Reaction of Hydrogen Peroxide with the Oxochromium(IV) Ion by Hydride Transfer

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Received January 28, 1993

Oxidation of hydrogen peroxide by pentaaquaoxochromium(IV), $(H_2O)_5CrO^{2+}$, in aqueous acidic solutions (0.10–1.0 M $HClO_4$) yields the superoxochromium(III) ion $(H_2O)_5CrOO^{2+}$. The same product is obtained in both the presence and the absence of oxygen. In 0.10 M $HClO_4$ the second-order rate constant at 25 °C is 190 ± 10 L mol^{-1} s^{-1} in O_2-saturated solutions and 172 ± 8 L mol^{-1} s^{-1} in Ar-saturated solutions, independent of acidity and ionic strength in the range 0.10–1.0 M ($HClO_4/LiClO_4$). In D_2O as solvent the rate constant is $k_D = 53 \pm 3$ L mol^{-1} s^{-1}, resulting in the kinetic isotope effect $k_H/k_D = 3.6$. Experiments in the temperature range 6.8–38.4 °C yielded $\Delta H^{\ddagger} = 25 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -116 \pm 8$ J mol^{-1} K^{-1}. A hydride-transfer mechanism is suggested for the oxidation of H_2O_2 by CrO^{2+}. It involves the coordination of H_2O_2 to Cr(IV) prior to the hydride abstraction step. The reaction of $HCrO_4^-$ with H_2O_2 under the same conditions also yields $(H_2O)_5CrOO^{2+}$, which was identified by its characteristic UV spectrum. Possible mechanisms for these reactions are discussed.

Introduction

Hydrogen peroxide usually oxidizes low-valent metal complexes in one-electron steps. Most such reactions follow the Fenton mechanism, producing hydroxyl radicals as intermediates.[1-4] Indeed, any other mechanism, such as that adopted by the reaction between Cu_{aq}^+ and hydrogen peroxide,[5] is considered exceptional. In any case, an open coordination site for peroxide seems to be a prerequisite.

On the other hand, high-valent metal complexes, such as those of Cr(VI), Fe(IV) and Cu(II), produce bound or free superoxide ions or molecular oxygen.[6-12] Peroxotitanium[13] and peroxovanadium[14] complexes are produced from hydrogen peroxide and oxotitanium(IV) and dioxovanadium(IV) ions.

$$VO_2^+ + H_2O_2 \rightarrow V(O)(O_2)^+ + H_2O \qquad (1)$$

$$V(O)(O_2)^+ + H_2O_2 \rightarrow V(O)(O_2)_2^- + 2H^+ \qquad (2)$$

Heating $V(O)(O_2)^+$ in dilute acid causes the peroxo group to disproportionate, yielding O_2 and vanadium(V) (eq 3). In

$$2VO(O_2)^+ \rightarrow 2VO_2^+ + O_2 \qquad (3)$$

concentrated acid, or upon treatment with the strongly oxidizing hexaaquacobalt(III) ion, VO^{2+} and O_2 are formed (eq 4).[15]

$$VO(O_2)^+ + Co(H_2O)_6^{3+} \rightarrow VO^{2+} + O_2 + Co(H_2O)_6^{2+} \qquad (4)$$

Decreasing the pH reduces the extent of peroxide coordination by virtue of pH equilibria, the coordinating forms being HO_2^- and O_2^{2-}.[6a]

Oxidation–reduction pathways have been found for other high-valent metals including Fe, Co, Ni, Cu, and Ag.[16-20] With coordination sites available, electron transfer involves $M{-}OOH^{n+}$ intermediates that rapidly yield O_2 or a superoxide adduct (eq 5).[18,19] On the other hand, H_2O_2 oxidizes $(bpy)_2(py)RuO^{2+}$, which

$$M^{n+1} + HOO^- \rightarrow M{-}OOH^n \rightarrow M^{n-1} + O_2 + H^+ \qquad (5)$$

lacks a coordination site, by H atom abstraction from noncoordinated H_2O_2 (eq 6).[21]

$$(bpy)_2(py)Ru{=}O^{2+} + H_2O_2 \rightarrow (bpy)_2(py)RuOH^{2+} + HO_2 \qquad (6)$$

