

## Kinetics and Mechanism of Chromate Reduction with Hydrogen Peroxide in Base

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$[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$  is reduced to  $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$  by hydrogen peroxide in strongly basic media where the acid dissociation of  $\text{H}_2\text{O}_2$  ( $\text{p}K_{\text{a}} = 11.65$ ) is appreciable. The reaction is first order in chromium(VI) and inhibited by hydroxide. The hydrogen peroxide dependence is defined by the form of the effective pseudo-first-order rate constant:  $k_{\text{eff}} = [\text{H}_2\text{O}_2]^3 / (K_1 + K_2[\text{H}_2\text{O}_2] + K_3[\text{HO}_2^-])$  with  $K_1 = 175(43) \text{ s} \cdot \text{M}^3$ ,  $K_2 = 403(18) \text{ s} \cdot \text{M}^2$ , and  $K_3 = 1422(34) \text{ s} \cdot \text{M}^2$ . Hydrogen peroxide anion initially attacks chromate, and subsequent equilibrium steps that exchange oxo groups for three peroxo groups precede a rate-determining, one-electron, intramolecular reduction step.

## Introduction

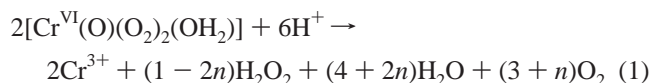
The complex chemistry of hydrogen peroxide and chromium involves ligand exchange, proton transfer, oligimerization, and redox reactions.<sup>1</sup> A consistent picture of the many oxidation and reduction reactions for this system is still emerging.

Like hydrogen peroxide itself, peroxo complexes are metastable, and hydrogen peroxide reactions with aqueous chromium species ultimately result in hydrogen peroxide decomposition. The metal cation may be reduced or oxidized in the process, but  $\text{H}_2\text{O}_2$  can also disproportionate without changing the oxidation state of the metal. Chromium commonly adopts the +3 or +6 oxidation state in water.  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$  is weakly acidic and rapidly oligimerizes in base.<sup>2</sup>  $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$  is weakly basic ( $\text{p}K_{\text{b1}} = 13.26$ ,  $\text{p}K_{\text{b2}} = 7.51$ ) and dimerizes in acidic media.<sup>3</sup>

The ligation of peroxo moieties initiates the chemical interaction of chromium and hydrogen peroxide. Chromium(III) and chromium(VI) both can coordinate to peroxide. Hydroperoxochromium(III) ion,  $[\text{Cr}^{\text{III}}(\text{O}_2\text{H})]^{2+}$ , spontane-

ously decomposes in minutes at room temperature.<sup>4,5</sup> Chromate reacts rapidly with hydrogen peroxide to exchange two oxo ligands and become diperoxochromate(VI), which then reacts further.<sup>6</sup> Unlike the bright yellow color of chromate,  $[\text{Cr}^{\text{VI}}(\text{O})(\text{O}_2)_2(\text{OH}_2)]$  ( $\text{p}K_{\text{a}} = 4$ ) is blue, and  $[\text{Cr}^{\text{VI}}(\text{O})(\text{O}_2)_2(\text{OH})]^-$  is violet.<sup>7,8</sup>

The reaction pathway of hydrogen peroxide and chromate depends strongly on the pH. Under extremely acidic conditions ( $\text{pH} < 1$ ), the diperoxochromate(VI) that forms reduces to chromium(III).<sup>9,10</sup> Peroxo ligand substitution is the rate-limiting step at this pH:<sup>11</sup>



Some disproportionation of hydrogen peroxide may occur catalytically during this multistep reaction; however, the variable  $n$  accounts for  $\text{H}_2\text{O}_2$  decomposition that may be integral with the mechanism but does not necessarily appear

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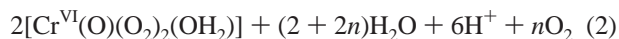
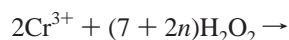
(1) Baloga, M. R.; Earley, J. E. *J. Am. Chem. Soc.* **1961**, *83*, 4906.  
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in the simplest reaction stoichiometry ( $n = 0$ ). Such a possibility exists because hydrogen peroxide may not act as a two-electron redox agent in this case.

Between a pH of 1 and 7, diperoxochromate(VI) predominantly undergoes intramolecular peroxide disproportionation whereby  $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$  is regenerated.<sup>12</sup> While the exact mechanism is unclear, the disproportionation of both peroxo ligands on diperoxochromate(VI) preserves both the metal oxidation state and the tetrahedral coordination.

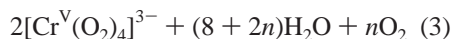
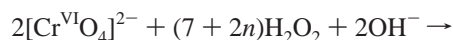
The reduction of chromate to chromium(III) still occurs to a limited degree above pH 1 (reaction 1). Spitalsky has confirmed that the final percentage of Cr(III) ranges from 28.3 to 100% of the total chromium depending on the acidity. Furthermore, the percentage of chromium(III) can also decrease if necessary to attain the predetermined level. Therefore, he also identified a compensating reaction whereby chromium(III) is oxidized to chromium(VI):<sup>13</sup>



This behavior of the chromium(III) and chromium(VI) concentrations is not a true thermodynamic equilibrium. Hydrogen peroxide redox reactions are essentially nonreversible because of the generation of water and/or molecular oxygen. Pairs of counter reactions such as reactions 1 and 2 create a catalytic cycle for the disproportionation of hydrogen peroxide.

