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Impact of Chromium Coordination on the Single-Electron Potentials for the Reduction of Oxygen to Water

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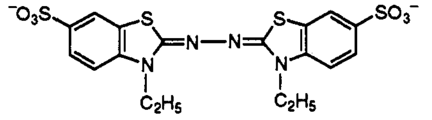
Abstract: Chemical equilibration of $CrOO^{2+}$ has allowed evaluation of the potential for the half-reaction $CrOO^{2+} + H^+ + e^- \rightarrow CrOOH^{2+}$ as +0.82 V *vs* NHE. Kinetic data for the reaction of CrO^{2+} and H_2O_2 allow refinement of the potential for the $CrO^{2+} + 2H^+ + e^- \rightarrow Cr^{3+} + H_2O$ reaction to lie within the range $1.71\ \text{V} \le E° \le 1.85$ V. With these values the potentials for each step of reduction of water to oxygen, as mediated by chromium complexation, are obtained. The chemical implications of these findings for the reactions and reactivity of the three chromium-containing species $CrOO^{2+}$, $CrOOH^{2+}$, and CrO^{2+} are presented.

Introduction

The activation of oxygen by metal ions and metal complexes continues to be an active field of investigation. It certainly holds large-scale commercial importance, especially for the autoxidation of alkyl benzenes catalyzed by cobalt salts and promoted by manganese salts.[1,2]

Those metal complexes that facilitate the reduction of O_2 appear to initiate this process by metal–oxygen binding.[3] It is useful, therefore, to examine the effect of the metal on the thermodynamics of the stepwise process of oxygen reduction to water. The goal is to learn the ways in which the particular metal may alter the potentials for each of the four steps of the single-electron cascade. It seems that aquachromium ions provide the only system as yet studied in sufficient detail to allow this analysis. We are now able to construct the full sequence, thanks to some additional findings obtained from equilibration experiments. These determinations employed $ABTS^{2-}$ (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate)), since its acid ionization constant, standard reduction potential, and absorption spectrum are well-known.[4–6]



$ABTS^{2-}$

Sufficient data are now available[7–17] for the species $CrOO^{2+}$, $CrOOH^{2+}$, and $Cr{=}O^{2+}$ to allow a complete breakdown of the single-electron steps. We shall present the equilibration results for reaction 1, the analysis of all the available thermodynamic data in the chromium–oxygen system, and the implications for the chemistry of oxygen–chromium derivatives. In addition to this objective, we wish to return to the issue of the "special stabilization" of such species as $CrOO^{2+}$ and perhaps $CrOOH^{2+}$. The unusually high binding constant for superoxide ion was apparently first recognized by Taube[7] from data[8] for the superoxocobalt cyclam complexes.

$$CrOO^{2+} + HABTS^- \rightarrow CrOOH^{2+} + ABTS^{\bullet -} \qquad K_1 \quad (1)$$

Experimental Section

Commercial $(NH_4)_2ABTS$ (Aldrich) was recrystallized from water and dissolved in 1.0 M perchloric acid to prepare solutions of $HABTS^-$. Solutions of $CrOO^{2+}$ were prepared from Cr^{2+} and O_2, with carefully controlled concentrations.[9–11] Different attempts were made to determine K_1 by spectral scanning and spectrophotometric titrations. They proved unsatisfactory because the reactant concentrations were calculated by the difference of two values close to one another and had unacceptably high uncertainties. The real difficulty is that the slow decomposition of $CrOO^{2+}$ over the several minutes needed for the measurements was sufficient to distort the readings by appreciable amounts.

Stopped-flow mixing was then used to generate $CrOO^{2+}$ in the mixing jet. The buildup of $ABTS^{\bullet -}$ to its equilibrium value was monitored. With the concentrations suitably chosen, this proved reliable and reproducible. These experiments were done by mixing $Cr(H_2O)_6{}^{2+}$ at pH 1 (0.1 M $HClO_4$), under argon, with an O_2-saturated solution of $HABTS^-$ also at pH 1. The solution contained 0.1 M methanol, to avoid the side reactions that lead to hydrogen chromate ions. A kinetic profile at 645 nm (ϵ 1.35 $\times 10^4$ L mol^{-1} cm^{-1}) was acquired each time, but only the final absorbance was used to determine $[ABTS^{\bullet -}]_{eq}$. This is a reliable assessment, since $ABTS^{\bullet -}$ does not react with O_2 or any other species in the system.

