Evidence for a Bond Homolysis Pathway for O$_2$ Release in the Decomposition of the Superoxochromium(III) Ion CrO$_2^{2+}$

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Abstract: The cation (H$_2$O)$_5$CrO$_2^{2+}$ has a considerable lifetime in aqueous solution in the absence of Cr^{2+}. One pathway for decomposition consists of bond homolysis, CrO$_2^{2+}$ → Cr^{2+} + O$_2$, with $k = 2.5 \times 10^{-4}$ s^{-1} at 25.0 °C ($\Delta H^{\ddagger} = 25.1 \pm 1.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9.7 \pm 3.6$ cal mol^{-1} K^{-1}). The resulting Cr^{2+} then reacts very rapidly with CrO$_2^{2+}$, with $k = 8 \times 10^8$ M^{-1} s^{-1}, estimated by kinetic modeling of the effect of [O$_2$]. A second pathway, which yields HCrO$_4^-$, proceeds by a bimolecular reaction between two CrO$_2^{2+}$ ions. It is characterized by a rate constant 6.0 ± 0.9 M^{-1} s^{-1} at 25 °C ($\Delta H^{\ddagger} = 12.0 \pm 1.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -14 \pm 6$ cal mol^{-1} K^{-1}). A structure of the activated complex for this pathway is proposed. The equilibrium constant for homolysis of CrO$_2^{2+}$ is $K_{\text{hom}} = 1.6 \times 10^{-12}$ M and that calculated from the thermodynamic data for heterolysis (CrO$_2^{2+}$ ⇌ Cr^{3+} + O$_2^-$) is $K_{\text{het}} = 3 \times 10^{-8}$ M. The latter, although kinetically unimportant, is suitable for thermodynamic analysis. The Lewis basicity of O$_2^-$ for Cr^{3+} is discussed on the basis of comparisons to cobalt(III)–ammine complexes, other (H$_2$O)$_5$CrX^{2+} complexes, and acid ionization constants. The data do not require a description of CrO$_2^{2+}$ as other than a superoxochromium(III) ion.

The reaction of chromium(II) ions with molecular oxygen in aqueous solution is a complex, multistep reaction.[1-4] The initial step, identified and studied by pulse radiolysis,[5,6] is the formation of a 1:1 complex. This reaction is not accompanied by a change in conductivity, signifying that there is neither loss nor uptake of protons (pH 2.6–4.3). The species produced can thus be formulated as CrO$_2^{2+}$. This initial reaction, Cr^{2+} + O$_2$ → CrO$_2^{2+}$, follows second-order kinetics with a rate constant of 1.6×10^8 M^{-1} s^{-1} at ~25 °C.[5,6]

The cation CrO$_2^{2+}$ shows surprising kinetic stability in acidic solutions, persisting for an hour or more provided Cr^{2+} is absent. We decided to undertake further studies of CrO$_2^{2+}$, anticipating the results would be of some general interest because this reaction bears on those by which metal ions bind O$_2$ and are oxidized by it.[7] The mechanism of decomposition of CrO$_2^{2+}$ is the subject of this report.

We shall present evidence to show that CrO$_2^{2+}$ decomposes by two concurrent, parallel pathways. One of these proves to be oxygen release by unimolecular homolysis:

$$\text{CrO}_2^{2+} \rightleftharpoons \text{Cr}^{2+}(\text{aq}) + \text{O}_2 \quad (k_1, k_{-1}) \tag{1}$$
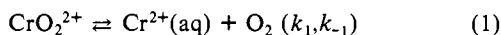
Results

Only very low concentrations of CrO$_2^{2+}$ can be prepared, generally ≤1 × 10^{-4} M.[8-10] On reason is that (as documented in the course of this work) the *bimolecular* self-reaction of CrO$_2^{2+}$ provides one pathway for its decomposition. This proves to be efficient enough to preclude the buildup of higher concentrations. A second reason is the very fast reaction between Cr^{2+} and CrO$_2^{2+}$, which severely limits the concentrations of Cr^{2+} that can be used in the preparation. We shall return to that reaction, eq 2, in a subsequent section.

$$\text{CrO}_2^{2+} + \text{Cr}^{2+}(\text{aq}) \rightarrow \text{CrOOCr}^{4+} \quad (k_2) \tag{2}$$

The Kinetics of Decomposition of CrO$_2^{2+}$. Kinetic data were obtained at [H$^+$] = 0.100 M and 1.00 M ionic strength, main-tained with lithium perchlorate. The rate itself and the form of the rate law were clearly dependent on the concentration of dissolved oxygen and to some extent also on the initial concentration of CrO$_2^{2+}$ itself. Kinetic data were obtained under several reaction conditions as follows.

(a) Oxygen-Free Solutions. Low concentrations (<2 × 10^{-5} M) of CrO$_2^{2+}$ decompose in strictly anaerobic solutions according to a first-order rate law, −d[CrO$_2^{2+}$]/dt = k_{app}[CrO$_2^{2+}$]. A mild but regular increase in k_{app} ((6.0–7.8) × 10^{-4} s^{-1} in 13 experiments) was found with the initial concentration of [CrO$_2^{2+}$] (in the range 13–20 µM). Subsequently, this was attributed to the intervention of a parallel kinetic pathway with a second-order dependence on [CrO$_2^{2+}$]. The second-order path assumes minor but not entirely negligible importance under anaerobic conditions at low [CrO$_2^{2+}$]. Extrapolation of the apparent first-order rate constant to [CrO$_2^{2+}$] = 0 affords a value of $(k_{\text{app}})_{\text{lim}}$ = 5.0 × 10^{-4} s^{-1}. With allowance for the stoichiometric factor, this gives k_1 = 2.5 × 10^{-4} s^{-1} at 25.0 °C.