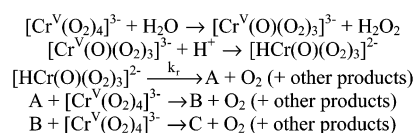
If hydrogen peroxide is added to a potassium chromate solution (the unbuffered pH will be weakly basic), the color remains yellow, and the evolution of oxygen gas occurs more slowly than under acidic conditions.<sup>9</sup> Diperoxochromate(VI) does not accumulate in solution because the ligand exchange reaction is slower than the disproportionation of the peroxo ligands.  $\text{H}_2\text{O}_2$  ( $\text{p}K_{\text{a}} = 11.65$ ) does not deprotonate appreciably at this pH.<sup>14</sup>

In more strongly alkaline conditions ( $\text{pH} > 10$ ), oxygen gas along with the brown-red tetrakis( $\eta^2$ -peroxo)chromate-(V) anion forms:<sup>15</sup>

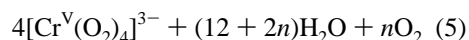
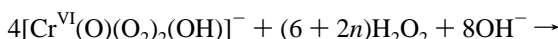
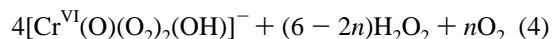


Unlike tetraperoxomolybdate or tungstate, this complex is  $d^1$ .<sup>6</sup> It has often been identified as an intermediate in chromium redox reactions with  $\text{H}_2\text{O}_2$ ,<sup>16</sup> however, the potassium salt,  $\text{K}_3\text{Cr}(\text{O}_2)_4$  (commonly  $\text{K}_3\text{CrO}_8$ ), can be stabilized in basic solution and isolated as a solid.<sup>17,18</sup> The complex anion has been observed in solution at neutral pH using electron paramagnetic resonance (EPR). Three other chro-

# Scheme 1



mium(V) complexes (intermediates in the reaction between chromate(VI) and hydrogen peroxide) have also been detected down to a pH of 4.<sup>19</sup> Diperoxochromate(VI) and tetraperoxochromate(V) can be interconverted by adjusting the pH, with the cycle consuming at least 1.5 peroxide units per metal center:<sup>20</sup>



Quane and Bartlett confirm that oxygen evolves even after a pseudo-equilibrium between the two chromium species is produced. This pair of counter reactions may be responsible for the mild catalytic properties of the tetraperoxochromate(V) species for hydrogen peroxide disproportionation.

Clues to the mechanism of the reaction between hydrogen peroxide and chromate(VI) in base can be ascertained from the reverse reaction. The decomposition of tetraperoxochromate(V) to chromate above pH 8 is first order in  $[\text{H}^+]$  and inhibited by  $[\text{H}_2\text{O}_2]$ .<sup>21</sup> While the matter of the sequential order of the protonation step is not settled, there is general agreement that the rate-determining step involves the oxidation of a protonated triperoxochromium(V) species. Brown et al. suggest the mechanism shown in Scheme 1.<sup>22</sup> A, B, and C are presumably intermediate chromium complexes. One rapid peroxo group exchange equilibrium precedes the rate-determining step.

While many mechanistic investigations have been conducted especially in acidic and mildly basic media, both a 1970 and a 1996 review of chromate reactions with hydrogen peroxide intimate that studies in strongly basic media remain largely inconclusive.<sup>23,24</sup> The aim of this work is to measure the kinetics of the one-electron reduction of chromate(VI) to tetraperoxochromate(V) with hydrogen peroxide in basic solution ( $\text{pH} \geq 10$ ) and to propose a mechanism that is consistent with known features of the chromium/hydrogen peroxide redox system.

## Experimental Methods

Stock solutions of chromate were prepared by dissolving  $\text{Na}_2\text{CrO}_4$  (Aldrich, 99.9%) in either 1.00 M NaOH or 1.00 M NaClO<sub>4</sub> and diluting to a chromate concentration of 800  $\mu\text{M}$ . Aliquots of

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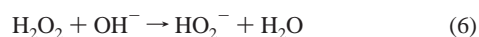
**Table 1.** Reagent Concentration and Rate Data<sup>a</sup>

