$

(Fenton, 1e)   (2e)

strongly ($K = 10^{10}$) than do any of the anions mentioned. The "extra" stability of superoxide complexes is even more prevalent for $(H_2O)Co([14]aneN_4)O_2{}^{2+}$. The parent cobalt(III) complex binds superoxide ($K = 10^{15.1}$)[12,13] more favorably than even hydroxide ($K = 10^{11}$), let alone fluoride and acetate ions. The extra stabilization of $MO_2{}^{2+}$ ions may arise from resonance forms like $M^{IV}(O_2{}^{2-})$.[12a]

The hydroperoxochromium(III) ion, CrO_2H^{2+}, is formed by the reduction of the superoxide complex with one-electron donors. The best yields of the hydroperoxide complex are obtained with a reducing agent like $Ru(NH_3)_6{}^{2+}$ (eq 5, $k_5 = 9.5 \times 10^5$ L mol^{-1} s^{-1}). The virtue of the ruthenium reagent is that it does not react further with CrO_2H^{2+}.[14] Several other reagents (such as $Fe_{aq}{}^{2+}$, eq 6) adopt an inner-sphere mechanism.[14]

$$CrO_2{}^{2+} + Ru(NH_3)_6{}^{2+} \overset{H^+}{\rightarrow} CrO_2H^{2+} + Ru(NH_3)_6{}^{3+} \qquad (5)$$

$$CrO_2{}^{2+} + Fe(H_2O)_6{}^{2+} \rightarrow [_{aq}CrOOFe_{aq}]^{4+} \overset{H^+}{\rightarrow} CrO_2H^{2+} + Fe^{3+} \qquad (6)$$
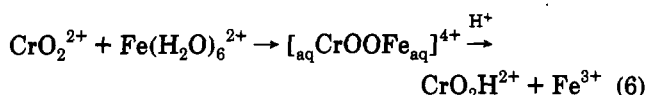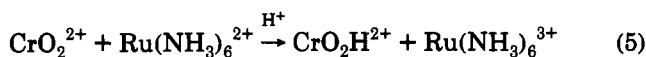
Reduction of CrO_2H^{2+} to Cr^{3+} is brought about by the same set of metal complexes that reduce hydrogen peroxide. They include $V_{aq}{}^{2+}$, VO^{2+}, $Co(cyclam)^{2+}$, $Ti_{aq}{}^{3+}$, and $Fe_{aq}{}^{2+}$. The reaction of CrO_2H^{2+} with $Fe(H_2O)_6{}^{2+}$ provides a good example,[15] and many others are analogous to it. The net reaction occurs with 1:2 stoichiometry (eq 7). The intriguing question is whether

$$CrO_2H^{2+} + 2Fe^{2+} + 3H^+ \rightarrow Cr^{3+} + 2Fe^{3+} + 2H_2O \qquad (7)$$
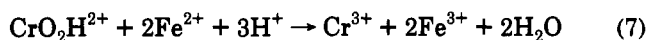
or not the reactions adopt the Fenton mechanism, a single-electron process. If so, then the chromyl ion (in this context, the chromium analog of the hydroxyl radical) is formed as an intermediate. Otherwise, a two-electron process with a ferryl intermediate may occur. These possibilities are diagrammed in Scheme III.

The Fenton mechanism has now been verified for the reactions of CrO_2H^{2+} with numerous reagents. The evidence consists of coincident isokinetic plots for these reactions and for hydrogen peroxide, which adopts the
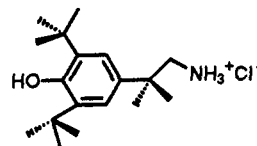
Fenton mechanism with the reagents listed.[16] Also, the oxochromium(IV) ion can be trapped by the hydrogen oxalate ion and by the water-soluble tri-*tert*-butylphenol[17] shown with the same competition ratios as found for the authentic CrO^{2+}, which shows that it is an intermediate here.[15]

The hydroperoxochromium(III) ion shows the same reactivity pattern and nearly the same absolute reactivity as does hydrogen peroxide.[18,19] One might have expected a much enhanced reactivity of CrO_2H^{2+} given that the highly electrophilic, tripositive metal ion replaces one hydrogen of the latter. However, the gas-phase ionization potentials, the solution reduction potentials, and the (estimated) acidity constants of the species involved all point to H_2O_2 being a better one-electron oxidant than CrO_2H^{2+}.