Reactions carried out *under these conditions* gave final solutions that were essentially nonabsorbing in the UV. The lack of a strong UV absorption suggests that only Cr(III) species are formed by this pathway. In particular, HCrO$_4^-$ is not formed.

Similar data over the temperature range 2.3–34.9 °C gave values of k_1 that were fit to the activated complex theory equation. The resulting activation parameters are $\Delta H_1^{\ddagger} = 25.1 \pm 1.1$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = +9.7 \pm 3.6$ cal mol^{-1} K^{-1}.

(b) Variation of [CrO$_2^{2+}$]. Experiments at [O$_2$] = 0 and higher [CrO$_2^{2+}$]$_0$ (to 4 × 10^{-5} M) deviated from first-order kinetics; they required a concurrent second-order component, which was barely perceptible in the experiments described previously. Within a single run the data fit the rate law

$$-\text{d}[\text{CrO}_2^{2+}]/\text{d}t = 2k_1[\text{CrO}_2^{2+}] + k''[\text{CrO}_2^{2+}]^2 \quad ([\text{O}_2] = 0) \tag{3}$$

The integrated form of eq 3 (see the Experimental Procedures) was used to evaluate k''. The second-order term points to a concurrent, bimolecular pathway for decomposition of CrO$_2^{2+}$, eq 4.

$$2\text{CrO}_2^{2+} + 4\text{H}_2\text{O} \rightarrow 2\text{HCrO}_4^- + 6\text{H}^+ \tag{4}$$

$$-\text{d}[\text{CrO}_2^{2+}]/\text{d}t = 2k_4[\text{CrO}_2^{2+}]^2 \tag{5}$$

With k_1 fixed at 2.5 × 10^{-4} s^{-1}, k'' = 2k_4 = 11.4 ± 3.4 M^{-1} s^{-1}. The second-order path in the 11 experiments contributed from 15.1 to 29.8% of the reaction. When the value of k'' is weighted in proportion to the extent to which it contributes to the whole, a weighted average is k_4 = 6.0 ± 0.9 M^{-1} s^{-1} at 25.0 °C.

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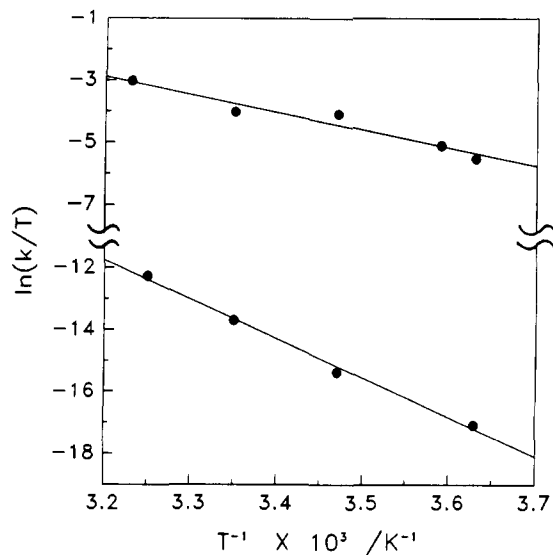(10) Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982,** *104,* 704.

Figure 1. The temperature dependences of k_1 (upper) and k_4 according to activated complex theory, as $\ln (k/T)$ vs. $1/T$.

The determinations of k_4, carried out as a function of temperature, gave $\Delta H_4^{\ddagger} = 12.0 \pm 1.7$ kcal mol^{-1} and $\Delta S_4^{\ddagger} = -14.4 \pm 5.8$ cal mol^{-1} K^{-1}. Figure 1 depicts the temperature dependences of k_1 and k_4 according to activated complex theory.

Increasing concentrations of $HCrO_4^-$ were detected spectrophotometrically at the end of the experiments in solutions containing higher initial concentrations of CrO_2^{2+}. It was subsequently proved that $HCrO_4^-$ is produced quantitatively in the reaction shown in eq 4.

(c) Effect of [O$_2$]. Three different but interrelated phenomena occurred when oxygen was added: (a) the reaction slowed substantially owing to an inverse dependence of the first term of eq 3 on [O$_2$]; (b) the second-order dependence on [CrO_2^{2+}] became more prominent; and (c) increasing proportions of $HCrO_4^-$ were observed in the UV spectra of the product solutions.

At the highest [O$_2$], 3.7 mM, only the second-order term of eq 3 is appreciable, and the data fit second-order kinetics. The rate constant k'' so determined at 25 °C is 10 M^{-1} s^{-1}, which agrees adequately with the determinations at higher [CrO_2^{2+}]$_0$ and [O$_2$] = 0.