The reaction of Cr(VI)[6a] with H_2O_2 first forms the oxodiperoxide CrO_5 ($K_f \sim 2 \times 10^8$ at 25 °C)[11] (eq 7). This is followed

$$HCrO_4^- + 2H_2O_2 + H^+ \overset{K_f}{\rightleftharpoons} CrO(O_2)_2 + 3H_2O \qquad (7)$$

by the reduction of Cr(VI) by the peroxo group to yield Cr(III) and O_2 via a Cr(III)–peroxyl radical intermediate.[11,12] A relatively stable diperoxochromium(IV) species, prepared from ammonium dichromate and hydrogen peroxide in aqueous ammonia, decomposes in acidic solution to Cr(VI), Cr(III), and O_2.[6a]

Only one example of the reaction of H_2O_2 with Cr(IV) has been reported. The diperoxo Cr(IV) complex $Cr(O_2)_2(en)H_2O$ reacts with H_2O_2 to produce the oxodiperoxo Cr(VI) species $CrO(O_2)_2(en)$ (k = 48 L mol^{-1} s^{-1}).[6c] In this reaction H_2O_2 oxidizes Cr(IV). However, in a different environment the reduction potentials may be reversed and H_2O_2 may reduce Cr(IV) to Cr(III) or Cr(II). An example of this type of chemistry was

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encountered in this work. We report the kinetics of oxidation of H_2O_2 by the hydrated oxochromium(IV) ion[22] $(H_2O)_5Cr{=}O^{2+}$. This reaction is particularly striking in that it forms $CrOO^{2+}$ in the presence *and absence* of O_2.

Experimental Section

Reaction of H_2O_2 with $(H_2O)_5CrO^{2+}$. Solutions of Cr^{2+} (0.01 M) in dilute perchloric acid were prepared by anaerobic reduction of Cr^{3+} with Zn/Hg. Injection of Cr^{2+} into an acidic aqueous solution saturated with O_2 gives rise to CrO^{2+},[23,24] as described in more detail later. A fresh solution of CrO^{2+} was prepared immediately prior to each experiment. The acid concentration and the ionic strength were both 0.10 M except in experiments designed to study the effects of these variables. The pH was maintained by perchloric acid, and the ionic strength, by lithium perchlorate. Commercial hydrogen peroxide (30%, Fisher) and $Tl_2(SO_4)_3$ were used without further purification. The kinetic isotope effect was determined by conducting experiments in D_2O and H_2O as solvents. The temperature was controlled in all the experiments by means of a thermostated cell holder connected to a circulating water bath set at the desired temperature.

In a typical kinetic experiment CrO^{2+} was formed *in situ* by injecting 100 μL of 0.10 M Cr^{2+} (final $[Cr^{2+}] = 0.2$ mM) into a spectrophotometric cell filled with an O_2-saturated (1.26 mM at 25 °C) solution containing at least 0.5 mM H_2O_2. Under these conditions Cr^{2+} and O_2 react to produce ~0.04 mM CrO^{2+} (~20% based on total Cr^{2+}). This is then followed by the reaction of interest between H_2O_2 and CrO^{2+}. For anaerobic experiments CrO^{2+} was prepared by injecting Cr^{2+} into a spectrophotometric cell that contained a solution of 2–3 equiv of air-free Tl^{3+}. Hydrogen peroxide (0.5–1.5 mM) was also present in the solution. In both of these procedures, the reaction with hydrogen peroxide was followed from the buildup of the product, $CrOO^{2+}$. This is the superoxochromium(III) ion,[22] well-known from earlier work.[24] The formation of $CrOO^{2+}$ was monitored at 290 nm, where its molar absorptivity is 3100 L mol^{-1} cm^{-1}.

Reaction of H_2O_2 with $HCrO_4^-$. The oxidation of H_2O_2 by $HCrO_4^-$ was studied in both the presence and the absence of O_2. In each experiment a solution containing 3×10^{-4} M $HCrO_4^-$ was allowed to react with 2.0 mM H_2O_2 in 0.1 M $HClO_4$. The absorption spectra of the products were recorded at 200–400 nm.