[OH <sup>-</sup> ] <sub>i</sub> <sup>b</sup> (M)	[H <sub>2</sub> O <sub>2</sub> ] <sub>i</sub> <sup>b</sup> (M)	[OH <sup>-</sup> ] <sub>eq</sub> <sup>c</sup> (M)	[HO <sub>2</sub> <sup>-</sup> ] <sub>eq</sub> <sup>c</sup> (M)	[H <sub>2</sub> O <sub>2</sub> ] <sub>eq</sub> <sup>c</sup> (M)	10 <sup>3</sup> k <sub>obs</sub> (s <sup>-1</sup> )	10 <sup>3</sup> k <sub>calc</sub> <sup>d</sup> (s <sup>-1</sup> )
0.667	3.257	0.00114	0.666	2.591	8.2	8.0
0.667	3.257	0.00114	0.666	2.591	8.1	8.0
0.571	3.164	0.00098	0.57	2.593	8.5	8.6
0.381	2.973	0.00065	0.38	2.593	10.1	9.9
0.286	2.875	0.00049	0.285	2.590	10.7	10.7
0.19	2.782	0.00033	0.19	2.592	11.5	11.7
0.095	2.684	0.00016	0.095	2.589	12.8	12.8
0.048	2.638	0.00008	0.048	2.590	13.1	13.5
0.01	2.601	0.00002	0.01	2.591	14.4	14.1
0.719 <sup>e</sup>	2.75	0.00157	0.717	2.033	4.2	4.2
0.667	2.698	0.00145	0.665	2.033	4.3	4.3
0.667	2.698	0.00145	0.665	2.033	4.4	4.3
0.573	2.605	0.00125	0.572	2.033	4.7	4.7
0.48	2.512	0.00105	0.479	2.033	4.9	5.0
0.387	2.419	0.00084	0.386	2.033	5.4	5.4
0.293	2.326	0.00064	0.293	2.033	6.0	6.0
0.2	2.233	0.00044	0.199	2.034	6.5	6.6
0.157	2.191	0.00034	0.156	2.035	6.9	6.9
0.114	2.14	0.00025	0.114	2.027	7.2	7.2
0.061	2.094	0.00013	0.061	2.033	7.7	7.8
0.014	2.047	0.00003	0.014	2.033	8.6	8.3
0.387	1.582	0.00143	0.385	1.197	1.4	1.4
0.293	1.489	0.00109	0.292	1.197	1.6	1.6
0.2	1.396	0.00074	0.199	1.197	1.8	1.8
0.106	1.303	0.00039	0.105	1.197	2.0	2.1
0.059	1.256	0.00022	0.059	1.197	2.3	2.3
0.013	1.21	0.00005	0.013	1.197	2.5	2.5
0.667	3.257	0.00114	0.666	2.591	8.0	8.0
0.571	2.791	0.00114	0.57	2.221	5.9	5.8
0.476	2.326	0.00114	0.475	1.851	3.4	4.0
0.381	1.861	0.00114	0.38	1.481	2.5	2.5
0.286	1.396	0.00114	0.285	1.111	1.8	1.3
0.19	0.93	0.00114	0.189	0.741	0.71	0.55
0.095	0.461	0.00114	0.094	0.366	0.13	0.11
0.00114	0	0.00114	0	0	0	0.00

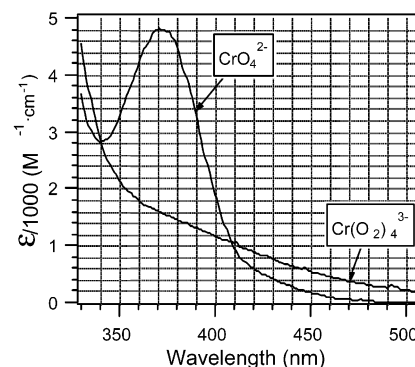
<sup>a</sup> Only significant figures are given. <sup>b</sup> Initial concentrations reflect amounts added to reaction. <sup>c</sup> Equilibrium concentrations satisfy the chemical equilibrium of reaction 6. <sup>d</sup> Calculated values are based on eq IV. <sup>e</sup> Ionic strength (IS) exceeds 0.67 M, however, no dependence on IS was detected in additional experiments.

these two solutions were premixed along with deionized water in a 1-cm cuvette before 30% H<sub>2</sub>O<sub>2</sub> (Aldrich) was added to initiate reaction 3 at 21 °C. The concentration range of H<sub>2</sub>O<sub>2</sub> was chosen so that the half-life of the reduction reactions would be of an appropriate duration for study with UV-vis spectroscopy (50–5000 s). A total volume of 2.1 mL was stirred with a 7-mm stir bar throughout the course of the reaction. Most reaction solutions were 530 μM in chromium (the maximum quantifiable concentration given the strong absorbance of chromate at 372 nm) with an ionic strength of 0.67 M.

Only the concentration of chromium species effectively changes over the course of the reaction. Chromate is always the limiting reagent with hydrogen peroxide and hydroxide present in at least 20-fold excess. However, to determine the actual concentration of these reagents, the dissociation of hydrogen peroxide in base, which becomes significant above pH 10, must be taken into account.<sup>14</sup>



This acid/base equilibrium ( $K_{\text{eq}} = K_a/K_w = 225 \text{ M}^{-1}$ ) is established very quickly and even compensates for the minor consumption of hydroxide and hydrogen peroxide (reaction 3). Table 1 lists the initial and equilibrium concentrations. All subsequent references to hydroxide and hydrogen peroxide concentrations denote equilibrium values.

