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Kinetic Study of an Intermediate Present in the Hydrogen Peroxide Oxidation of Chromiun(III) to Chromium(VI)

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The oxidation of chromium(III) by hydrogen peroxide in basic media occurs via a branching mechanism. Following the initial formation of a chromium(III)–peroxide intermediate, chromium(IV) and chromium(V) intermediates are produced in the two pathways, respectively. The latter intermediate was monitored spectrophotometrically at 500 nm and identified as chromium(V) by use of ESR. A detailed mechanism and rate constants for the various reactions are presented.

There have been numerous investigations of oxidation–reduction reactions involving chromium(VI).[1,2] These systems are inherently interesting because of the possibility of intermediates which can be either deduced by product analysis, as was done by Ardon and Plane[3] and by Hegedus and Haim[4] in proposing a chromium(IV) intermediate, or observed directly, as was done by Wiberg and Schafer[5] in proposing a chromium(V) intermediate.

The oxidation of chromium(III) to chromium(VI) by hydrogen peroxide

$$2Cr(III) + 3H_2O_2 \rightarrow 2Cr(VI) + 6OH^- \qquad (1)$$

was investigated by Baloga and Earley.[6] This study was carried out in basic media, where the chromium(III) becomes more labile and where polynuclear complexation occurs. It was found that increasing polymerization of chromium(III) had an inhibitory effect on the initial rate of oxidation. The hydroxide and hydrogen peroxide dependencies were determined using a chromium(III) solution which had been "aged" in base for 1 h prior to its oxidation. As the degree of polymerization was not known, it was not possible to develop a detailed mechanism. The aim of the present study was to obtain detailed mechanistic information on the oxidation of monomeric chromium(III) to chromium(VI) in basic media.

Experimental Section

Materials. Stock solutions of $Cr(H_2O)_6^{3+}$ were prepared by the hydrogen peroxide reduction of sodium chromate (Baker Chemical Co.) in perchloric acid and the concentrations were determined spectrophotometrically using a Beckman DU spectrophotometer at 408 nm (ϵ 15.6) and at 574 nm (ϵ 13.4), the positions of maximum absorbance of the monomer.[7]

Hydrogen peroxide solutions of the desired concentrations were prepared from commercially available 30% H_2O_2 solution (Fisher Chemical Co) without added stabilizers. The hydrogen peroxide was standardized by titration with potassium permanganate.

Carbonate-free sodium hydroxide stock solutions were standardized using potassium hydrogen phthalate. Periodically, the carbonate concentration was determined by titration of sodium hydroxide with hydrochloric acid to a phenolphthalein end point followed by titration to a methyl orange end point.[8] The levels of carbonate found to be present were such as to have a negligible effect on the kinetics of the reaction. In kinetic runs where appreciable amounts of carbonate were added, no catalytic effect was observed and the carbonate functioned solely as a base.

Spectral Study. A Cary Model 14 recording spectrophotometer was used to obtain the spectra of all solutions. Basic, metastable chromium(III) monomer (CrO_2^-) has an absorbance maximum at 594 nm (ϵ 24.1). The product of the reaction had the same spectrum as chromate, with its absorbance maximum at 374 nm.

Kinetic Measurements. The kinetics of the oxidation of chromium(III) to chromium(VI) by hydrogen peroxide were followed by use of the stopped-flow technique. Of the two reacting solutions, one solution consisted of $Cr(H_2O)_6^{3+}$ and hydrogen peroxide diluted to the desired concentrations from their respective stock solutions. The resultant pH was approximately 3. The spectra of these solutions, taken at various times, showed no change in absorptivity or positions of peak maxima. The absorptivities and positions of peak maxima were those typical of monomeric chromium(III). The second solution consisted of sodium hydroxide stock solution diluted to the desired concentration. Ionic strength was adjusted using sodium perchlorate. This experimental method ensured that chromium(III) monomer was the species being oxidized because no base was added before initiation of the reaction. When the reactants were mixed in the absence of hydrogen peroxide, a flat trace was observed at all wavelengths and the absorptivities were characteristic of CrO_2^-. Rates of reaction were followed by measuring absorbance changes at 374, 500, and 594 nm. The reactions were followed using an Aminco Minimonochromator with an Aminco-Morrow stopped-flow apparatus[9] attached. The detector used was an R-136 photomultiplier tube (PMT) powered by a Harrison 6515 A dc power supply. The PMT output was fed into an Aminco Linear-Log kinetic photometer and the logarithmic (absorbance) signal was then displayed using a Tektronix R564B storage oscilloscope. The filtering components built into the kinetic photometer ensured a background noise level no greater than ±0.001 OD. All kinetic runs were performed at 25.0 ± 0.1 °C. There was a small temperature jump of less than 1 °C upon mixing of solutions.