The rate constant k_ψ of eq 8 was obtained by fitting the absorbance–time data to the first-order kinetic expression $\text{Abs}_t = \text{Abs}_\infty - (\text{Abs}_0 - \text{Abs}_\infty)\exp(-k_\psi t)$, where Abs = absorbance

$$d[CrOO^{2+}]/dt = k_\psi[CrO^{2+}] \qquad (8)$$

Results

In the presence of O_2 the oxidation of H_2O_2 by CrO^{2+} produces $CrOO^{2+}$ (eq 9), which was detected by its absorption bands at

$$CrO^{2+} + H_2O_2 \xrightarrow{k_9} CrOO^{2+} + H_2O \qquad (9)$$

$$-\frac{d[CrO^{2+}]}{dt} = (k_{dec} + k_9[H_2O_2])[CrO^{2+}] \qquad (10)$$

290 nm ($\epsilon = 3100$ L mol^{-1} cm^{-1}) and 245 nm ($\epsilon = 7000$ L mol^{-1} cm^{-1}).[25] When H_2O_2 was in large excess over CrO^{2+}, the rate of formation of $CrOO^{2+}$ followed first-order kinetics. The pseudo-first-order rate constants varied linearly with H_2O_2 concentration at constant ionic strength, as expected from eqs 9 and 10. A plot of k_ψ *vs* $[H_2O_2]$ at 25.0 °C and 0.1 M ionic strength has a slope of $k_9 = 191 \pm 10$ L mol^{-1} s^{-1} in H_2O and 53 ± 3 L mol^{-1} s^{-1} in D_2O, giving $k_H/k_D = 3.6$, as shown in Figure 1.

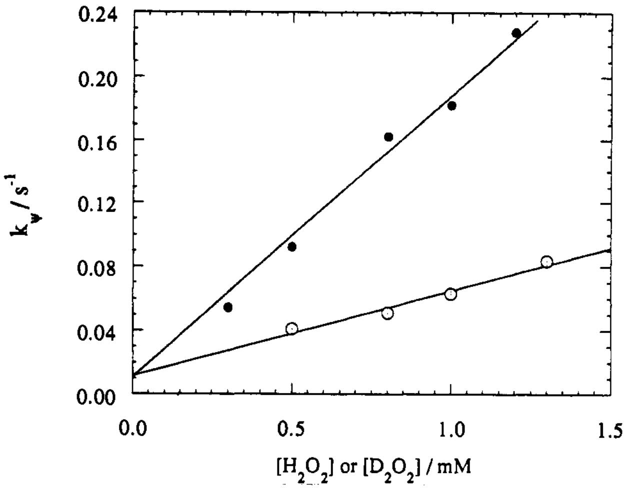

Figure 1. Dependence of k_ψ on the concentration of H_2O_2 in H_2O (filled circles) and of D_2O_2 in D_2O (open circles) for the reaction of hydrogen peroxide with CrO^{2+} in 0.10 M perchloric acid at 25 °C.

Table I. Dependence on the Peroxide Concentration of the Pseudo-First-Order Rate Constants (k_ψ) for the Oxidation of H_2O_2 and D_2O_2 by CrO^{2+} in 0.1 M $HClO_4$ or $DClO_4$ at 25 °C

$[H_2O_2]/10^{-4}$ M	k_ψ/s^{-1}	$[D_2O_2]/10^{-4}$ M[a,b]	k_ψ/s^{-1}
3.0	0.054[b] (0.058)[c]	5.0	0.041
5.0	0.092[b] (0.098)[c]	8.0	0.051
8.0	0.162[b]	10	0.063
10.0	0.182[b] (0.180)[c]	13	0.083
12.0	0.228[b]		

[a] In D_2O. [b] In the presence of O_2. [c] In the absence of O_2.

Table II. Ionic Strength Dependence of k_9 and k_{dec} in 0.1 M $HClO_4$ at 25 °C[a]

ionic strength/M ($HClO_4$/$LiClO_4$)	k_{dec}/s^{-1}	k_9/L mol^{-1} s^{-1}
0.1	0.009 ± 0.001	191 ± 10
0.4	0.018 ± 0.001	182 ± 13
0.6	0.023 ± 0.002	184 ± 9
1.0	0.029 ± 0.003	188 ± 2

[a] The rate law is given by eq 10.