(d) Variations of [O$_2$]. A series of reactions was monitored in which [CrO_2^{2+}]$_0$ was approximately constant ($\sim 2 \times 10^{-5}$ M), and [O$_2$] was varied between 0 and 3.7×10^{-3} M. (The highest O$_2$ concentration used 3.5 atm pressure of O$_2$ in a specially designed quartz cell.) The recorded absorbance-time traces are depicted in Figure 2. They illustrate both the rate-inhibiting effect of increased [O$_2$] and a reaction order with respect to [CrO_2^{2+}] that increases above unity at higher [O$_2$].

Superimposed on the experimental points shown in Figure 2 are curves calculated from the subsequently described fit by numerical integration to the final composite rate law in eq 6. The

$$\frac{-d[CrO_2^{2+}]}{dt} = \frac{2k_1[CrO_2^{2+}]}{1 + (k_{-1}/k_2)([O_2]/[CrO_2^{2+}])} + 2k_4[CrO_2^{2+}]^2$$

(6)

satisfactory fit over a wide range of [O$_2$] and [CrO_2^{2+}] lends credence to eq 6, in which the rate constants are designated according to the elementary reaction steps in the kinetic scheme by which these results are to be interpreted.

Evidence for a Cr^{2+} Intermediate. Homolysis of CrO_2^{2+} would necessarily yield Cr^{2+}, eq 1. Cr^{2+} would occur transiently, however, since we believe that it is consumed in a secondary and presumably very rapid reaction, eq 2. An experiment was done in which 4.84×10^{-5} M CrO_2^{2+} was allowed to decompose (at 25 °C, 0.10 M H$^+$, 0.25 M ionic strength) under oxygen-free conditions in the presence of 0.050 M (NH$_3$)$_5$CoBr^{2+}. These conditions favor the capture of Cr^{2+} formed in the homolytic pathway.

A measurable concentration of Co^{2+} (2.04×10^{-5} M) was, indeed, determined. This is evidence for the formation of a re-
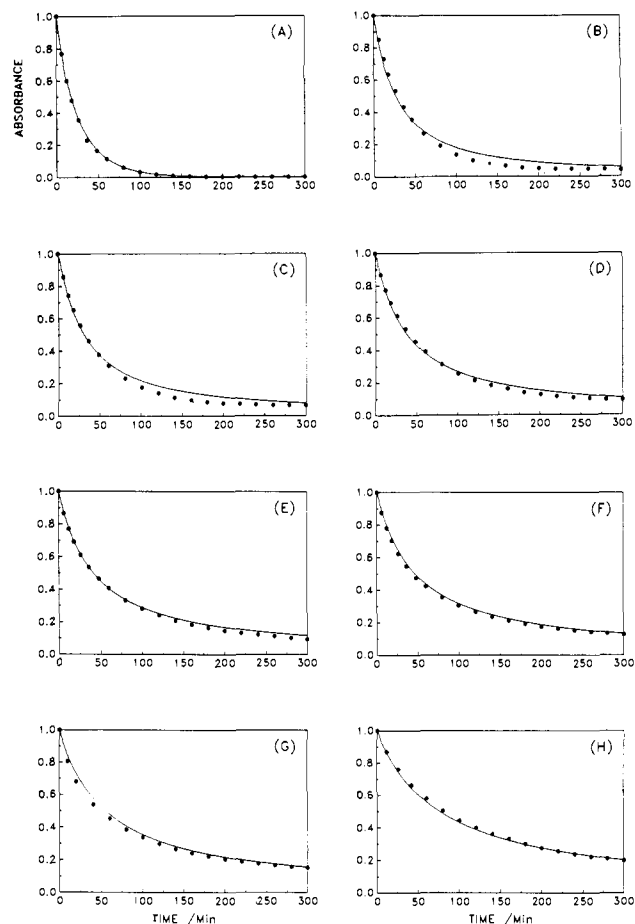

Figure 2. Absorbance-time traces (normalized to the same absorbance change of 1.0 unit, arbitrary scale) showing the kinetic inhibition by increased [O$_2$]. The experiments A–H correspond to increasing values of O$_2$: 0, 0.0525, 0.105, 0.210, 0.315, 0.683, 1.05, and 3.70 mM. The curves drawn through the experimental data are the final best fits (calculated with the numerical integration program KINSIM) using the full rate law, eq 6, and the best values of all four rate constants.

ducing intermediate, and we suggest that the known,[11] rapid reduction of (NH$_3$)$_5$CoBr^{2+} by Cr^{2+} is responsible. The concentration of Co^{2+} matches exactly that calculated (by numerical integration[12] of the differential rate equations) for the reaction sequence shown given the rate constants k_1, k_{-1}, k_2 (8×10^8 M^{-1} s^{-1}, see below), k_4, and k_{Co} (2×10^6 M^{-1} s^{-1} estimated at $\mu = 0.25$ M).[11b]

Numerical Modeling of Kinetic Data. The kinetic scheme consisting of the reactions of eq 1, 2, and 4 was tested to see that it adequately reproduced the experimental absorbance-time profiles depicted in Figure 2. A closed-form solution of the differential rate equation was not feasible. A program for their numerical solution, KINSIM,[12] was applied to the proposed reaction scheme. The chemical equations included in this analysis were those along path 1 (the reactions shown in eq 1 and 2) and path 2 (the bimolecular reaction of eq 4).