Free radicals generated during the reactions were detected and monitored with time using a JEOL Ltd. JES-SM-1 continuous-flow system in conjunction with a JES 3X JEOL ESR spectrometer.

A Hewlett-Packard 9810A calculator with a 500-step program memory was used both to evaluate rate constants and, in conjunction with a Hewlett-Packard 9862A calculator plotter, to simulate kinetic runs.

Results

Investigation of this system was initiated at 374 and 594 nm, where product and reactant, respectively, have absorbance maxima. Preliminary results indicated that the loss of reactant did not correspond to the gain of product. This prompted the construction of a time spectrum (Figure 1) which revealed the presence of at least one intermediate which could be studied in the range 475–525 nm.

The results at 374 and 594 nm were apparently complicated by the presence of more than one absorbing species. The wavelength 500 nm was chosen since the intermediate appears to have its maximum absorbance there, whereas that of the reactant and product are negligible. At this wavelength, the reaction appeared to be that of a straightforward buildup of an intermediate followed by its loss at a much slower rate. Accordingly, attention was focused on the system at 500 nm and the study limited to this intermediate.

For each kinetic run at 500 nm, rate constants were calculated based on the first three half-lives. Invariably, the second and third half-lives were in agreement with each other. The first half-life was longer due to an induction period which will be discussed later. Columns 5 and 6 of Table I contain the observed rate constants for the rapid buildup of intermediate at 500 nm calculated from the first and second half-lives, respectively. In all of the reactions tabulated, pseudo-first-order conditions were established with chromium in limiting quantity and hydroxide in excess over hydrogen peroxide. Under these conditions it was found that for the second and subsequent half-lives the rate of gain of inter-

Table I. Kinetic Data at 500 nm[a,b]–Rapid Gain

$10^3[Cr]_T$, M	$[H_2O_2]_T$, M	$[OH^-]_c$, M	$10^4[H_2O_2]$,[c] M	$k^{(1)}_{obsd}$, s^{-1}	$k^{(2)}_{obsd}$, s^{-1}	$k^{(1)}_{obsd}$(calcd),[d] s^{-1}
1.00	0.0293	0.407	3.16	1.5	1.7	1.6
1.00	0.0488	0.388	5.53	3.2	3.5	2.8
1.00	0.0195	0.0835	9.86	6.6	7.3	4.9
1.00	0.0975	0.340	12.5	7.7	9.2	6.2
1.00	0.0195	0.0319	23.9	11	11	11
1.50	0.0195	0.188	4.49	2.0	2.3	2.3
1.50	0.0195	0.103	8.08	4.1	4.6	4.1
2.50	0.0488	0.380	5.64	3.8	4.6	2.9
2.50	0.0488	0.166	12.7	8.1	8.1	6.3
2.50	0.0975	0.332	12.9	7.7	8.7	6.4
2.50	0.0975	0.283	15.1	7.7	8.7	7.4
2.50	0.184	0.235	34.2	16	21	16
2.50	0.0920	0.113	34.8	17	22	16
2.50	0.0488	0.0506	39.4	17	20	18
2.50	0.244	0.190	55.7	25	30	25

[a] All runs at 25.0 ± 0.1 °C. [b] Ionic strength is 2.2 M. [c] Calculated using eq I. [d] Calculated using eq IV and values for rate constants given in Table IV.

Table II. Kinetic Data at 500 nm[a,b]–Slow Loss

10^3-$[Cr]_T$, M	$[H_2O_2]_T$, M	$[OH^-]_T$, M	10^4-$[H_2O_2]$, M	ΔA, OD	k_3, s^{-1}
1.00	0.0293	0.407	3.16		0.13
1.00	0.0488	0.388	5.53		0.12
1.00	0.0195	0.0835	9.86	0.040	0.085
1.00	0.0975	0.340	12.5		0.11
1.00	0.0195	0.0319	23.9	0.083	0.073
1.50	0.0195	0.188	4.49	0.033	0.083
1.50	0.0195	0.103	8.08	0.053	0.081
2.50	0.0488	0.380	5.64	0.076	0.12
2.50	0.0488	0.166	12.7	0.14	0.095
2.50	0.0975	0.332	12.9	0.16	0.12
2.50	0.0975	0.283	15.1	0.17	0.10
2.50	0.184	0.235	34.2	0.30	0.096
2.50	0.0920	0.113	34.8	0.29	0.090
2.50	0.0488	0.0506	39.4	0.32	0.076
2.50	0.244	0.190	55.7	0.40	0.13

[a] All runs at 25.0 ± 0.1 °C. [b] Ionic strength is 2.2 M.