**Figure 1.** Molar absorptivity of chromate(VI) and tetrakis(η<sup>2</sup>-peroxo)-chromate(V).

The amounts of hydroxide and hydrogen peroxide in the reaction cuvette were chosen so that the equilibrium concentrations could be easily compared. Three distinct series of rate measurements with constant [H<sub>2</sub>O<sub>2</sub>] were taken as well as one series with constant [OH<sup>-</sup>]. Samples with a peroxide concentration of 2.591 M and a pH of 11.06 were used to ascertain the temperature dependence of the rate constant from 16 to 40 °C. Three additional reactions at the same concentrations were run with chromium concentrations of 265, 132, and 76 μM. Kinetic experiments were also conducted in the presence of the radical scavenger benzoquinone to test for radical reactions.

UV-visible spectra of starting and ending solutions were obtained from 300 to 800 nm with a Cary 50 UV-visible spectrophotometer. Spectra could also be taken during the course of a reaction. EPR of the product solution was measured at room temperature at a frequency of 9.771 GHz and a power of 3.17 mW. A modulation field of 5 G and a modulation frequency of 100 kHz were used.

Time traces at 372 and 500 nm were monitored simultaneously. These wavelengths correspond to the largest absorbance fractions for [Cr<sup>VI</sup>O<sub>4</sub>]<sup>2-</sup> and [Cr<sup>V</sup>(O<sub>2</sub>)<sub>4</sub>]<sup>3-</sup>, respectively (see Figure 1). Data points were measured with the delay time set to zero, which resulted in 48 points per minute at each wavelength.

The data were processed and analyzed with Igor Pro.<sup>25</sup> Non-random error caused by oxygen gas evolution resulted in numerous spikes in the absorbance that were deleted with a user-defined macro: any data point over 2% higher than both of its neighbors is deleted. Generally, 0–10% were eliminated. The time traces could then be fit to analytical functions.

## Results

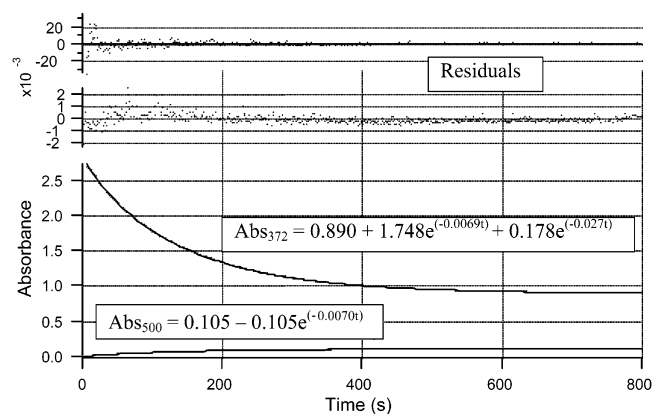
**Spectroscopy.** Figure 1 shows the graph of the molar absorptivity of the end product of the reaction of Na<sub>2</sub>CrO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> in base, along with that of the starting chromate. The maximum at 372 nm that corresponds to the ligand to metal charge-transfer band in [Cr<sup>VI</sup>O<sub>4</sub>]<sup>2-</sup> has disappeared, and although a shoulder has grown in above 500 nm, no new maxima are observed. Several references confirm that the product spectrum is that of tetraperoxochromate(V) and not diperoxochromate(VI).<sup>26–28</sup> If the pH is less than 10, then the reaction does not go completely to [Cr<sup>V</sup>(O<sub>2</sub>)<sub>4</sub>]<sup>3-</sup>.

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**Figure 2.** Sample absorbance data at 372 and 500 nm for the reaction of chromate in 2.035 M  $\text{H}_2\text{O}_2$ , 0.156 M  $\text{HO}_2^-$ , and 0.00034 M base. Data and residuals are represented with dots, and the analytical fits to the data are drawn as continuous curves.

**Table 2.** Molar Absorptivity,  $\epsilon$  ( $\text{M}^{-1}\cdot\text{cm}^{-1}$ )

wavelength (nm)	$[\text{CrO}_4]^{2-}$	$[\text{Cr}(\text{O}_2)_4]^{3-}$
340	2400	2400
372	4800	1600
408	1040	1040
500	0	200

When full spectra were taken throughout the course of the reaction, no intermediates could be observed. Isosbestic points at 340 and 408 nm confirm that the effective reaction that is monitored experimentally is the reduction of chromium(VI) to chromium(V) (see Figure 1). Table 2 lists pertinent molar absorptivities for the reactant and product.

The EPR spectrum for the product solution verifies that the species is tetraperoxochromate(V). The measured  $g$  value for the  $3d^1$  electron is 1.973(1), and the hyperfine splitting caused by the chromium-53 nucleus is 55.3 MHz.<sup>29</sup>

**Kinetics.** Figure 2 shows typical time traces at 372 and 500 nm along with the analytical fit to the data. The former wavelength tracks the disappearance of reactant while the latter tracks the appearance of product. A small induction time of approximately 1 s is exhibited. No ionic strength dependence could be detected, and no other medium effects were noted for the chosen concentration ranges.

