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Disproportionation of Aquachromyl(IV) Ion by Hydrogen Abstraction from Coordinated Water

Attila Nemes and Andreja Bakac*

Ames Laboratory, Iowa State University, Ames, Iowa 50011

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In aqueous solutions, the aquachromyl(IV) ion, $Cr_{aq}O^{2+}$, disproportionates to Cr_{aq}^{3+} and $HCrO_4^-$. The reaction exhibits second-order kinetics with an inverse $[H^+]$ dependence, $-d[Cr_{aq}O^{2+}]/dt = 38.8[Cr_{aq}O^{2+}]^2[H^+]^{-1}$ at 25 °C. The combination of the rate law and substantial kinetic isotope effect, $k_H/k_D = 6.9$, suggests a mechanism whereby a hydrogen atom is abstracted from a coordinated molecule of water or hydroxo group within a singly deprotonated transition state. The buildup of chromate is more complicated and somewhat slower than the loss of chromyl, suggesting the involvement of intermediates.

Introduction

The unstable IV and V oxidation states of aquachromium are inevitably involved as intermediates in the reduction of chromate and oxidation of Cr_{aq}^{3+}. In the reactions of chromate with alcohols,[1,2] oxalate,[3,4] and various other substrates,[5] a number of research groups have demonstrated the involvement of Cr(IV)[4,6,7] and Cr(V),[1−3] often complexed to the substrate, in the overall process. ESR spectroscopy was used successfully[1,3,5] to identify Cr(V), which may not be produced directly in the substrate/$HCrO_4^-$ reaction but rather by the disproportionation of Cr(IV) and reduction of $HCrO_4^-$ by Cr_{aq}^{2+}.[5,7−9] The possibility that Cr(V) is the active carcinogen in Cr(VI)-induced cancers has prompted a large number of ESR studies[10] in search of Cr(V) in the reduction of chromate by various biologically relevant organic substrates.[11−16] Cr(V) was indeed identified in almost every study designed to detect it, although the sheer presence of Cr(V) in such systems provides no information as to its role in DNA-damaging processes.

In aqueous solutions containing 0.01 M formate/formic acid, Cr(V) disproportionates, eq 1, in a pH-dependent process as determined recently by pulse radiolysis.[17] This work provided a $pK_a = 3.8$ for the (presumably) tetrahedral $H_2CrO_4^-$ and a bimolecular rate constant $k = 3.4 \times 10^8\ M^{-1}\ s^{-1}$ for the reaction between tetrahedral $HCrO_4^{2-}$ and octahedral "H_3CrO_4". The question[1,5,6,9] of whether the reaction of eq 1 lies to the left or right has thus been settled by experiment,[17] although one cannot rule out the possibility that the actual species in this medium are not the pure aqua forms but rather the formato complex(es). Such an assignment would be consistent with the known tendency of Cr(IV) and Cr(V) to engage in complex formation with inorganic and organic substrates.[18,19]

$$2Cr(V) \rightarrow Cr(VI) + Cr(IV) \qquad (1)$$

The ESR silence of Cr(IV) makes it more difficult to detect this oxidation state spectroscopically. Nevertheless, careful trapping and competition studies provided strong evidence for transient generation of Cr(IV) in reductions of chromate with organic substrates.[4,6,7] Several years ago we discovered an independent route for the generation of $Cr(IV)_{aq}$ from Cr_{aq}^{2+} and O_2[7,20] and shown this surprisingly persistent species to be identical to that produced in the chromate/2-propanol reaction. A 0.1 mM solution of $Cr(IV)_{aq}$, which we believe to be an aquachromyl ion $Cr_{aq}O^{2+}$, has a half-life of ~20 s at pH 1.[7]

Two different pathways for the decay of $Cr(IV)_{aq}$ have been discussed. One is the reverse of eq 1,[6,21,22] which was shown to be thermodynamically unfavorable on the basis of estimated reduction potentials for the Cr(VI), Cr(V), Cr(IV) sequence,[9] and the other is disproportionation,[4,6,7,23] eq 2.

$$2Cr(IV)_{aq} \rightarrow Cr(III)_{aq} + Cr(V)_{aq} \qquad (2)$$

Now that a method for generating bulk concentrations of $Cr_{aq}O^{2+}$ is available,[7] it should be possible to determine