The small intercept in these plots corresponds to the decomposition of CrO^{2+}. Analysis of the data on this basis yields $k_{dec} = 0.01$–0.03 s^{-1} at 25.0 °C.[26] The effects of the acidity and ionic strength on k_ψ were studied over the range 0.10–1.0 M ($HClO_4$/$LiClO_4$) by changing one parameter at a time. The pseudo-first-order rate constant was found to be independent of $[H^+]$ and proportional to the ionic strength (Figure 2). Further analysis showed that only k_{dec} increases with ionic strength and that the second-order rate constant k_9 is independent of ionic strength. This is as expected from the charge types involved. The variation of k_9 with temperature over the range 6.8–38.4 °C yielded the activation parameters $\Delta H^* = 25 \pm 3$ kJ mol^{-1} and $\Delta S^* = -116 \pm 8$ J mol^{-1} K^{-1} (Figure 3).

Even in the absence of O_2, the reaction of CrO^{2+} with H_2O_2 yielded $CrOO^{2+}$ as in reaction 9. Just as in the presence of O_2,

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(22) The formula for the oxochromium(IV) ion is written in several places as the pentaaqua ion, which we believe but have not proved it to be. The superoxochromium(III) ion $(H_2O)_5CrOO^{2+}$ has been shown to be a chromium(III) species with an η^1-superoxide ion. (We write its formula as shown in this paper, lest the notation $(H_2O)_5CrO_2^{2+}$ be confused for an oxo complex.) Because of the reactions that CrO^{2+}, $CrOOH^{2+}$, and $CrOO^{2+}$ undergo, we *assume* that they are all six-coordinate. The noncomittal notation CrO^{2+} has been used except in circumstances where the specification of the solvation is helpful.

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(26) The range of k_{dec} given represents the value at the concentrations of oxochromium(IV) ion that were used. The decomposition pathway is a minor component under these conditions; thus we have no clear proof that the decomposition pathway has a first-order dependence on $[CrO^{2+}]$. Indeed, there is some indication that the order of the decomposition reaction with respect to $[CrO^{2+}]$ is >1.

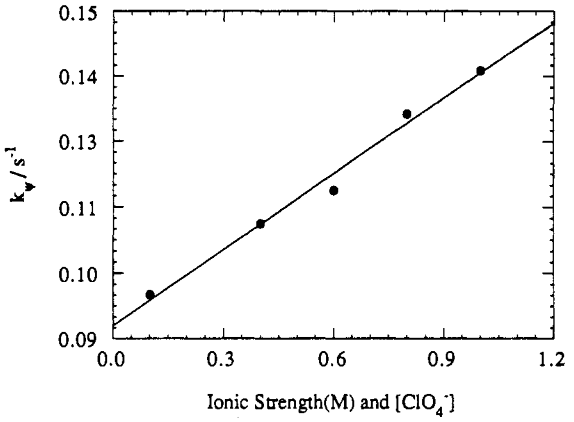


Figure 2. Ionic strength dependence of the observed rate constants k_ψ for the reaction of H_2O_2 (0.50 mM) with CrO^{2+} in 0.10 M perchloric acid at 25 °C. The sole source of the dependence is k_{dec} (eq 10).

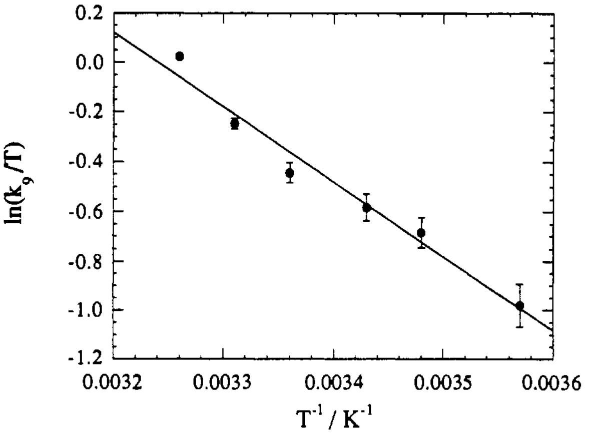


Figure 3. Plot of ln (k_9/T) against $1/T$ at 0.1 M $HClO_4$ for the reaction of H_2O_2 with CrO^{2+}.

the formation of $CrOO^{2+}$ followed pseudo-first-order kinetics when peroxide was in excess. The second-order rate constant was determined to be $k_9 = 172 \pm 7$ L mol^{-1} s^{-1}.