Results and Discussion

Recent evidence has been presented in support of what we believe are previously unrecognized reaction parallels between metal alkyl complexes and species that are often referred to as metal oxygen adducts.[18] The superoxo complex $(H_2O)_5Cr{-}OO^{2+}$ can be compared with alkyl chromium ions, $(H_2O)_5Cr{-}R^{2+}$. The first consists of covalently bound Cr^{3+} and $O_2{}^{\bullet -}$ ions,[9] and the second, similarly regarded, are covalent complexes of Cr^{3+} and an alkyl carbanion.[19] This localized valence description of

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$CrOO^{2+}$ was evident in the reaction chemistry, and it has been confirmed by the resonance Raman spectrum.[20]

The most persuasive parallel between the two is found in oxidative homolysis[18] and in the homolysis reactions. The example chosen for spontaneous homolysis is for the 2-propyl complex, so as to illustrate the numerical similarity most emphatically:

$$\text{Cr–OO}^{2+} \underset{1.6 \times 10^{8}\ \text{L mol}^{-1}\ \text{s}^{-1}}{\overset{2.5 \times 10^{-4}\ \text{s}^{-1}}{\rightleftarrows}} \text{Cr}^{2+} + \text{O}_2 \qquad (2)$$

$$\text{Cr–CHMe}_2^{\ 2+} \underset{2.3 \times 10^{8}\ \text{L mol}^{-1}\ \text{s}^{-1}}{\overset{1.7 \times 10^{-4}\ \text{s}^{-1}}{\rightleftarrows}} \text{Cr}^{2+} + \text{Me}_2\text{CH}^{\bullet} \qquad (3)$$

Equation 1 shows the principal equilibrium when solutions of $CrOO^{2+}$ and $HABTS^-$ are mixed. The reverse reaction does occur, but the fairly ready decomposition of $CrOOH^{2+}$ renders it unsuitable for quantitative measurement of the equilibrium position. The equilibrium constant for eq 1 was determined from the absorbance of the $ABTS^{\bullet -}$ radical, with the other concentrations calculated from the stoichiometry. Only in the stopped-flow mixing method, where the initial concentrations are accurately known, is this reliable. Each experiment was repeated several times to improve precision, and three sets of concentrations were used. The results are these:

$[CrOO^{2+}]_0$/ 10^{-4} M	$[HABTS^-]_0$/ 10^{-4} M	$[ABTS^{\bullet -}]_{eq}$/ 10^{-4} M	no. detns	K_1- (std dev)
1.52	1.46	0.772(8)	11	1.16(27)
0.422	0.283	0.170(17)	4	1.01(32)
1.65	3.53	1.26(7)	4	1.75(45)
				av K_1: 1.29(38)

There appears to be a mild trend in K_1 value with concentration, which, however, does not lie outside the error. In any event, this trend has been ignored and K_1 taken as a constant. With this equilibrium constant and the known potential for the $ABTS^{\bullet -}$/$HABTS^-$ half-reaction (eq 4) it is possible to calculate the potential for the chromium couple, shown in eq 5.

$$\text{ABTS}^{\bullet -} + \text{H}^+ + \text{e}^- \rightarrow \text{HABTS}^- \qquad E^\circ = 0.81\ \text{V} \qquad (4)^4$$

$$\text{CrOO}^{2+} + \text{H}^+ + \text{e}^- \rightarrow \text{CrOOH}^{2+} \qquad E^\circ = 0.82\ \text{V} \quad (5)$$

Another standard potential for a couple in the aquachromium system has been calculated[9] on the basis of eq 2, given its equilibrium constant from kinetic values. The value of K_2, combined with the standard electrode potentials for $Cr(H_2O)_6^{3+}$/$Cr(H_2O)_6^{2+}$ (–0.42 V) and $O_2(aq)/O_2^{\bullet -}$ (–0.16 V at this standard state[21-23]), gives this potential:

$$\text{Cr}^{3+} + \text{O}_2(\text{aq}) + \text{e}^- \rightarrow \text{CrOO}^{2+} \qquad E^\circ = +0.27\ \text{V} \quad (6)$$