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experimentally the fate of $Cr_{aq}O^{2+}$ in such solutions. Unfortunately, we have recently discovered that this species has no prominent features in the UV−visible spectrum, despite our earlier statements[7] to the contrary. Solutions of $Cr_{aq}O^{2+}$ always contain some $Cr_{aq}OO^{2+}$ and $HCrO_4^-$, both of which absorb strongly in the UV. The interference from these two absorbing impurities has led to our erroneous spectral assignment. Also, a species believed to be Cr_{aq}(IV) was recently generated by pulse radiolysis at pH ≥ 3 and shown to absorb only modestly in the UV.[24]

In this work we have utilized the known reaction of $Cr_{aq}O^{2+}$ with methanol, eqs 3 and 4, to monitor $Cr_{aq}O^{2+}$ for kinetic purposes by converting it to the strongly absorbing $Cr_{aq}OO^{2+}$. This approach has allowed us to determine precisely the kinetics and likely mechanism of decomposition of $Cr_{aq}O^{2+}$.

$$Cr_{aq}O^{2+} + CH_3OH \rightarrow Cr_{aq}{}^{2+} + CH_2O + H_2O \qquad (3)$$

$$Cr_{aq}{}^{2+} + O_2 \rightleftarrows Cr_{aq}OO^{2+} \qquad (4)$$

Experimental Section

Solutions of $Cr_{aq}O^{2+}$ were prepared by injecting the appropriate amount of $Cr_{aq}{}^{2+}$ (typically 90 μL of 5 or 20 mM solution) into a spectrophotometric cell containing an air- or O_2-saturated solution of dilute aqueous perchloric acid and, when necessary, lithium perchlorate to adjust the ionic strength. The yield of $Cr_{aq}O^{2+}$ was typically 20−30%, the rest of the chromium having been converted to (mostly) $Cr_{aq}{}^{3+}$ and some $Cr_{aq}OO^{2+}$ (10−15%). At constant conditions, the yields of $Cr_{aq}O^{2+}$ were highly reproducible (±10%). This was essential for kinetic experiments, most of which utilized a separate solution for each concentration−time point, as follows.

A freshly prepared solution of $Cr_{aq}O^{2+}$ was aged inside the thermostated cell holder in the sample compartment of a Shimadzu 3101 PC spectrophotometer. At a predetermined time, methanol (40 μL) was injected to convert the remaining $Cr_{aq}O^{2+}$ to $Cr_{aq}OO^{2+}$, eq 3 and 4, and the absorbance increase was recorded at 290 nm. Approximately 10−12 such measurements were carried out for each kinetic run.

In a similar set of experiments, methanol was replaced with a solution of sodium iodide and the formation of I_3^- was monitored at 350 nm. All three chromium species ($Cr_{aq}O^{2+}$, $Cr_{aq}OO^{2+}$, and $HCrO_4^-$) oxidize iodide to I_3^- ($\epsilon_{350} = 2.6 \times 10^4$ M^{-1} cm^{-1}). At our standard conditions, 0.033 M I^- and 0.10 M H^+, the reactions with $Cr_{aq}O^{2+}$ and $Cr_{aq}OO^{2+}$ were complete upon mixing, but that with chromate required ∼10 min for completion. The addition of iodide to an aged solution of $Cr_{aq}O^{2+}$ thus caused a jump in absorbance at 350 nm followed by a slower absorbance increase. With the concentration of $Cr_{aq}OO^{2+}$ approximately constant for the duration of the experiment (to within 20% on the basis of spectral data), the changes in the jump were taken to represent the changes in the concentration of $Cr_{aq}O^{2+}$.

Results

The decomposition of $Cr_{aq}O^{2+}$ produces chromate. From the absorbance increase at the 350 nm maximum of $HCrO_4^-$ ($\epsilon_{350} = 1.61 \times 10^3$ M^{-1} cm^{-1}),[17] we obtained a stoichiometric ratio $\Delta[Cr_{aq}O^{2+}]/\Delta[HCrO_4^-] = 2.8 \pm 0.3$ (average of eight determinations).

Kinetics. (a) Using Methanol Indicator Reaction. Figure 1 (bottom) shows a kinetic curve obtained under typical conditions: 0.10 M $HClO_4$; ∼0.03 mM $Cr_{aq}O^{2+}$; 25 °C. The data obeyed second-order kinetics and were fitted to eq 5, where Abs_t, Abs_0, and Abs_∞ represent absorbances at times t, time zero, and after completion of the reaction, respectively. The average of several such runs yielded $k_{obs} = 482$ M^{-1} s^{-1}. The calculated standard deviation is only 3%, but an uncertainty of ±15% in all of our kinetic data is more reasonable considering the need to use a fresh reaction solution for each kinetic point, see Experimental Section, and the sensitivity of second-order rate constants to concentrations.