Those metal complexes that do not have an accessible primary coordination sphere, such as $Ru(NH_3)_6{}^{2+}$ and $Co(sepulchrate)^{2+}$, do not react with CrO_2H^{2+}. This is a characteristic of hydrogen peroxide and of species that resemble it.[18,20,21]

The oxochromium(IV) or chromyl ion, CrO^{2+}, was identified long ago as a transient in the reduction of chromium(VI)[22] and in the oxidation of chromium(III).[23] It had been trapped chemically (e.g., by Mn^{2+}) and proposed[2] to yield $(H_2O)_4Cr(OH)_2Cr(H_2O)_4{}^{4+}$ upon reduction with Cr^{2+}, but it had hitherto not been observed directly. Some chromium(IV) complexes stabilized by complexation to ligands like porphyrins[24] and 2-ethyl-2-hydroxybutyrate[25] have been studied, although the act of stabilization destroys much of its inherent reactivity.

We have developed four independent reactions to produce the chromyl ion directly, in the absence of stabilizing ligands. The species so obtained lasts for only a few minutes, but this is sufficient time in which to characterize its reactivity. These four reactions are shown in Scheme IV. Each of these reactions produces, insofar as we can tell by the UV spectrum and the reaction rates, the same reactive chromyl ion.

(12) (a) Taube, H. *Prog. Inorg. Chem.* **1986**, *34*, 607. (b) Wong, C. L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

(13) An earlier report,[7] based on the data in ref 12b, gives $K_4 = 10^{13.8}$. The use of the new data [Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1990**, *121*, 2273] for oxygen binding to $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$ yields $K_4 = 10^{15.1}$.

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(15) Wang, W.-D.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1993**, *32*, 2005.

(16) Wang, W.-D.; Bakac, A.; Espenson, J. H. *Inorg. Chem.*, in press.

(17) The water-soluble phenol is [2-methyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl]ammonium chloride: Traylor, T. G.; Lee, W. A.; Stynes, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 755. Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1990**, *112*, 178.

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(25) (a) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679. (b) Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1991**, *30*, 1039 and references therein.

Scheme IV

Scheme V
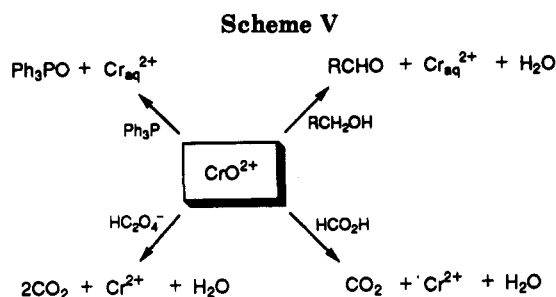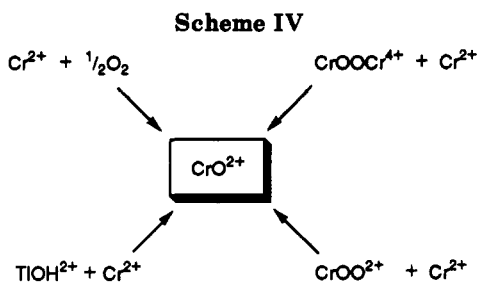
The formulation of the chromium(IV) entity as an oxo cation is based on chemical arguments, not direct proof. It is believed to be analogous to the adjacent vanadyl ion, and its chemical reactions are consistent with the formula CrO^{2+}.

The oxochromium(IV) ion oxidizes triphenylphosphine by transfer of an oxygen atom.[26] It reacts with alcohols and aldehydes as a *hydride ion* acceptor. In these reactions the immediate chromium product is *divalent* chromium, Cr^{2+}. That is to say, these reactions bypass chromium(III), despite its thermodynamic stability. Scheme V diagrams the reactions that are being referred to.