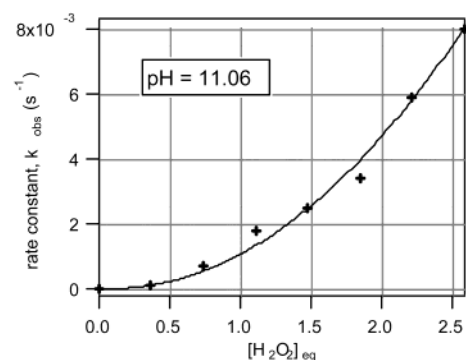
Time traces at 500 nm, which correspond exclusively to  $[\text{Cr}^{\text{V}}(\text{O}_2)_4]^{3-}$ , increase monotonically from 0 to 0.1 AU and can be fit with a single exponential function:

$$[\text{Cr}^{\text{V}}](t)/[\text{Cr}_{\text{total}}] = (1 - \exp(-k_{\text{obs}}t)) \quad (\text{I})$$

Time traces at 372 nm decrease exponentially from 2.6 to 0.9 AU because the reactant absorbs more strongly than the product at this wavelength (see Table 2). The time dependence of the chromium(VI) concentration exhibits the same rate as that of the chromium(V), but a second smaller exponential term is often required to fit the data adequately:

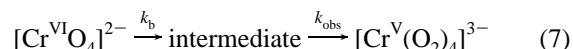
$$[\text{Cr}^{\text{VI}}](t)/[\text{Cr}_{\text{total}}] = (1 - B) \exp(-k_{\text{obs}}t) + B \exp(-k_{\text{b}}t) \quad (\text{II})$$

The second term invariably exhibits a faster rate ( $k_{\text{b}} > k_{\text{obs}}$ )



**Figure 3.** Observed (+) and calculated first-order rate constant data for the reduction of chromate vs the equilibrium concentration of hydrogen peroxide at constant hydroxide concentration.

and accounts for no more than 20% of the total magnitude ( $0 < B < 0.2$ ). The double exponential character of this time trace suggests that there are significant concentrations of at least three different chromium species that have different absorptivities at 372 nm. The faster rate,  $k_{\text{b}}$ , must correspond to a reaction step that occurs before that with the slower rate,  $k_{\text{obs}}$ :



The intermediate is presumably a chromium(VI) species because the absorptivities at both wavelengths ( $\epsilon_{372} \approx 4400 \text{ M}^{-1}\cdot\text{cm}^{-1}$ ,  $\epsilon_{500} \approx 0 \text{ M}^{-1}\cdot\text{cm}^{-1}$ ) are very nearly that of the reactant chromate. Since the latter rate is measured both in the disappearance of product as well as in the appearance of  $\text{Cr}^{\text{V}}$ , it is used to establish the rate law for the reduction.

Exponential fits to the kinetic traces indicate that the rate law is first order in chromium(VI):

$$\text{rate} = k_{\text{obs}}([\text{H}_2\text{O}_2], [\text{OH}^-], [\text{HO}_2^-])[\text{Cr}^{\text{VI}}] \quad (\text{III})$$

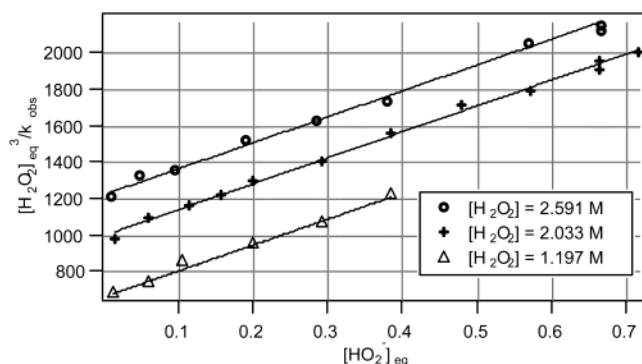
The rate constant,  $k_{\text{obs}}$ , is a function of the concentrations of hydrogen peroxide, hydrogen peroxide anion ( $\text{HO}_2^-$ ), and hydroxide, all of which are effectively constant during the course of an experiment. Since these three concentrations are related by equilibrium 6,  $k_{\text{obs}}$  can be written in terms of just two of them. The first two will be used as they are generally the same order of magnitude.  $k_{\text{obs}}$  itself is independent of initial  $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$  in the range of 76–530  $\mu\text{M}$ , consistent with pseudo-first-order kinetics.

Upon inspection of individual series of data, the reduction of chromate to tetraperoxochromate(V) appears to be approximately second order in hydrogen peroxide and inhibited by hydroxide or hydrogen peroxide anion ( $[\text{OH}^-] \propto [\text{HO}_2^-]$  at constant  $[\text{H}_2\text{O}_2]$ ). Figure 3 shows how the rate increases with the concentration of hydrogen peroxide, and Figure 4 shows how the inverse of  $k_{\text{obs}}$  increases linearly with the concentration of hydrogen peroxide anion. Detailed analysis reveals a more exact form of the rate equation.