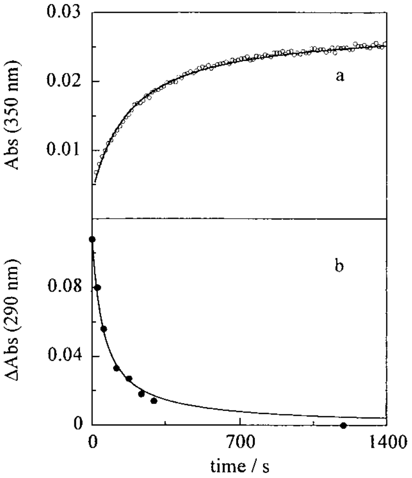

Figure 1. Kinetic traces and second-order fits for (a) formation of $HCrO_4^-$ at 350 nm and (b) disappearance of $Cr_{aq}O^{2+}$ followed by MeOH indicator reaction at 290 nm. Conditions: $[HClO_4] = 0.10$ M, 25 °C, $[Cr_{aq}O^{2+}]_0 = 3.7 \times 10^{-5}$ M (a) and 3.4×10^{-5} M (b). ΔAbs in (b) is the difference in absorbance measured after and before the addition of MeOH.

$$Abs_t = Abs_\infty + \frac{Abs_0 - Abs_\infty}{1 + k_{obs}[Cr_{aq}O^{2+}]_0 t} \qquad (5)$$

Another set of experiments in 0.10 M $HClO_4$ utilized the highest concentration of $Cr_{aq}O^{2+}$ that was experimentally attainable, 0.16 mM, and gave $k_{obs} = 283$ M^{-1} s^{-1}. The agreement (40% deviation) with the rate constant obtained at a 5-fold lower initial concentration is acceptable, although the reaction was accompanied by a ∼40% loss of $Cr_{aq}OO^{2+}$, which is more than double the percentage that disappeared at 0.03 M $Cr_{aq}O^{2+}$. At the high reactant concentrations, $Cr_{aq}OO^{2+}$ may get involved in post-rate-determining steps, thereby changing the stoichiometric factor and thus the observed rate constant. All the subsequent experiments utilized the lower of the two concentrations of $Cr_{aq}O^{2+}$ (∼0.03 mM). Further lowering of $[Cr_{aq}O^{2+}]$ so as to confirm the rate law over a wider range of concentrations made the absorbance changes too small for precise kinetic measurements.

The reaction rate increases with a decrease in $[H^+]$. Kinetic measurements were carried out in the range $0.020 < [H^+] < 0.10$ M at 0.10 M ionic strength. A plot of the rate constant against the inverse concentration of $[H^+]$ is linear with a zero intercept and a slope of 38.8 s^{-1}, Figure 2.

An increase in the ionic strength from 0.020 to 0.10 M caused the rate constant at 0.020 M H^+ to decrease from 2.42×10^3 to 1.99×10^3 M^{-1} s^{-1}. For a reaction between two dications to give a proton and a transition state with a 3+ charge, as indicated by the inverse acid dependence, the rate constant is expected to increase by 30% as the ionic strength increases from 0.02 to 0.10 M.[25] With an estimated error of ±15% for all the rate constants, the closeness of the two values neither supports nor rules out the presumed 2+ charge on the chromyl ions.

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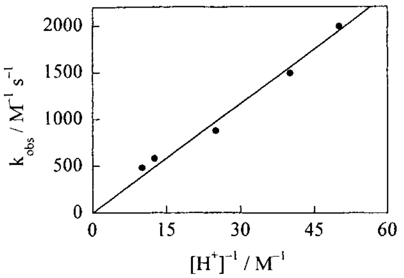

Figure 2. Plot of k_{obs}, determined by MeOH indicator reaction, against $[H^+]^{-1}$ for the disappearance of $Cr_{aq}O^{2+}$, with $\mu = 0.10$ M ($HClO_4$ + $LiClO_4$), 25 °C.