The generation of Cr^{2+} was demonstrated by chemical trapping.[26] Molecular oxygen was used to convert it to CrO_2^{2+}, a species easily recognized by its UV spectrum. Thus when each of the reactions in Scheme V was run in an oxygen-saturated solution, CrO_2^{2+} was obtained in *quantitative* yield.[26] Since in these experiments CrO_2^{2+} is formed only when O_2 is present, this establishes chromium(II) ion as an intermediate. Of course, if one uses a distinctly one-electron reagent, such as Fe^{2+}, then the product of the CrO^{2+} reactions is chromium(III).[15]

The oxidations of alcohols by CrO^{2+} show a significant kinetic isotope effect when the α-hydrogen atom is deuterated; $k_H/k_D = 2.6$–3.5. This is consistent with a *hydride ion* abstraction mechanism, but not unique proof of it; the transition state that we have proposed[26] is the following:
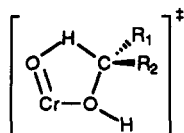
The alternative, hitherto[22] regarded as the likely mechanism by which chromium(IV) oxidizes alcohols and other organic compounds, is a single-electron process. In it, a *hydrogen atom* would be transferred. The structure of the transition state might in general terms be as shown above, but its consequence would be

(26) Scott, S. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 4205.

Scheme VI
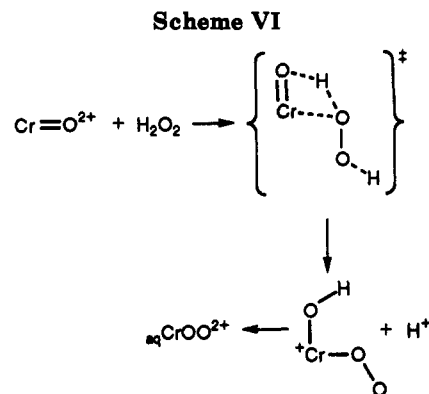
the formation of chromium(III) and an aliphatic radical rather than chromium(II) and the carbonyl compound. These alternatives are shown in eqs 8a and 8b. Radicals

$$CrO^{2+} + RCH_2OH \rightarrow CrOH^+ + RCHO + H^+ \quad (8a)$$

$$CrO^{2+} + RCH_2OH \rightarrow CrOH^{2+} + RC^\bullet HOH \quad (8b)$$

cannot be trapped in this reaction, and the rate constants vary little from one alcohol to the next. This is a powerful argument against reaction 8b, since the greatly differing stability of an incipient radical would be expected to show up in the kinetics.

As it turns out, eq 8a is also favored thermodynamically, although of course the kinetic preference need not be the same as the thermodynamic one. Given the one-electron potentials for Cr^{3+}/Cr^{2+} (-0.42 V) and $^\bullet CH_2OH/CH_3OH$ (1.29 V),[27] and taking into account the difference in the degree of hydrolysis of the chromium products, it can be shown, by means of the Nernst equation, that the standard free energy change of eq 8a is more favorable than that of eq 8b by 28 kJ mol^{-1} for R = H.[26]

Having thus established the preferred pathway between chromium(IV) and alcohols, we return to the old question[22] of the details of the mechanism by which chromium(VI) oxidizes alcohols. We ran the reaction of $HCrO_4^-$ and 2-propanol in 2 M perchloric acid under an oxygen atmosphere, specifically to look for CrO_2^{2+}. It is indeed formed, and in quantitative yield. This shows that the chromium(IV) intermediate in the oxidation chemistry behaves the same as the one prepared by the routes in Scheme IV. We take this as proof of the sequence $Cr^{VI} \rightarrow Cr^{IV}O^{2+} \rightarrow Cr^{2+} \rightarrow CrO_2^{2+}$.
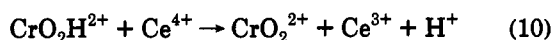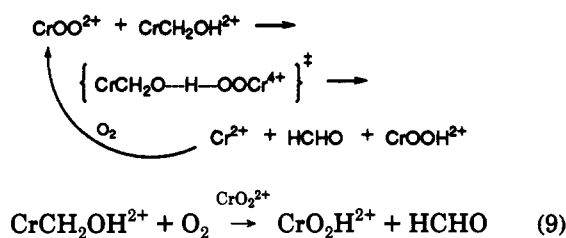
The oxochromium(IV) ion reacts with hydrogen peroxide to form the superoxochromium(III) ion. This happens not only in the presence of O_2, but also in its absence. Thus chromium(II) is not itself an intermediate. The mechanism proposed for this reaction is shown in Scheme VI.[28]

The oxidation of $(H_2O)_5CrCH_2OH^{2+}$ by O_2 is catalyzed by CrO_2^{2+}. The reaction forms the hydroperoxochromium(III) ion, according to the (approximate) stoichiometry given by eq 9. This product was reoxidized to CrO_2^{2+} by Ce^{4+} (eq 10), which shows that the CrOO unit remained intact, at least briefly, following the catalyzed oxygen reaction. Scheme VII shows the

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(28) Al-Ajlouni, A. M.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1993**, *32*, 3162.