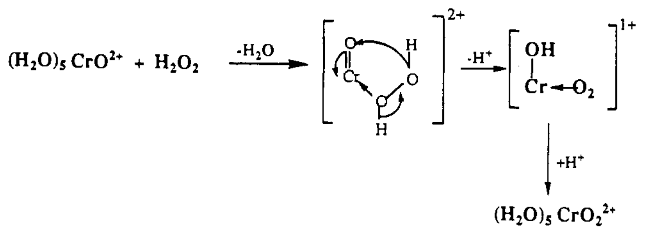
The oxidation of H_2O_2 by $HCrO_4^-$ in aqueous solution was also carried out in the presence and in the absence of O_2. In both experiments the colorless solution rapidly turned blue and then faded relatively slowly, owing to the formation and decomposition of oxodiperoxochromium(VI), $OCr(O_2)_2$.[11] The UV spectra recorded during these experiments showed that $CrOO^{2+}$ was formed in both cases.

Discussion

As an oxidant, CrO^{2+} is more reactive kinetically than $HCrO_4^-$. Whereas it takes several hours to reduce a dilute solution of $HCrO_4^-$ by 2 mM methanol in 0.10 M $HClO_4$ at 25 °C, with CrO^{2+} the reaction is complete in 3 min.[23] This is not surprising, in that Cr(IV) is thermodynamically more oxidizing than Cr(VI). Some relevant reduction potentials: Cr(VI)/Cr(V), 0.55 V;[27] Cr(VI)/Cr(III), 1.33 V; Cr(IV)/Cr(III), ca. 1.5–1.7 V. Some of the differences seen in these potentials reflect the major changes in coordination number and geometry that accompany some of the reduction steps but not others.[24]

The values of the rate constant k_9 under O_2 (191 ± 10 L mol^{-1} s^{-1}) and Ar (172 ± 7 L mol^{-1} s^{-1}) are acceptably close to allow us to conclude that O_2 plays no role in the rate-controlling reaction. These values are the same within the experimental error. The rate constant obtained under argon has the greater systematic error from the substantial background absorbance of both Tl^{3+} and Tl^+, which are present only in the air-free experiments.

Scheme I



The activation parameters were determined only in the presence of O_2. The large negative value of $\Delta S^\ddagger$, −116 J mol^{-1} K^{-1}, suggests a bimolecular rate-controlling step. The low value of $\Delta H^\ddagger$, 25 kJ mol^{-1}, indicates a mechanism featuring compensating bond breaking and bond making, as proposed below. As a guide to the mechanism of the hydrogen peroxide reaction, we turn to what was previously established for CrO^{2+}. The activation parameters obtained in this study are similar to those obtained in oxidation of alcohols by CrO^{2+} ($\Delta H^\ddagger$ = 33–38 kJ mol^{-1}, $-\Delta S^\ddagger$ = 95–112 J mol^{-1} K^{-1}). A hydride-transfer mechanism was proposed for these reactions. The only exception is the case of cyclobutanol ($\Delta H^\ddagger$ = 46 kJ mol^{-1}, $\Delta S^\ddagger$ = −61 J mol^{-1} K^{-1}), which reacts by hydrogen atom abstraction *via* a carbon-centered radical intermediate.[24]

The one-electron reduction of CrO^{2+} produces Cr(III), which is inert toward further oxidation or reduction by other reagents present in the solution. On the other hand, the two-electron reduction of CrO^{2+} produces Cr^{2+}, which binds O_2 rapidly (k = 1.6 × 10^8 L mol^{-1} s^{-1}) and completely, forming $CrOO^{2+}$.[25] Formation of $CrOO^{2+}$ from Cr^{2+} normally occurs upon reaction with O_2. Our results show that $CrOO^{2+}$ is formed from CrO^{2+} and H_2O_2 both in the presence *and absence* of O_2. From these results we conclude that the source of oxygen in $CrOO^{2+}$ is H_2O_2 and not the free O_2 in solution. There is no evidence that Cr^{2+} is involved as an intermediate.