Replacing the solvent water with D_2O (96% D) caused the rate constant to decrease by a factor of 5.4 to $k_{obs} = 89.4\ M^{-1}\ s^{-1}$ at 0.10 M H^+. If the isotopic composition of the hydrogens involved in the reaction is identical to that of the solvent, as one would expect, then some of the reaction in 96% D_2O still involves the remaining H isotope. The corrected value of k_D is 70.1 $M^{-1}\ s^{-1}$ (i.e. $89.4 - \{0.04 \times 482\}$) yielding a kinetic isotope effect (kie), $k_H/k_D = 6.9$.

The initial concentration of $Cr_{aq}O^{2+}$ was reproducibly about 50% lower in D_2O than in H_2O solutions containing the same initial concentrations of O_2 and ${Cr_{aq}}^{2+}$. The isotope effect on the yield of chromyl suggests that some step(s) in its formation from ${Cr_{aq}}^{2+}$ and O_2 may involve hydrogen ion or hydrogen atom transfer which competes with other, nonproductive steps.

(b) Using Iodide Indicator Reaction. This method is somewhat less precise than the methanol method because both $Cr_{aq}O^{2+}$ and $Cr_{aq}OO^{2+}$ decompose to yield chromate, albeit on different time scales, and both oxidize I^- to ${I_3}^-$ in the fast initial step of the indicator reaction; see Experimental Section. The overall 3:1 stoichiometry in the reactions of iodide with both $Cr_{aq}OO^{2+}$ and ${HCrO_4}^-$, compared to only 1:1 for $Cr_{aq}O^{2+}/I^-$ reaction, artificially amplifies (triples) the minor concentration changes associated with the self-decay of $Cr_{aq}OO^{2+}$. The rate constants obtained in these measurements for the disappearance of $Cr_{aq}O^{2+}$ and the appearance of ${HCrO_4}^-$ have values 324 $M^{-1}\ s^{-1}$ and 255 $M^{-1}\ s^{-1}$, respectively at 0.10 M H^+.

The spectral data, which provided directly the concentrations of $Cr_{aq}OO^{2+}$ and ${HCrO_4}^-$ in the absence of iodide, and iodometric data, which yielded $\{[Cr_{aq}O^{2+}] + [Cr_{aq}OO^{2+}]\}$ and $[{HCrO_4}^-]$, were combined and used to calculate the total oxidizing power of the solution at each kinetic point. No new species or reactions were needed to account for the data.

(c) Monitoring Chromate. The increase in absorbance at 350 nm was slower (by a factor of 4−8) than that observed by use of methanol and iodide indicator reactions, Table 1 and Figure 1 (top). Kinetic traces are described well by the second-order rate expression of eq 5. Specifically, there was no obvious delay in the onset of chromate formation, as would be expected if chromate were temporarily retained by an intermediate. Addition of extra chromate (0.33 mM) at the beginning of the reaction at 0.10 M H^+ had no effect on the appearance of the traces or the rate, ruling out slow release of chromate from an equilibrated complex with any of the available oxidation states of chromium. Also, chromate complexes with transition metal aqua ions,[26,27] including ${Cr_{aq}}^{3+}$,[28] exhibit intense absorption bands in the UV−visible region, but the repetitive scanning of the reaction mixture throughout the course of the reaction failed to detect any extra absorbance in the 200−380 nm region.

Table 1. Rate Constants for the Disappearance of $Cr_{aq}O^{2+}$ and Formation of ${HCrO_4}^-$ [a]

$[H^+]$/M	$10^{-2}k_{obs}/M^{-1}\ s^{-1}$	
	$Cr_{aq}O^{2+}$ decay[b]	${HCrO_4}^-$ formation[c]
0.10	4.82[d,e]	1.09[f,g]
0.10	0.894[h]	1.12[h]
0.10		1.14[i]
0.10	2.83[j]	0.463[j]
0.080	5.82	1.66
0.040	8.76	1.42
0.025	14.9	2.82[d]
0.020	19.9	3.28
0.020	24.2[k]	2.62[d,k]

[a] 25 °C, $[Cr_{aq}O^{2+}]_0 = (2.0-3.5) \times 10^{-5}$ M, $\mu = 0.10$ M ($HClO_4$ + $LiClO_4$), except where noted. All the rate constants have an estimated 15% error. [b] Using MeOH indicator reaction; see text. [c] Determined at 350 nm. [d] Average of two determinations. [e] Idometric determination gave $k_{obs} = 324\ M^{-1}\ s^{-1}$. [f] Average of three determinations. [g] Iodometric determination gave $k_{obs} = 255\ M^{-1}\ s^{-1}$. [h] In D_2O (96% D). [i] In the presence of added ${HCrO_4}^-$ (0.33 mM). [j] $[Cr_{aq}O^{2+}]_0 = 1.6 \times 10^{-4}$ M. [k] $\mu = 0.020$ M.