The missing element in this analysis is the electrode potential for the CrO^{2+}/Cr^{3+} couple, including in this notation the formula of an oxocation, which is known[12,13,15] to be present in independently prepared solutions. Over many years, this potential has been estimated on the basis of the potentials of those reagents that will, and will not, intercept CrO^{2+} when it is an intermediate. For example, the finding that Mn^{2+} is converted to Mn^{3+} in certain chromic acid oxidations (those in which CrO^{2+} in an intermediate)[24] allows one to conclude that the potential in question is more positive than +1.5 V. This places the potential for eq 7 in the range 1.5–1.9 V.

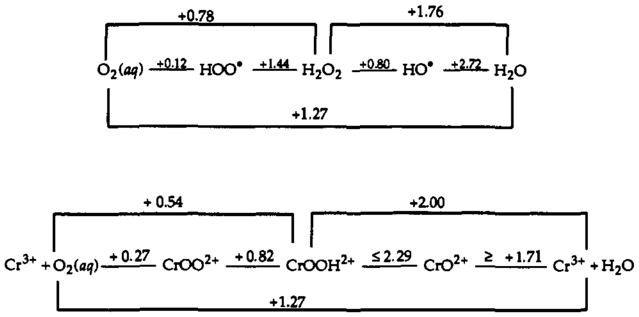

Figure 1. Latimer diagrams for the reduction of aqueous oxygen at pH 0 and 298 K and for the same overall four-electron process as mediated by chromium coordination. The overall four-electron potentials are required to be the same by thermodynamics. In both cases the reference state is $[O_2(aq)] = 1\ \text{mol L}^{-1}$.

$$\text{CrO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{Cr}^{3+} + \text{H}_2\text{O} \qquad (7)$$

This range can be narrowed further by considering the findings, and their implications, for reaction 8:[15]

$$\text{CrO}^{2+} + \text{H}_2\text{O}_2 \rightleftarrows \text{CrOO}^{2+} + \text{H}_2\text{O} \qquad (8)$$

This reaction appeared to proceed to completion. On a longer time scale, a much slower reaction consumed $CrOO^{2+}$. We rule out this being the reverse of eq 8, driven to the left by the known decomposition of CrO^{2+}, because the major route for decomposition of $CrOO^{2+}$ is to evolve O_2, as in eq 2.[9] Presumably $CrOO^{2+}$ decays by no route other than its ordinary ones here as well. Thus, k_{-8} can at best be a small fraction of k_2, these rate constants referring to the equations numbered correspondingly. If we say that the reverse of eq 8 contributes less than 10% of the decomposition, then $k_{-8} \leq 0.1k_2$. From this and the two-electron potential for H_2O_2 at pH 0, another potential can be obtained:

$$\text{CrOO}^{2+} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CrO}^{2+} + \text{H}_2\text{O} \qquad E^\circ \leq +1.56\ \text{V} \quad (9)$$

The combination of the potentials in eqs 5 and 9 yields the potential for $CrOOH^{2+}/CrO^{2+} \leq +2.29$ V, and probably no less than +2.15 V. This value, together with other known values, gives the potential for $CrO^{2+}/Cr^{3+} \geq 1.71$ V. This lies within the range cited, and E° is in fact probably no higher than +1.85 V. All of the values have pH 0 as the reference. The full Latimer diagram for oxygen to water, without[21] and with the assistance of chromium, is shown in Figure 1. Since both overall four-electron reactions are identical with one another, Cr^{3+} entering in the first step and re-emerging in the last, both have $E^\circ = +1.27$ V, corresponding to $O_2(aq)/H_2O$ at pH 0.