To conduct the simulations, the known value[5,6] of k_{-1} was used and values of k_1 and k_4 as reported herein were used. The only unknown rate constant was k_2. The failure of attempts to measure k_2 directly (next section) and the ranges of oxygen concentration over which the rate-inhibitory effect of increasing [O$_2$] was noted suggest that k_2 is quite large. The value of k_2 used in the simulation was adjusted until the absorbance-time profiles for all runs matched satisfactorily, as shown in Figure 2. This method gives $k_2 = 8 \times 10^8$ M^{-1} s^{-1}. The precision of this value of k_2 is judged

(11) (a) Candlin, J. C.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766. (b) The value $k_{Co} = 2.0 \times 10^6$ M^{-1} s^{-1} was used in the experimental simulation. This estimate was required since the ionic strength of the experiment was 0.250 M.

(12) Barshop, B. A.; Wrenn, R. F.; Frieden, C. J. *Anal. Biochem.* **1983**, *130*, 134.

to be no better than about ±50%, however, on the basis of the variations in it that could be made without the deviations becoming unacceptably great.

Reaction of Cr^{2+} and CrO_2^{2+}. The overall reaction of Cr^{2+} and O_2 occurs with a 4:1 stoichiometry.[4] The species CrO_2^{2+} persists as long as reported above only in the absence of excess Cr^{2+}. The direct reaction between Cr^{2+} and CrO_2^{2+} would thus be expected to occur with an overall 3:1 stoichiometry. A ratio 3.2:1 was confirmed by spectrophotometric titration, as shown in Figure 3. This supports the net reaction in eq 7.

$$CrO_2^{2+} + 3Cr^{2+} + 2H_2O = 2Cr_2(OH)_2^{4+} \qquad (7)$$
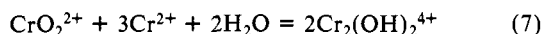
Attempts to evaluate k_2 directly were thwarted, however, because the reaction between Cr^{2+} and CrO_2^{2+} occurs too rapidly for the stopped-flow technique. This is consistent with the very high estimate from the numerical modeling, $k_2 = 8 \times 10^8$ M^{-1} s^{-1}.

Is the Complex Kinetic Scheme Needed? An attempt was made to analyze the kinetics over the full range of $[O_2]$ by the use of a simplified kinetic model in which $k'' = 0$. (In that version, the second-order dependence on $[CrO_2^{2+}]^2$ arises from one limit of the first term, namely $(2k_1k_2/k_{-1})[CrO_2^{2+}]^2/[O_2]$, which applies when $k_{-1}[O_2] \gg k_2[CrO_2^{2+}]$.) This was not successful, as illustrated in Figure 4 for three of the kinetic runs over the full range of $[O_2]$. The experimental absorbance–time profiles are not matched by the parameter set applicable either at one end of the $[O_2]$ range or the other. That is, no adjustment of k_2 alone sufficed to account for the variations with $[CrO_2^{2+}]$ and $[O_2]$ without the term $2k_4[CrO_2^{2+}]^2$.

Production of $HCrO_4^-$. An additional but perhaps more subjective basis arises for asserting that the incorporation of the kinetic term $2k_4[CrO_2^{2+}]^2$ is reasonable from a chemical viewpoint rather than the mathematical approach just described. The proportion of the starting material that is converted to $HCrO_4^-$ shows a close correspondence to the proportion of the reaction calculated to proceed by the second-order pathway.

The results of these calculations, again performed by numerical integration[12] for each run using the final parameter set, are shown in Figure 5, which illustrates the agreement between experimental and calculated values of $[HCrO_4^-]$. The close correspondence between the two lends credence to the formulation given, in that different products, $Cr_2(OH)_2^{4+}$ and $HCrO_4^-$, are formed by the independent pathways. It is not necessary to consider the competing reaction between Cr^{2+} and $HCrO_4^-$, even though it has a very high rate constant.[13]

Discussion

Character of CrO_2^{2+}. Although $(H_2O)_5CrO_2^{2+}$ has not been isolated for structural characterization, a theoretical analysis[14] suggests that it contains η^1-bonded O_2. We return to the question of the electronic structure of CrO_2^{2+} at the end of the Discussion, where it is then considered from the experimental point of view. For the moment, we adopt, as did the authors who discuss the electronic structures of dioxygen, superoxo, and peroxo complexes in general,[14] a notation[15] that finesses the issue. Thus we write $\{CrO_2^{2+}\}^6$, there being a total of six metal d and ligand π^* and σ^* electrons. Other chromium complexes analogous to CrO_2^{2+} are known.[16-20] These include $Cr(TPP)(py)O_2$, which has been

(13) The competing reaction between Cr^{2+} and $HCrO_4^-$ [Hegedus, L. S.; Haim, A. *Inorg. Chem.* 1967, *6*, 664] is not important. Although the rate constant is very high, the rate itself is not competitive with those for the other Cr^{2+} reactions (k_2 and k_{Co} steps) at these concentrations.