A further guide to the mechanism is found in the kinetic isotope effect (kie). We suggest that this is a primary kie for D_2O_2 *versus* H_2O_2. The kie need not necessarily arise from D_2O_2, however, in that both the solvent and the coordinated water molecules are also deuterated, given the design of the experiment. On the one hand, the kie appears to be far too large to be attributed to the cumulative secondary kie's of water molecules coordinated to the oxochromium(IV) ion. On the other, if it is instead a primary kie of a coordinated water molecule, we have been unable to construct a mechanism that would facilitate the conversion of reactants to products. Thus we postulate that the H–OOH bond is indeed centrally involved in the activation step.

The moderate primary kie (k_H/k_D = 3.6) supports the proposed oxygen–hydrogen bond breaking in the rate-controlling step. Also, the low value of $\Delta H^\ddagger$ is indicative of the coordination of H_2O_2 to chromium prior to hydride abstraction. The molecular orbital analysis has shown that such coordination would lower the activation energy for hydride abstraction by the oxo ligand.[28] A mechanism consistent with all the data is presented in Scheme I. A rapidly formed CrO^{2+}–H_2O_2 complex is proposed to undergo rate-controlling intramolecular hydride transfer. This yields $(HO)CrO_2^+$, which upon protonation becomes $CrOO^{2+}$. This mechanism agrees with the previous work on catalyzed disproportionation and oxidation of H_2O_2 by high-valent transition metal complexes[9,11] and on the oxidation of alcohols by CrO^{2+}.[24]

The decomposition of the $OCr(O_2)_2$ compound (i.e., CrO_5) formed in the H_2O_2–$HCrO_4^-$ reaction is not completely understood. It decomposes at low temperatures (≤0 °C) in 3–6 M $HClO_4$ to yield the polynuclear peroxochromium(III) species CrO_2Cr^{4+} and $CrO_2CrO_2Cr^{5+}$.[10] On the other hand, the decomposition of CrO_5 at room temperature was proposed[11] to

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yield a trivalent chromium(III) complex with a coordinated peroxyl radical. In the notation of these authors, it was written as $Cr^{III}(O_2^{\bullet})^{2+}$. This intermediate reacts rapidly with CrO_5 and finally yields Cr^{3+}, H_2O_2, and O_2 (eq 11).

$$Cr^{III}(O_2^{\bullet})^{2+} + CrO_5 + 4H^+ \rightarrow 2Cr^{3+} + 2H_2O_2 + O_2 \quad (11)$$

Additional experiments on the previously studied oxidation of H_2O_2 with $HCrO_4^-$ were also carried out in this work under the same conditions used for the H_2O_2–CrO^{2+} reaction. In our hands the reaction yielded $CrOO^{2+}$. This suggests that it and the proposed $Cr^{III}(O_2^{\bullet})^{2+}$ are identical. Assuming that they are, one wonders why a different, polynuclear product was formed at 0 °C.[11] We considered the possibility that the reported CrO_2Cr^{4+}, formally a dimer of the oxochromium(IV) ion, might dissociate at room temperature into two molecules of CrO^{2+} (eq 12). This would then be followed by reaction 9 and yield $CrOO^{2+}$.

$$CrO_2Cr^{4+} \overset{K_{eq}}{\rightleftharpoons} 2CrO^{2+} \quad (12)$$

According to this interpretation the reaction yields different products at 0 and 25 °C because of the temperature effect on the equilibrium of eq 12.

This proposal had to be discarded, however, because our experiments with the μ-peroxo complex CrO_2Cr^{4+}, prepared as in the published report,[10] does not yield measurable amounts of CrO^{2+} at 25 °C. It is possible that the use of high concentrations of reactants in ref 11 is the reason for the formation of different products.

Acknowledgment. Support for this research was provided by the National Science Foundation under Grant CHE 9007283. Some of the experiments were done with facilities of Ames Laboratory.