From these potentials and other thermodynamic values, the electrode potentials, equilibrium constants, and standard free energies of a number of reactions related to these can be calculated. Table 1 summarizes the thermodynamic data, some entries being directly measured and others obtained by calculation. One comparison that aptly illustrates the mediating role of metal ions in oxygen reactions concerns the binding of the monoanions $O_2^{\bullet -}$ and HO_2^-. The relevant reactions and their equilibrium constants are as follows:

$$\text{Cr}^{3+} + \text{O}_2^{\ \bullet -} \rightarrow \text{CrOO}^{2+} \qquad K = 3 \times 10^{7}\ \text{L mol}^{-1} \quad (10)$$

$$\text{Cr}^{3+} + \text{HO}_2^{\ -} \rightarrow \text{CrOOH}^{2+} \qquad K = 6 \times 10^{3}\ \text{L mol}^{-1} \quad (11)$$

One might imagine that trivalent chromium will have an effect parallel to that of protons. That is, we note for $H^+ + HO_2^- \rightarrow H_2O_2$, as compared to $H^+ + O_2^{\bullet -} \rightarrow HOO^{\bullet}$, that HO_2^- is more basic toward protons than $O_2^{\bullet -}$ is by a factor of 10^7 (compare

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Table 1. Thermodynamic Parameters[a,b] for Reactions and Half-Reactions Involving Chromium Complexes and Oxygen

entry	source	reaction	$E°/V^a$	K	$\Delta G°$/kJ mol^{-1}
A	mesd, eq 1	$CrOO^{2+} + HABTS^- \rightarrow CrOOH^{2+} + ABTS^{\bullet-}$		1.3	−0.6
B	k_f, k_r, eq 2	$Cr^{2+} + O_2(aq) \rightarrow CrOO^{2+}$		6.4×10^{11}	−67
C	B & $E°$'s	$Cr^{3+} + O_2^{\bullet-} \rightarrow CrOO^{2+}$		3×10^7	−43
D	ref 21	$HOO^\bullet \rightarrow H^+ + O_2^{\bullet-}$		2.0×10^{-5}	+27
E	C & D	$Cr^{3+} + HOO^\bullet \rightarrow CrOO^{2+} + H^+$		6×10^2	−16
F	k_f, not k_r, eq 8	$CrO^{2+} + H_2O_2 \rightarrow CrOO^{2+} + H_2O$		$\geq 8 \times 10^6$	−39
G	ref 21	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.76		−340
H	F & G	$CrOO^{2+} + 2H^+ + 2e^- \rightarrow CrO^{2+} + H_2O$	≤+1.56		−301
I	A	$CrOO^{2+} + H^+ + e^- \rightarrow CrOOH^{2+}$	+0.82		−80
J	H & I	$CrOOH^{2+} + H^+ + e^- \rightarrow CrO^{2+} + H_2O$	≤+2.29		−221
K	B & I & $E°$'s	$CrOOH^{2+} + 3H^+ + 2e^- \rightarrow Cr^{3+} + 2H_2O$	+2.00		−386
L	J & K	$CrO^{2+} + 2H^+ + e^- \rightarrow Cr^{3+} + H_2O$	≥+1.71		−165
M	G & K	$Cr^{3+} + H_2O_2 \rightarrow CrOOH^{2+} + H^+$		9×10^{-9}	+46
N	ref 21	$H_2O_2 \rightarrow H^+ + HO_2^-$		1.5×10^{-12}	+67
O	eq 6	$Cr^{3+} + O_2(aq) + e^- \rightarrow CrOO^{2+}$	+0.27		−26
P	M & N	$Cr^{3+} + HO_2^- \rightarrow CrOOH^{2+}$		6×10^3	−21

[a] *vs* NHE. [b] Standard State for O_2 is 1 mol L^{-1}.

entries D and N in Table 1). If Cr^{3+} were simply a Lewis acid, presumably a harder one than H^+, the same trend, perhaps enhanced, would be expected. Clearly this is not so, since $K_{11} \ll K_{10}$ (entries C and P). Thus an electron-transfer role for chromium is implicated. The difference between K_{10} and K_{11} signals either that $CrOO^{2+}$ is stabilized by another electronic interaction or that $CrOOH^{2+}$ is destabilized, or both. We have already pointed out that the equilibrium constant for reaction 10 is much higher than those for analogous complexation reactions between Cr^{3+} and other monoanions.[9] The value of K_{11}, on the other hand, is in the range for other basic anions, such as acetate and fluoride ions.[9] Perhaps K_{11} should instead be compared to the binding constant for a much more basic anion like hydroxide ion. From that comparison, embodied in eq 12, it is seen that K_{11} is indeed relatively small in comparison:

$$Cr^{3+} + OH^- \rightarrow CrOH^{2+} \qquad K = 10^{10}\ \mathrm{L\ mol^{-1}} \quad (12)$$

We commented earlier[14,16] on the relative oxidizing powers of H_2O_2 and $CrOOH^{2+}$. Our stated inference that H_2O_2 is the more powerful is obviously incorrect. As the $E°$ values in Figure 1 show, $CrOOH^{2+}$ is a more potent one-electron oxidant than H_2O_2 by well more than 1 V. Put another way, CrO^{2+} may be a more "stable" product than $HO^\bullet$. At least, it is the one that survives long enough for laboratory manipulation, whereas hydroxyl radical is a sub-microsecond transient.