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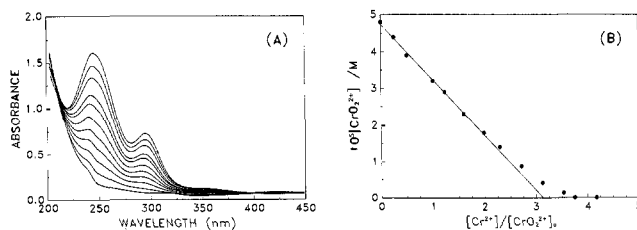**Figure 3.** Spectrophotometric titration of CrO_2^{2+} with Cr^{2+}: (A) UV spectrum of CrO_2^{2+} with successive injections of Cr^{2+}; (B) titration plot at 290 nm. The endpoint corresponds to a reactant ratio 3.2:1 Cr^{2+}: CrO_2^{2+} (cf. eq 7).
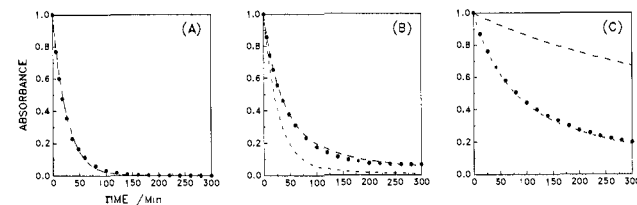

Figure 4. Attempted kinetic fits of (relative) absorbance–time data over the full range of $[O_2]$ is illustrated for three experiments at $10^3[O_2] =$ (A) 0, (B) 1.05, and (C) 3.7 M. Each run was fit to eq 6, requiring that $k_4 = 0$. The two sets of dashed lines (calculated with k_1 and k_{-1} set at their known values) show two values of k_2, indicated by short and long dashes, one that fits B satisfactorily but C very poorly, $k_2 = 10^{9.2}$ M^{-1} s^{-1} and vice versa, with $k_2 = 10^{10.2}$ M^{-1} s^{-1}. (The two fits coincide for A.) Thus there exists no one value of k_2 at which theory and experiment agree over the range of $[O_2]$ without the term $k_4[CrO_2^{2+}]^2$.
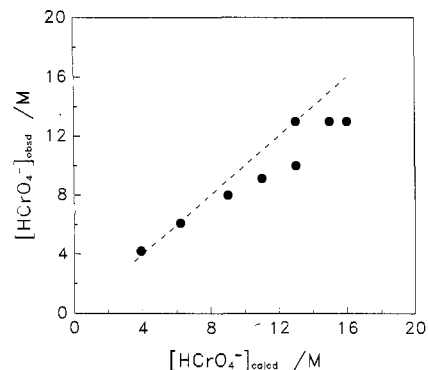

Figure 5. A comparison between the observed and calculated yields of $HCrO_4^-$. The calculated yield is the proportion of the reaction proceeding by the kinetic term $k_4[CrO_2^{2+}]^2$, in which the best fit values of the four rate constants in eq 4 were used for numerical simulation in the program KINSIM.

assigned an η^1 structure on the basis of its IR spectrum.

The chemical evidence is also consistent with the η^1 structure, particularly: (a) the rapid reaction ($k_2 = 8 \times 10^8$ M^{-1} s^{-1}) between CrO_2^{2+} and Cr^{2+} is consistent with it; (b) the initial step in the decomposition reaction of CrO_2^{2+} (k_1) is *not* assisted by H^+, contrary to the expectation for the unimolecular dissociation of a peroxo complex; (c) the ammine analogue $[(NH_3)_5CrO_2^{2+}]$ reacts with $Cr(NH_3)_6^{2+}$ to yield $[(NH_3)_5CrO_2Cr(NH_3)_5]^{4+}$;[19] (d) the UV spectrum of CrO_2^{2+} has features resembling those of O_2^- and HO_2.[21]

The Unimolecular Reaction. Three lines of evidence have been obtained to support the suggested bond-homolysis step. First, the form of the rate law indicates two successive kinetic steps with activated complexes $[CrO_2^{2+}]^{\ddagger}$ and $[Cr_2O_2^{4+}]^{\ddagger}$. The inverse dependence of rate on $[O_2]$ implies that O_2 is released in the first step, as in eq 1. Depending on $[O_2]/[CrO_2^{2+}]$ (relative to k_{-1}/k_2), one or the other of the two steps is rate-limiting in a given experiment.

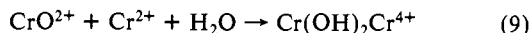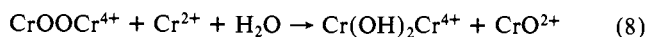Second, the large value of $\Delta H_1^{\ddagger}$ and especially the substantial

(21) (a) Bielski, B. H. J. *Photochem. Photobiol.* 1978, *28*, 645. (b) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* 1985, *14*, 1041.

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and positive value of $\Delta S_1{}^{*}$ are consistent with unimolecular homolysis. The related dissociations of organochromium(2+) ions have been well-characterized as bond-homolysis reactions, $CrR^{2+} \rightarrow Cr^{2+} + R^{\bullet}.$[22,23] Their activation parameters are similar to those found[22,23] for k_1, although ΔS^{*} is less positive (10 as compared to ~ 27 cal mol^{-1} K^{-1}). This is consistent with the nature of the released radical: O_2 should disrupt the solvent structure of water less than an aliphatic radical does.

Third, we detected a reducing intermediate. We presume this to be Cr^{2+}, because it converts $(NH_3)_5CoBr^{2+}$ to Co^{2+}(aq).