We considered a possibility that, despite the good quality of second-order fits, the traces are distorted by the slow formation of chromate in the parallel, slow decay of $Cr_{aq}OO^{2+}$, which caused the "infinity" reading to keep increasing and resulted in an unreasonably small rate constant. This explanation would require that the total yield of chromate be greater than that calculated by the 3:1 stoichiometry, contrary to the experimental observations. In fact, the ratio $[{HCrO_4}^-]_{formed}/[Cr_{aq}O^{2+}]_{consumed}$, calculated from the data collected on two almost identical solutions at 350 and 290 nm, Figure 1, kept changing throughout the reaction, being the smallest at the beginning and reaching a value close to 0.33 when the absorbance at 350 nm stopped changing.

Interestingly, when the reaction was conducted in D_2O, the loss of chromyl and formation of chromate took place with similar rate constants, Table 1.

Discussion

The second-order kinetics for the disappearance of chromyl, combined with the 3:1 stoichiometry for chromate formation, strongly support the disproportionation reaction of eq 2 followed by either oxidation of $Cr_{aq}(V)$ by $Cr_{aq}O^{2+}$, eq 6, or disproportionation of $Cr_{aq}(V)$,[17] eq 1. In addition to electron transfer, reactions 1 and 6 also include a change in geometry and coordination number[17] as the octahedral Cr(V) is oxidized to tetrahedral Cr(VI). Also, some rapid acid−base chemistry is required to generate thermodynamically stable hydrolytic forms of chromate and chromium(III).

$$Cr_{aq}(V) + Cr_{aq}O^{2+} \rightarrow {HCrO_4}^- + {Cr_{aq}}^{3+} \tag{6}$$

The disproportionation of chromyl was considered in the early works by Haight[6] and Klaning[4] and later gained some support by our observation that aged solutions of chromyl contained large amounts of chromate.[7] Also, a species believed to be Cr_{aq}(IV) was generated pulse radiolytically and observed to decay to chromate, the buildup of which followed second-order kinetics with $k = 1.2 \times 10^7\ M^{-1}\ s^{-1}$ at pH 3.7.[24] (The published value[24] was corrected by a factor of 3 to make it directly comparable to our data in Table 1.)

The significant kinetic isotope effect and inverse acid dependence in the present work clearly show that the reaction

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Scheme 1

$$\mathrm{Cr_{aq}O^{2+} \rightleftarrows HOCr_{aq}O^{+} + H^{+}} \qquad K_a \qquad (S1)$$

$$\mathrm{HOCr_{aq}O^{+} + Cr_{aq}O^{2+} \rightarrow OCr^{V}{}_{aq}O^{+} + Cr_{aq}{}^{III}OH^{2+}} \qquad k_{S2} \qquad (S2)$$

$$\mathrm{Cr_{aq}OH^{2+} + H^{+} \rightleftarrows Cr_{aq}{}^{3+}} \qquad (S3)$$

does not take place by simple electron transfer.[29,30] Such a reaction would generate both products in thermodynamically unfavorable hydrolytic forms, $\mathrm{Cr^{III}{}_{aq}O^{+}}$ and $\mathrm{Cr^{V}{}_{aq}O^{3+}}$, which is probably one reason for a more complicated mechanism.

The data are consistent with Scheme 1, which involves deprotonation of a coordinated molecule of water followed by hydrogen atom transfer to the chromyl oxygen. Either reaction 1 or reaction 6 completes the scheme.

The hydrogen transferred in the redox step may come from the coordinated hydroxo group, as in eq S2, or from one of the coordinated molecules of water, in which case the initial Cr(V) product would have the formula $\mathrm{(HO)_2Cr_{aq}O^{+}}$. Further deprotonation of both $\mathrm{Cr_{aq}(O)_2{}^{+}}$ and $\mathrm{(HO)_2Cr_{aq}O^{+}}$ would be required to reach the thermodynamically stable hydrolytic form of octahedral chromium(V) for which pulse radiolysis suggests a formula "$\mathrm{H_3CrO_4}$"[17]; i.e., there are two more protons in this complex than in the $\mathrm{HCrO_4{}^{-}}$ from which it was derived.