Scheme VII

$$CrOO^{2+} + CrCH_2OH^{2+} \longrightarrow$$

$$\left\{ CrCH_2O\text{---}H\text{---}OOCr^{4+} \right\}^{\ddagger} \longrightarrow$$

$$O_2 \qquad Cr^{2+} + HCHO + CrOOH^{2+}$$

$$CrCH_2OH^{2+} + O_2 \xrightarrow{CrO_2^{2+}} CrO_2H^{2+} + HCHO \qquad (9)$$

$$CrO_2H^{2+} + Ce^{4+} \rightarrow CrO_2{}^{2+} + Ce^{3+} + H^+ \qquad (10)$$

mechanism that we have suggested.[29] This system catalyzes the concurrent oxidation of methanol, but rather inefficiently.

Surprisingly, the oxygen-free system of $CrO_2{}^{2+}$ and $CrCH_2OH^{2+}$ reacts more rapidly than when O_2 is present. A chain reaction occurs; scavenging experiments suggest that Cr^{2+} is a chain-carrying intermediate. The suggested mechanism[29] is depicted in Scheme VIII.

The (μ-peroxo)dichromium(4+) ion, [(H₂O)₅-CrOOCr(OH₂)₅]⁴⁺, was obtained along with other complexes from the reaction of hydrogen chromate ions with hydrogen peroxide.[30] It was not found in any of our work on the $Cr^{2+}O_2$ system, but this may not be definitive if it is destroyed by rapid, subsequent reactions. Its independently-detected fast reaction with Cr^{2+} (Scheme IV) is an example of why it might not be observed. We should comment, however, that $CrOOCr^{4+}$ does not decompose to CrO^{2+}. Therefore, the CrO^{2+} that results from Scheme I is formed either directly or in a very rapid reaction of a nonaccumulating intermediate.
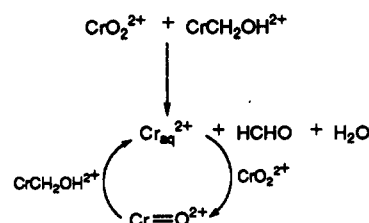
The decomposition of the oxochromium(2+) ion has not been studied in sufficient detail to identify the products and intermediates, let along a detailed mechanism. The possibility of an intermediate peroxo complex needs to be considered, albeit as a long shot.

The species claimed[31] to be $_{aq}CrOCr_{aq}{}^{4+}$ has been shown to be a semiquinone complex.[32] There is every

Scheme VIII

$$CrO_2{}^{2+} + CrCH_2OH^{2+}$$

$$\downarrow$$

$$Cr_{aq}{}^{2+} + HCHO + H_2O$$

$$CrCH_2OH^{2+} \Big(\qquad \Big) CrO_2{}^{2+}$$

$$Cr{=}O^{2+}$$

reason to expect that a μ-oxo species exists, in that ligand-stabilized versions of it are now well-known.[33] Among the hydrolytic dimers of chromium(III) is a protonated form of it.[34,35] It remains to be seen whether it can be formed by the reaction of CrO^{2+} with Cr^{2+}.

To Summarize and Speculate. In the final analysis, the chromium(II) ion does not opt for simple electron transfer in its reaction with O_2; were that so, $Cr(H_2O)_6{}^{3+}$ would be the product. This O_2 reaction begins, as so many do, with binding to the metal. Then the second feature of chromium chemistry comes into play—its kinetic inertness toward ligand substitution. Thus a long-lived $CrO_2{}^{2+}$ results, which, like its analog $HO_2{}^{\bullet}$, shows considerable oxidizing ability. A considerable concentration of CrO^{2+} can be realized. It is the Lewis analog of the hydroxyl radical and a strong but less powerful oxidizing agent. The incorporation of the transition metal center enriches the chemistry of CrO^{2+}, however, and it can abstract hydride ion from some reagents, which $HO^{\bullet}$ cannot.

Since the ultimate product of the $Cr^{2+}-O_2$ reaction is known to be $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$, we must wonder whether it results more or less directly from the reaction of CrO^{2+} and Cr^{2+}. We do know that the reaction of Tl^{3+} with Cr^{2+} eventually forms the di-μ-hydroxo complex; this work has shown the CrO^{2+} is formed in the first step. This route to the eventual product remains a very real possibility.

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