The reversibility of O_2 binding and release is the most important issue established by this work. This appears to be the only instance in which such behavior has been established for a chromium complex in homogeneous solution. The first clear evidence for the reversible binding of molecular oxygen by a chromium(II) ion was reported for divalent chromium ion exchanged onto zeolite A.[24] Each chromium(II) ion contained in the zeolite reversibly binds one molecule of oxygen.

The Reaction between Cr^{2+} and $CrO_2{}^{2+}$. The initial step of this reaction is shown in eq 4. The 3:1 stoichiometry for this reaction, expected from the stoichiometry of the overall O_2–Cr^{2+} reaction, was directly confirmed by spectrophotometric titration of $CrO_2{}^{2+}$ with Cr^{2+}, as cited above. In combination with the kinetic scheme, with a 1:1 reaction between $CrO_2{}^{2+}$ and Cr^{2+} (eq 2), the overall 3:1 reaction requires additional step(s). We speculate that, following eq 2, steps such as the following occurs:

$$CrOOCr^{4+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} + CrO^{2+} \quad (8)$$

$$CrO^{2+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} \quad (9)$$

The reactions, although proposed without direct evidence obtained in the course of this work, appear reasonable. The first (eq 8) finds analogy in the reactions of other metal ions with oxygen.[25-27] Moreover, it can be viewed as the attack of chromium on the O–O bond of the dinuclear chromium peroxide complex. As such, it is analogous to the attack of Cr^{2+} on the O–O bond of hydrogen peroxide and alkyl hydroperoxides.[28,29]

The analogy between the chromium(IV) species, the chromyl ion CrO^{2+}, and hydroxyl (and alkoxy) radicals can be recognized; note their similarity to the ferryl ion FeO^{2+}.[30] The second reaction (eq 9) is simply the reaction of this chromium(IV) species and chromium(II). These reactions are formulated to yield directly the observed product, the dinuclear complex containing two bridging OH groups.[4] The distinction between this and the authentic μ-oxo species Cr–O–Cr^{4+} is now recognized.[31] Although experiments were not done to explore these points further, we also note that further slow changes in UV spectra were seen in many of the kinetic runs, after $CrO_2{}^{2+}$ had *completely* reacted. These could be arrested by addition of Cr^{2+}, which is consistent with the chemistry suggested.

Activation Parameters and Bond Strengths. The following numerical quantities (M, s, thermochemical units) referring to eq 1 were determined or calculated from experimental data.

kinetic parameters	k (298 K)	$\Delta G_{298}{}^{*}$	ΔH^{*}	ΔS^{*}
forward (k_1)	2.5×10^{-4}	22.4	25.1	9.7
reverse (k_{-1})	1.6×10^{8}	6.3	2 ± 2 (est)	-15 ± 6
equilibrium parameters	K_1 (298 K)	$\Delta G°_{298}$	$\Delta H°$	$\Delta S°$
	1.6×10^{-12}	16.1	23 ± 2	25 ± 10

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The numerical values and their assignments do not absolutely require that $CrO_2{}^{2+}$ homolyzes. On the other hand, they do lend support to it, in comparison with bona-fide homolytic dissociation reactions of M–R bonds,[22,32,33] as cited above.

The Bimolecular Pathway. This step is responsible for formation of $HCrO_4{}^{-}$ and so proceeds by a mechanism quite different from the Cr(III)-forming reactions along the path that begins with bond homolysis. In a formal sense $CrO_2{}^{2+}$ and $HCrO_4{}^{-}$ are equivalent, in that these species are related not by oxidation–reduction, but by simple hydrolysis:

$$CrO_2{}^{2+} + 2H_2O = HCrO_4{}^{-} + 3H^{+} \quad (10)$$
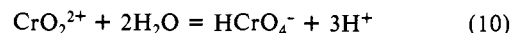
The structures of the two are quite different, however, and one would anticipate that a mechanism considerably more intricate than hydrolysis would be needed for their interconversion. That contention is supported by the second-order kinetics for the rate of the net transformation, as in eq 4. This reaction step proceeds with a substantially lower enthalpy of activation (compensation of bond-making and bond-breaking) and by the negative entropy of activation (consistent with the additional organizational entropy of a bimolecular reaction).

A plausible transition state for this reaction step is one in which the pair of $CrO_2{}^{2+}$ ions interact to create a new Cr–O bond from the O–O bond of the other partner:
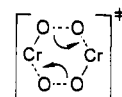

If this is a reasonable representation of the transition state, then its dissociation as shown will lead to a dioxo species, $(H_2O)_nCr(O)_2{}^{2+}$. Loss of protons from the dioxochromium(VI) ion will (according to the process depicted) occur spontaneously, preceded or followed by dissociation of coordinated water, ultimately yielding $HCrO_4{}^{-}$.

Alternatively, bimolecular decomposition of $CrO_2{}^{2+}$ might proceed analogously to the disproportionation of HO_2, i.e.

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad (11)$$

$$2CrO_2{}^{2+} \rightarrow CrO_2Cr^{4+} + O_2 \quad (12)$$
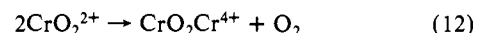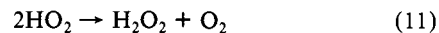
Here the immediate product is a μ-peroxo dichromium complex. The same dimetallic species, however, is believed to be formed in the reaction between $CrO_2{}^{2+}$ and Cr^{2+}, eq 2, along the other pathway for $CrO_2{}^{2+}$ decomposition. There, however, it does not lead to $HCrO_4{}^{-}$. Clearly, the same species cannot react in different ways in similar circumstances, and thus the path shown in eq 12 seems unlikely.