The difference in oxidizing capacity of $CrOOH^{2+}$ or H_2O_2 does not reveal itself in the kinetics of their reactions. Neither of these species appears capable of undergoing outer-sphere electron transfer, or at least that mechanism has never been demonstrated. Since outer-sphere electron-transfer reactions are the only ones for which driving forces would be expected to matter, the lack of an effect of driving force on reactions that proceed by other mechanisms can be understood. In actuality, both $CrOOH^{2+}$ and H_2O_2 are reduced by inner-sphere (group transfer) mechanisms. In the event such a pathway is unavailable, no reaction occurs even if the partner is one like $Ru(NH_3)_6^{2+}$, which offers an additional substantial driving force of its own. In the systems that we have examined, both $CrOOH^{2+}$ and H_2O_2 adopt Fenton mechanisms and are remarkably similar in reactivity toward numerous transition metal partners.[14,17]

To reverse this argument: were the rate-controlling step in the $CrOOH^{2+}$ and H_2O_2 mechanisms really internal electron transfer following precursor complex formation, then $CrOOH^{2+}$ reactions, with so much greater driving force, would be much more rapid. This feature is not observed, the two being comparable, with $CrOOH^{2+}$ usually slightly less reactive.

We have illustrated the marked propensity of CrO^{2+} to undergo a two-electron conversion to Cr_{aq}^{2+} when it reacts with an O atom acceptor like Ph_3P or a hydride ion donor like most (but not all) alcohols and aldehydes. No analogous route[25] can exist for $HO^\bullet$, whose reactions[13] are typified by addition to aromatic rings or by H atom abstraction, especially from aliphatic C–H bonds. The advantage of these two-electron routes for CrO^{2+} is that they create a pathway of lower overall standard free energy, enabling the system to avoid free radical intermediates which occur at higher energy.

There are some reactions in which CrO^{2+} and $HO^\bullet$ appear to react in parallel. The ring opening of cyclobutanol has already been commented upon,[13] and organic radicals are certainly produced in both reactions. A second reagent is $Fe(H_2O)_6^{2+}$, which reacts with hydroxyl radicals as in eq 13:[26]

$$Fe(H_2O)_6^{2+} + HO^\bullet \rightarrow (H_2O)_5Fe\text{–}OH^{2+} + H_2O \quad k = 2.3 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}} \quad (13)$$

The $Fe(H_2O)_6^{2+}$ reaction occurs more slowly than those of many other metal ions with $HO^\bullet$, presumably because it is limited by water dissociation. Certain other reactions of $Fe(H_2O)_6^{2+}$ with radicals (*e.g.*, $Br_2^{\bullet-}$)[27] are known to proceed by the inner-sphere mechanism and are similarly limited. That being so, we are inclined to write by analogy, for the $Fe(H_2O)_6^{2+}$ reaction[14,17] with $Cr{=}O^{2+}$, a scheme with an oxo-bridged intermediate:

$$Fe(H_2O)_6^{2+} + (H_2O)_5CrO^{2+} \rightarrow \{Fe\text{–}O\text{–}Cr\}^{4+} \xrightarrow{2H^+} Cr^{3+} + Fe^{3+} + H_2O \quad (14)$$

The intervention of an oxo-bridged intermediate has not yet been proved, however, although precedents can be cited. The reaction between $V(H_2O)_6^{2+}$ and VO^{2+} yields the dimetallic ion VOV^{4+},[28] and that between $Cr(H_2O)_6^{2+}$ and CrO^{2+} yields, eventually, $Cr(OH)_2Cr^{4+}$, possibly by way of the unproved $CrOCr^{4+}$.[29,30]

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