Provided $\mathrm{Cr_{aq}(V)}$ is oxidized rapidly by $\mathrm{Cr_{aq}O^{2+}}$, as in eq 6, the rate law for Scheme 1 is given by eq 7, where $\mathrm{[Cr_{aq}O^{2+}]_{tot}}$ represents the total concentration of chromyl. If, on the other hand, $\mathrm{Cr_{aq}(V)}$ disproportionates, eq 1, then the kinetic factor of 3 in eq 7 would be replaced by 1.5.

$$-\mathrm{d[Cr_{aq}O^{2+}]_{tot}}/\mathrm{d}t = \frac{3k_{S2}K_a[\mathrm{H^+}][\mathrm{Cr_{aq}O^{2+}}]_{tot}{}^2}{(K_a + [\mathrm{H^+}])^2} \qquad (7)$$

The pK_a of $\mathrm{Cr_{aq}O^{2+}}$ is not known, but a value around 5 or higher would seem reasonable for a chromium complex bearing an overall 2+ charge. Thus, under the experimental conditions, $[\mathrm{H^+}] \gg K_a$, the rate law reduces to eq 8 which exhibits an inverse first order dependence on $[\mathrm{H^+}]$, as observed.

$$-\mathrm{d[Cr_{aq}O^{2+}]}/\mathrm{d}t = \frac{3k_{S2}K_a[\mathrm{Cr_{aq}O^{2+}}]_{tot}{}^2}{[\mathrm{H^+}]} = k_{obs}\,[\mathrm{Cr_{aq}O^{2+}}]_{tot}{}^2 \qquad (8)$$

The plot of k_{obs} against $[\mathrm{H^+}]^{-1}$ in Figure 2 yields $3k_{S2}K_a = 38.8\ \mathrm{s^{-1}}$. Taking p$K_a \geq 5$, we obtain $k_{S2} \geq 10^6\ \mathrm{M^{-1}\ s^{-1}}$. This value greatly exceeds the previously measured rate constants for hydrogen abstraction by chromyl from aldehydes,[31] phenols,[32] and macrocyclic rhodium(III) hydrides,[33] all of which feature strongly reactive element–hydrogen bonds. On these grounds, the rate constant $k_{S2} > 10^6\ \mathrm{M^{-1}\ s^{-1}}$ for hydrogen abstraction from coordinated water or hydroxide would seem unreasonably large.

Another possibility is the loss of a proton and transfer of hydrogen atom in a concerted process. An obvious case, illustrating hydrogen atom transfer from a hydroxo group, is shown in eq 9.

$$\mathrm{2Cr_{aq}O^{2+} \rightleftarrows [Cr_{aq}O\cdots H\cdots OCr_{aq}O^{3+}] + H^{+} \rightarrow Cr_{aq}OH^{2+} + Cr_{aq}(O)_2{}^{+}} \qquad (9)$$

A related mechanism in Scheme 2 involves a hydroxo-bridged transition state formed by deprotonation of a molecule of $\mathrm{H_2O}$ coordinated to one chromyl and dissociation of water from the other.

The scheme assumes that the water dissociates from the labile position trans to the oxo group and that a hydrogen is transferred from one of the four water molecules lying in a plane perpendicular to the Cr–O–Cr axis. The next reasonable step might be the dissociation to products, presumably $\mathrm{Cr_{aq}(OH)_2{}^{+}}$ and $\mathrm{Cr_{aq}(O)(OH)^{2+}}$, on the basis of the substitutional properties of chromium(III) and chromium(V), although it is possible that a reasonably long-lived $\mathrm{Cr^{III}Cr^{V}}$ successor complex is involved, allowing the rearrangement and proton balancing to take place prior to the release of products.

The reaction would again exhibit a second-order dependence on $\mathrm{Cr_{aq}O^{2+}}$, eq 10.

$$-\mathrm{d[Cr_{aq}O^{2+}]}/\mathrm{d}t = \frac{nk_1k_2[\mathrm{Cr_{aq}O^{2+}}]^2}{k_{-1}[\mathrm{H^+}] + k_2} \qquad (10)$$

For the condition $k_2 \ll k_{-1}[\mathrm{H^+}]$, the dependence on $[\mathrm{H^+}]$ becomes cleanly inverse first order and, at constant $[\mathrm{H^+}]$, $k_{obs} = nK_1k_2$, where $n = 3$ or 1.5, depending on the fate of Cr(V), as discussed earlier.