Heterolytic Dissociation of $CrO_2{}^{2+}$. Consider the reaction

$$CrO_2{}^{2+} \rightleftharpoons Cr^{3+} + O_2{}^{-} \quad (13)$$
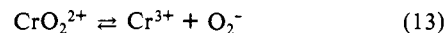
This equilibrium is written as producing free superoxide ions for the purposes of the treatment given below. Of course, in these strongly acidic solutions the predominant species is HO_2 (pK_a = 4.8).[21] It is the very rapid disproportionation of HO_2 (k = 8.3 $\times 10^{5}$ M^{-1} s^{-1})[21] that would ultimately drive the decomposition of $CrO_2{}^{2+}$ to completion despite the fact that it would start by a very endergonic step (eq 13 or the equivalent $CrO_2{}^{2+} + H^{+} = Cr^{3+} + HO_2$). The point is moot, in any event, since this is not an important path under any conditions examined.

Nonetheless useful comparisons, both kinetic and thermodynamic, can be made by continuing with the analysis of the reaction as written in eq 13. The value of K_{13} can be obtained from the kinetically derived value of K_1 (above) and the standard reduction potentials for the Cr^{3+}/Cr^{2+} and O_2(aq)/$O_2{}^{-}$ couples, -0.41 and -0.16 V, respectively. This gives $K_{13} = 3 \times 10^{-8}$ M, more favorable than K_1 by some $10^{4.2}$. Of course, both homolysis and heterolysis are endergonic reactions, with respective values of $\Delta G°$ of 16.1 and 10.3 kcal mol^{-1}. If either is the initial step in any kinetic

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Decomposition of the Superoxochromium(III) Ion

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sequence, it would need to be compensated by subsequent, sufficiently exergonic reaction(s) so as to drive the overall dissociation process. Interestingly, however, the kinetic data show that homolysis, although less favorable thermodynamically, provides the better initial step. This logic points to a severe *kinetic* disadvantage for heterolytic dissociation.

A substantial kinetic barrier for k_{13} is indeed consistent with a reverse rate limited by the very slow substitution rate of Cr-$(H_2O)_6^{3+}$. If a typical value of $\sim 10^{-6}$ M^{-1} s^{-1} is taken for k_{-13}, then $k_{13} \sim 10^{-14}$ s^{-1}. There is no need to refine k_{-13}, since any credible estimate would support the conclusion that k_{13} is expected to be negligibly small.

We next consider a treatment of O_2^- coordination to Cr(III) based on that recently given by Taube[7] for cobalt macrocycles.[34] Consider the binding constant between Cr^{3+} and O_2^- in comparison with other X^- ions (of these, $X^- = OH^-$ affords an interesting comparison, since it is often one of the most strongly bound). The comparative data (formation constants, M^{-1}) for chromium and one of the cobalt macrocycles[34] are as follows:

	O_2^-	OH^-
$Cr(H_2O)_6^{3+}$	$10^{7.5}$	10^{10}
$Co([14]aneN_4)(H_2O)_2^{3+}$	$10^{13.7}$	10^{11}

This comparison for the cobalt complexes provided one basis for Taube's contention that something is astonishing about the cobalt–oxygen interaction. The enhanced stability was taken to suggest a charge-transfer interaction, as in $Co(IV)-O_2^{2-}$. In that context, the reversal in ordering between the chromium and cobalt systems is remarkable. Whatever else may be inferred from this, an analogous metal(IV)–peroxide state appears relatively much less important for chromium.

From a different viewpoint we consider the Lewis acidity of $Cr(H_2O)_6^{3+}$ toward O_2^- relative to its acidity toward, for example, acetate ions.[35,36] These anions are comparable bases toward the hydrated proton (HO_2 and $HOAc$ have pK_a's of 4.8 ± 0.1). Compared to $CrOAc^{2+}$, however, CrO_2^{2+} forms with a higher stability constant (log K's are <4.7 and 7.5, respectively). The larger value for the latter may signal an appreciable charge-transfer interaction in the superoxo complex, although one also needs to keep in mind that aqueous superoxide anion is very strongly hydrogen-bonded, comparable to fluoride ions.[37]

In fact, one can consider the binding of fluoride and other simple anions in the same context as the superoxide interaction. Consider the complexes $(H_2O)_5CrX^{2+}$ and $(NH_3)_5CoX^{2+}$, chosen because extensive stability constant data are available for both series,[38,39] because of the close analogy between the pentaammine cobalt complexes and saturated tetraamine cobalt macrocycles (to return to the Taube–Endicott[34] example), and because the electronic nature of the ground state[40] seems incontrovertibly $M^{III} \cdot X^-$ for the simple anions, other perhaps than superoxide. The values of the ratio K_{Cr}/K_{Co} are as follows:

X^-	OH^-	F^-	Cl^-	Br^-	NCS^-
K_{Cr}/K_{Co}	65	850	0.088	0.006	0.39

The preference shown by F^- toward $Cr(H_2O)_6^{3+}$ is striking, considering the other anions; even the very hard base OH^- does not show as large an enhancement. Might fluoride ions in the aquochromium complex retain partially the hydrogen-bonding interactions characteristic of the free anion, utilizing cis water molecules in the coordination sphere? If so, the relative stability of the amminecobalt bonding of fluoride ions would be correspondingly lower. This would rationalize the large stability constant of CrO_2^{2+} compared to those for other CrX^{2+} ions ($10^{7.5}$ vs. $10^{4.3}$ for fluoride), in that coordination of aqueous (i.e., hydrated) superoxide ions to the aquo complex does not completely sacrifice the hydrogen-bonded interactions of the anion.