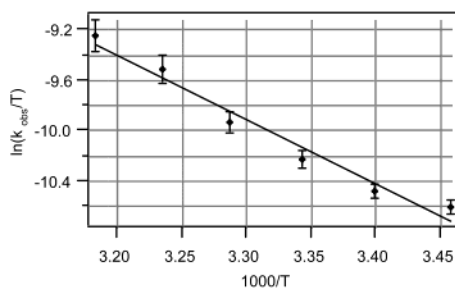
A graph of  $[\text{H}_2\text{O}_2]^p/k_{\text{obs}}$  versus  $[\text{HO}_2^-]$  yields straight lines for multiple series of data at constant  $[\text{H}_2\text{O}_2]$ . If  $p = 3$ , the slopes of the three data series at different hydrogen peroxide concentrations are all equal within experimental error (Figure 4). The intercepts increase linearly with  $[\text{H}_2\text{O}_2]$ , and the

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**Figure 4.** Observed (+) and calculated first-order rate constant data for the reduction of chromate vs the equilibrium concentration of hydrogen peroxide anion at constant hydrogen peroxide concentration. The slope for all three series of data is the same. The different intercepts vary linearly with  $[H_2O_2]_{eq}$ .



**Figure 5.** Eyring plot for the rate of production of tetraperoxochromate(V) from chromate(VI) with hydrogen peroxide in base. Basic Arrhenius behavior is observed with  $\Delta H^\ddagger = 43(4)$  kJ/mol and  $\Delta S^\ddagger = -140(12)$  J/K·mol.

effective rate at 21 °C can therefore be accurately modeled as a function of the reagent concentrations:

$$k_{obs}(s^{-1}) = \frac{[H_2O_2]^3}{175(43) + 403(18)[H_2O_2] + 1422(34)[HO_2^-]} \quad (IV)$$

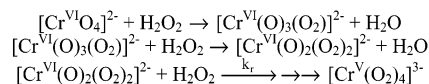
The numerical values in the denominator were refined for the entire data set, and Table 1 lists the observed and calculated rates. Figures 3 and 4 also show the calculated fits to the observed data. Equation IV beautifully accounts for the series of data at constant hydroxide concentration (Figure 3) as well those at constant hydrogen peroxide concentration (Figure 4). No other rate equation could be found that accurately models the observed kinetics.

Figure 5 shows an Eyring plot for  $k_{obs}$  that is approximately linear over the temperature range from 16 to 41 °C and establishes basic Arrhenius behavior for the reduction reaction. To the extent that the observed rate corresponds to a single reaction,  $\Delta H^\ddagger = 43(4)$  kJ/mol and  $\Delta S^\ddagger = -140(12)$  J/K·mol.

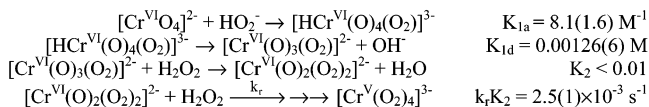
## Discussion

Tetraperoxochromate(V) can be synthesized from chromate by reduction with hydrogen peroxide and stabilization with base.<sup>17</sup> The reaction involves the exchange of four oxo ligands for four peroxo ligands along with a one-electron reduction of the chromium. Both peroxide and hydroxide

## Scheme 2



## Scheme 3



play a dual role in this synthesis. Four peroxide units are incorporated into the final product, and peroxide is the reducing agent. Hydroxide inhibits the reaction kinetically by competing for coordination sites but also stabilizes the final product thermodynamically relative to diperoxochromate(VI) (reactions 4 and 5).<sup>21</sup>

The mechanism obviously involves several steps. A minimum of four ligand exchanges must accompany the redox step, and the empirical rate law points to three ligand exchanges before the rate-determining step. Scheme 2 depicts one straightforward possibility.

This mechanism yields the following effective first-order rate constant after the concentration of  $[Cr^{VI}(O)_2(O_2)_2]^{2-}$  from the rate-determining step is written in terms of the total chromium(VI) concentration that is monitored experimentally at 372 nm. (For a more detailed mathematical analysis, see ref 22 or the Supporting Information.)

$$k_{eff} = \frac{k_r K_1 K_2 [H_2O_2]^3}{K_1 K_2 [H_2O_2]^2 + K_1 [H_2O_2] + 1} \quad (V)$$

An equivalent form for the rate constant expression results if any or all of the exchange steps involve hydrogen peroxide anion and hydroxide instead of hydrogen peroxide and water. However, base inhibition can only be accounted for if hydroxide is a leaving group in at least one step. Some protonated species are involved since the reaction does not proceed unless the equilibrium hydrogen peroxide concentration is appreciable.

If the first exchange step is considered to be an association step with hydrogen peroxide anion followed by a dissociation step, then the effective rate constant takes on a form consistent with the empirical rate law (Scheme 3).

$$k_{eff} = \frac{k_r K_{1a} K_{1d} K_2 K_{eq} [H_2O_2]^3}{K_{1a} K_{1d} K_2 K_{eq} [H_2O_2]^2 + K_{1a} K_{1d} K_{eq} [H_2O_2] + K_{1a} [HO_2^-] + 1} \quad (VI)$$

Associative intermediates involving a hydrogen peroxide anion are plausible for this 16-electron complex. For a peroxo group to replace an oxo ligand, a proton must also be transferred from a bound hydrogen peroxide anion to a bound oxo ligand before hydroxide can dissociate. The equilibrium constants are deduced by comparison with the empirical rate law (eq IV). The square term in the denominator is negligible if  $K_2$  is less than 0.01. All these equilibrium constant values

are quite reasonable, but  $K_2$  could not be determined accurately from our data.