In terms of the oxidation states, the putative $\mathrm{Cr^{III}Cr^{V}}$ successor complex would be analogous to that expected in the $\mathrm{Cr_{aq}{}^{2+}/HCrO_4{}^{-}}$ reaction. Despite some careful mechanistic work on this reaction,[34–36] which included isotopic labeling and product analysis, we are not aware of any data pertaining to the existence of a binuclear or polynuclear intermediate(s). We note, however, that the related $\mathrm{Fe_{aq}{}^{2+}/HCrO_4{}^{-}}$ reaction involves an observable intermediate, presumably an $\mathrm{Fe^{III}Cr^{V}}$ species, although an oxo-bridged $\mathrm{Fe^{III}{-}O{-}Cr^{III}}$ complex could not be ruled out.[37] Similarly, the reaction between $\mathrm{U_{aq}O_2{}^{2+}}$ and $\mathrm{Cr_{aq}{}^{2+}}$ produces at least two intermediates, one of which is believed to be a $\mathrm{Cr^{III}U^{V}}$ species with a lifetime of 4–8 min at 0 °C.[38]

If a similar $\mathrm{Cr^{III}Cr^{V}}$ complex is generated in the present system, it may dissociate to the hydrolytically stable forms of Cr(III) and Cr(V), react with $\mathrm{Cr_{aq}O^{2+}}$, or disproportionate. The experimental observations support any scheme that allows Cr(V), free or complexed, to react rapidly with either $\mathrm{Cr_{aq}O^{2+}}$ or another molecule of Cr(V) to yield an intermediate which releases chromate slowly.

The results of the two experiments in $\mathrm{D_2O}$, Table 1, also support the presence of an intermediate. On this slower time scale the disappearance of $\mathrm{Cr_{aq}O^{2+}}$ and release of $\mathrm{HCrO_4{}^{-}}$ seem to take place simultaneously. Apparently, the second stage—release of $\mathrm{HCrO_4{}^{-}}$ from the intermediate—is now fast relative to its formation. This result implies that there is no significant isotope effect associated with the second stage, consistent with the chemistry involving mainly Cr–O bond breaking.

Regardless of the exact nature and lifetimes, or even the existence of the intermediate(s) in post-rate-determining steps, the initial steps in the mechanism seem clear and reasonable.

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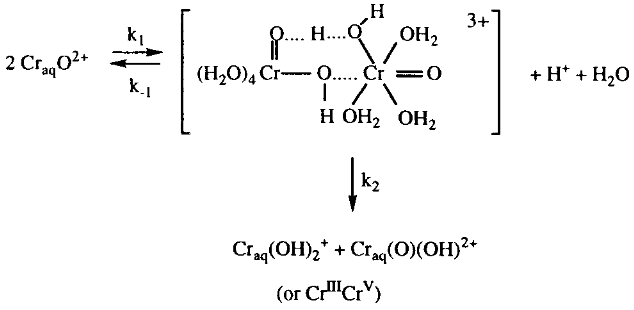
Scheme 2



From the rate law and substantial kinetic isotope effect, we conclude that two bonds involving hydrogen are broken in a bimolecular process. One hydrogen is released as hydrogen ion, and the other is transferred as hydrogen atom. It is the combination of the kie's for these two steps that results in an overall kie of 6.9.

Hydrogen atom abstraction, or proton-coupled electron transfer, has been proposed previously as a mechanism for comproportionation of polypyridyl complexes of oxoruthenium(IV) and aquaruthenium(II).[30,39] These reactions are characterized by large kinetic isotope effects, which require the O−H bond to be substantially cleaved in the transition state. The proposed hydrogen atom abstraction by tyrosine radical from hydroxide or a molecule of water coordinated to manganese in photosystem II[40,41] now appears less likely on the basis of recent crystal structure report.[42]

The rate constant for Cr_{aq}(IV) disproportionation at pH 3.7, extrapolated from our data, is 2×10^5 M^{-1} s^{-1}, almost 2 orders of magnitude less than the value measured directly in pulse radiolysis experiments at that pH.[24] This result suggests that either the nature of the species or the mechanism changes between pH 1.7 and 3.7. Further work is needed before this point can be addressed.

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