To relate this point to electronic structures, consider the values of K_{Cr}/K_{Co} for $X^- = OH^-$ vs. O_2^-, now using K_{Co} for $(H_2O)_2Co([14]aneN_4)^{3+}$.[41] The relevant values are 13 (OH^-) and $10^{-6.2}$ (O_2^-). On the one hand, we have just pointed out that K_{Cr} for O_2^- is exceptionally *large* (relative to values for CrX^{2+}); on the other, this very *small* value of K_{Cr}/K_{Co} for superoxide ions emphasizes just how truly astonishing is the stability constant between O_2^- and $(H_2O)_2Co([14]aneN_4)^{3+}$. We believe it further strengthens Taube's case[7] for charge-transfer stabilization of that complex. At the same time, however, this anlysis does not make a compelling or an appealing case for the formulation of $(H_2O)_5CrO_2^{2+}$ as other than a superoxo chromium(III) complex.[42]

Experimental Procedures

Preparation and Characterization of CrO_2^{2+}. Solutions of $\le 1 \times 10^{-4}$ M CrO_2^{2+} were prepared by the rapid injection of a dilute solution of Cr^{2+} (10 mL, ≤ 1 mM) into oxygen-saturated aqueous perchloric acid (30 mL, 0.1 M H^+). Sufficient lithium perchlorate was used to obtain an ionic strength of 1.00 M. A fresh solution was prepared for nearly every experiment. In each case the UV spectrum was recorded, and samples containing appreciable concentrations of $HCrO_4^-$ were discarded. CrO_2^{2+} has a UV spectrum in good agreement with that reported:[5,6] λ_{max} 290 and 247 nm (ϵ 3100 and 7400 M^{-1} cm^{-1}).

Attempts to increase the concentration of CrO_2^{2+} by the use of higher $[Cr^{2+}]$ only increased the concentration of $HCrO_4^-$, an undesirable side product. Higher concentrations of dissolved oxygen (up to 0.05 M by the use of 50 atm pressure of O_2 in a bomb) also showed excessive $HCrO_4^-$ formation. Contamination by $HCrO_4^-$ is evident by its absorbance maximum at 353 mm, absent in pure solutions of CrO_2^{2+}. The solution of CrO_2^{2+} was then bubbled with a vigorous stream of argon to remove all traces of oxygen.

Kinetics. The subsequent reactions of CrO_2^{2+} were monitored spectrophotometrically, usually at the 290-nm absorption maximum. Some reactions were evaluated with $[O_2] = 0$. In other cases, a known concentration of oxygen was maintained throughout by a calibrated O_2-Ar gas mixture to provide the desired $[O_2]$. To maintain constant $[O_2]$ in a kinetic run, the gas mixture was passed continuously through the reaction cell.

First-order and second-order kinetic data were evaluated by standard procedures. For data following a mixed first- and second-order rate law (eq 3), the following equation was used:

$$[CrO_2^{2+}]_t = \frac{2k_1[CrO_2^{2+}]_0}{e^{(2k_1 t)}(2k_1 + k''[CrO_2^{2+}]_0) - k''[CrO_2^{2+}]_0} \quad (14)$$

(34) Wong, C. L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

(35) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

(36) Thermodynamic data do not appear to be available for $(H_2O)_5CrOAc^{2+}$, however, although the kinetics of its (heterolytic) dissociation have been studied.[35] Since aquation proceeded to completion at 0.04 M H^+, a conservative estimate affords a stability constant for $Cr^{3+} + OAc^- = CrOAc^{2+}$ of $K < 5 \times 10^4$ M^{-1}.

(37) (a) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393. (b) Yamdagni, R.; Payzant, J. D.; Kebarle, P. *Can. J. Chem.* **1973**, *51*, 2507.

(38) Swaddle, T. W.; King, E. L. *Inorg. Chem.* **1965**, *4*, 532. Stability constants for $(H_2O)_5CrX^{2+}$ complexes have been summarized by: Swaddle, T. W.; Guastalla, G. *Inorg. Chem.* **1968**, *7*, 1915.

(39) Stability constants for $(NH_3)_5CoX^{2+}$ complexes have been summarized by: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 165.

(40) An analysis of the energetics of electron transfer in $(NH_3)_5CoX^{2+}$ complexes has been given: (a) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321. (b) Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic: New York, 1970.

(41) Where known, stability constants toward a given X^- are comparable for $Co(NH_3)_5OH_2^{3+}$ and $(H_2O)_2Co([14]aneN_4)^{3+}$.

(42) An interesting possibility, but one that we are unable to address properly, is whether the ground state of this ion might be formulated as the hydroxo–hydroperoxo tautomer $(H_2O)_4Cr(OH)(OOH)^{2+}$.