The effective rate constant assumes the expected form for constant hydrogen peroxide and hydroxide conditions:

$$1/k_{\text{eff}} = C_1 + C_2[\text{HO}_2^-] \text{ for constant } [\text{H}_2\text{O}_2] \quad (\text{VII})$$

$$k_{\text{eff}} = \frac{[\text{H}_2\text{O}_2]^3}{C_3 + C_4[\text{H}_2\text{O}_2]} \text{ for constant } [\text{OH}^-] \quad (\text{VIII})$$

The equilibrium values suggest that a considerable concentration of monoperochromate species does accumulate in solution. The existence of the second exponential rate term for the disappearance of chromate corroborates such a preequilibrium step (eq II). The molar absorptivity at 372 nm for monoperochromate complexes would probably be only slightly different from that of chromate. The fast rate accounts for a small shift in the spectrum that would accompany the accumulation of such intermediates before the rate-determining step.  $[\text{Cr}^{\text{VI}}(\text{O})(\text{O}_2)_2(\text{OH})]^-$  absorbs strongly at 372 nm ( $\epsilon_{372} = 740 \text{ M}^{-1}\cdot\text{cm}^{-1}$ ) and also 500 nm ( $\epsilon_{500} = 500 \text{ M}^{-1}\cdot\text{cm}^{-1}$ ) so its presence would certainly be noticed in the 500 nm time trace.<sup>20</sup>

The initial product of the rate-determining step would be a five-coordinate triperoxochromate(VI). The negative value of  $\Delta S^\ddagger$  from the Eyring plot (Figure 5) is consistent with a bimolecular rate-determining step and five-coordinate intermediate. However, it is not yet clear if preequilibria or medium effects cause the slight curvature of the Eyring plot.

The mechanism of Scheme 3 accounts for the observed rate law and indicates that the redox active species is a triperoxo complex. The existence of diperochromate(VI) suggests that the chromium is not reduced after two ligand exchanges. The fact that the oxidation of tetraperochromate(V) requires only one ligand exchange before the rate-determining step further points to a triperoxo species as the critical redox intermediate.<sup>30</sup>

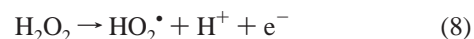
The mechanism of oxo/peroxo exchange in strong base is distinct from mechanisms in more acidic media. Below pH 7,  $[\text{HCr}^{\text{VI}}\text{O}_4]^-$  and  $\text{H}_2\text{O}_2$  react rapidly to form diperochromate(VI).<sup>30</sup> The pH range from 7 to 9 spans a mechanistic crossover region where hydrogen peroxide remains protonated and chromate does not. In this region, chromate does catalyze the disproportionation of hydrogen peroxide, but a change of color indicative of diperochromic acid does not occur, so the ligand exchange reaction must be the rate-limiting step. Above pH 10, we find that the hydrogen peroxide anion attacks unprotonated chromate.

The overall stoichiometry of the reaction implies that the mechanism not only consists of multiple steps but also involves significant complexity. However, pseudo-first-order rate constants for reactions carried out in dilute solutions down to 76  $\mu\text{M}$  chromium are all equal, which strongly suggests that the reaction is truly first order in chromium and that no chromium–chromium interactions contribute to the overall mechanism. Furthermore, the reduction of

chromium is a single-electron reduction, while hydrogen peroxide is normally a two-electron redox agent. If a single reducing agent reduces two different chromium species, then either the agent or a chromium(IV) species must migrate through solution to another chromium(VI) species. Both of these potential mechanisms would exhibit a second-order dependence on the concentration of chromate that we cannot see. The rate equation remains first order even for initial chromate concentrations as low as 76  $\mu\text{M}$ .

An alternative hypothesis can be inferred from iron systems such as superoxide dismutase (SOD).<sup>31</sup> Iron(II/III) complexes are known to undergo one-electron intramolecular redox reactions with molecular oxygen, superoxide, and peroxide,<sup>32,33</sup> and the same occurs for some chromium complexes. Superoxo complexes have already been proposed to rationalize aqueous chromium(III) oxidation schemes.<sup>34</sup> The decomposition of tetraperochromate(V) in water produces  $\text{O}_2^-$  and singlet oxygen.<sup>35</sup> One-electron redox occurs for chromium in the solid state as well. The products of thermally decomposed potassium tetraperochromate(V) include chromate along with superoxide  $\text{KO}_2$ .<sup>36</sup> In the case of aqueous chromium(VI), a superoxo ligand would result from the transfer of a single electron from a coordinated  $\text{O}_2^{2-}$  to  $\text{Cr}^{\text{VI}}$ .

A mechanism that involves superoxide essentially allows hydrogen peroxide to act as a one-electron redox agent. The reductive half reaction resembles the hydrogen peroxide disproportionation reaction, except that superoxide is produced instead of molecular oxygen:



Superoxide itself has a  $\text{pK}_a$  of 4.75(8) so in basic solution it exists exclusively in the anionic form.<sup>37</sup> Its rapid disproportionation in water produces  $\text{H}_2\text{O}_2$  and singlet  $\text{O}_2$  ( $^1\Delta_g$  or  $^1\Sigma_g$ ),<sup>38</sup> unless the reaction is catalyzed by SOD in which case the product oxygen is purportedly in the ground state.<sup>39</sup> Superoxide, singlet oxygen, and hydroxyl radicals (which are produced in the Haber–Weiss reaction between superoxide and peroxide<sup>39</sup>) all potentially contribute to the toxicity of chromium.<sup>40</sup>

The one-electron reduction of reaction 9 appears to be integral to the oxidation of aqueous tetraperochromate(V), which generates  $\text{O}_2^-$ .<sup>35</sup> After one ligand exchange, a peroxo ligand can reduce to two oxo ligands at the expense

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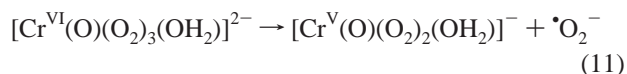
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of  $\text{Cr}^{\text{V}}$  and a second peroxo ligand. Superoxide anion can then dissociate into solution leaving behind monoperoxo-chromate(VI):



Tetraperoxo-chromate(V) is efficiently converted into chromate(VI) with only one more ligand exchange step. The mechanism is also consistent with previous isotopic labeling experiments that indicate at least half of the oxygen atoms on the product chromate(VI) come from the peroxo oxygen ligands around the chromate(V).<sup>22</sup>

Superoxide is potentially an initial byproduct of chromium reduction reactions, too.<sup>41</sup> If a triperoxo-chromate(VI) complex undergoes an intramolecular redox, then superoxide could dissociate into solution:



Reaction 11 is an intramolecular pathway to diperoxo-chromate(V), which has been identified in acidic solution by EPR<sup>19</sup> and modeled computationally.<sup>42</sup> Reduction reactions were unaffected when carried out in the presence of the radical scavenger benzoquinone, indicating further that if superoxide is produced in the rate-determining step, it quickly disproportionates before it interacts with a second chromium species.

Hydrogen peroxide as a one-electron reducing agent provides a simple mechanism for the reduction of chromate that is first order in chromium. The stoichiometry of such redox reactions can be adjusted to account for oxygen gas evolution that results from the disproportionation of superoxide. For example, in reaction 3,  $n$  would equal 1. Four hydrogen peroxides per chromium become ligands, a fifth reduces the chromium, and 0.5 equiv is regenerated through superoxide decomposition.

Hydrogen peroxide reacts in various competitive ways with chromium, and different pathways predominate depending on the acidity. The substitution of peroxo ligands can occur at any pH. Such substitutions remove electron density from the metal center as do protonations, while intramolecular disproportionation of peroxo ligands effectively replace it. The diperoxo-chromate(VI) is the pivotal species in the competition between the variety of reactions within the hydrogen peroxide system because metal reduction accompanies the withdrawal of further electron density.

Extremely acidic conditions combine with further peroxo substitution to pull away sufficient electron density and promote the reduction to chromium(III) (reaction 1). Under more mildly acidic conditions ( $1 < \text{pH} < 7$ ), however, the disproportionation of hydrogen peroxide within the chromium coordination sphere is fast enough to preserve the two oxo ligands required to support the hexavalent oxidation state. In mildly basic solution, the substitution reaction slows to the point where the diperoxo species does not even accumulate. However, under strongly basic conditions ( $\text{pH} > 10$ ), a distinct peroxo substitution reaction that involves the attack of the unprotonated chromate dianion by the hydrogen peroxide anion, along with possible base inhibition of the disproportionation reaction, allows for the exchange of more than two oxo ligands (Scheme 3). One-electron metal reduction ensues as the third and fourth oxo ligands are exchanged. The four peroxo groups sterically protect the chromium center and provide sufficient electron density to stabilize the pentavalent state but apparently not the hexavalent state. Pentavalent chromium does not reclaim more electron density by further reduction or catalysis of hydrogen peroxide disproportionation.

The chemistry of peroxochromates is remarkable. Chromium has several possible oxidation states, and hydrogen peroxide can function as a reducing or oxidizing agent. Permanent reduction of chromate with hydrogen peroxide occurs at either extreme of the pH scale but not in between. Both reactions entail one-electron reductions, but the mechanisms and products are quite distinct. Convincingly, no reactions that convert chromium(V) to chromium(III) without going through a chromium(VI) intermediate have ever been reported.

The redox chemistry of chromium and hydrogen peroxide in basic media has been understood qualitatively for nearly a century. Now, a consistent mechanistic understanding further reveals the competition between acid/base, ligand exchange, and disproportionation reactions and hints at the critical role of superoxide and its byproducts in the chemistry of chromium.

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**Supporting Information Available:** Detailed derivation of the rate law for Scheme 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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