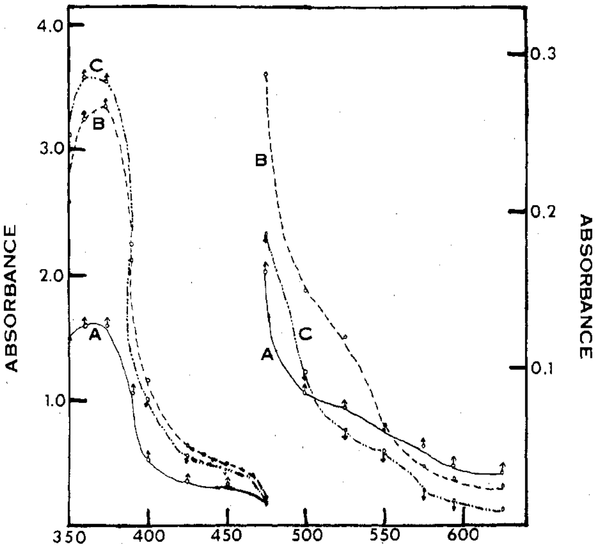


Figure 1. Time spectra [plots of absorbance vs. wavelength for various times]: A, 0.1 s; B, 1.0 s; C, 5.0 s. Refer to axis on the right for right-hand curves.

mediate was first order in chromium and hydrogen peroxide and inverse first order in hydroxide. Column 6 of Table II contains the observed rate constant for the loss of intermediate. The loss step was found to be first order in intermediate only.

Table III. Effect of a Chelating Agent[a,b]

10^3-$[Cr]_T$ M	$[H_2O_2]_T$, M	$[OH^-]_T$, M	[en], M	ΔA^{500}, OD	ΔA^{594}, OD
2.5	0.0975	0.441		0.16	0.05
2.5	0.0975	0.441	0.25	0.024	0.04

[a] All runs at 25.0 ± 0.1 °C. [b] Ionic strength is 2.2 M.

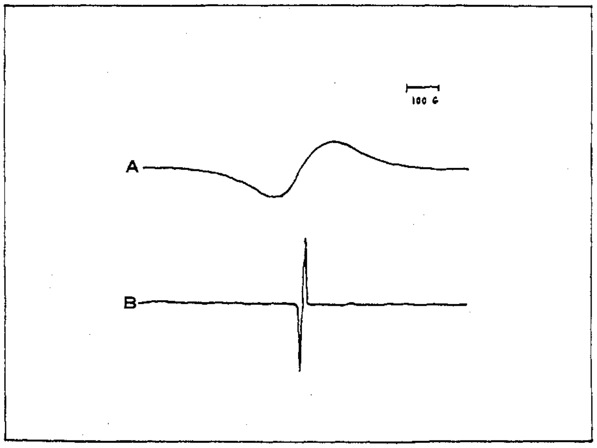


Figure 2. ESR spectra: A, Cr(III) and hydrogen peroxide in acidic media; B, chromium and hydrogen peroxide in base 0.1 s after mixing; the g value for the peak is 1.977.

In addition, it should be noted that the gain and loss steps are effectively decoupled.

A noteworthy feature of the kinetic traces at 500 nm is the variability of the total change in absorbance. The symbol ΔA in Table II column 5 represents the maximum change in absorbance (in OD from zero absorbance) that was observed. At constant initial chromium concentrations, $[Cr(III)]_0$, the absorbance maxima are proportional to the total hydrogen peroxide concentrations and inversely proportional to the total hydroxide concentrations.

The effect of a chelating agent on this system was studied by adding ethylenediamine to the sodium hydroxide solution before mixing with chromium–hydrogen peroxide solution and observing the results at 500 and 594 nm (Table III).

A comparison of the two reaction mixtures, identical except for the presence of chelate in one of them, shows a drastic decrease in the absorbance change at 500 nm. The effect at 594 nm is much less pronounced. It was not possible to determine any rate constants for the reactions because of excessive noise in the kinetic traces.

An ESR study was undertaken to gain additional information on the intermediate observed at 500 nm. Figure 2A shows the ESR spectrum of a solution containing chromium(III) and hydrogen peroxide in the absence of base. A basic solution of chromium(III) in which hydrogen peroxide is absent yields a similarly broad spectrum. Figure 2B shows the ESR spectrum obtained by monitoring a basic solution of chromium(III) and hydrogen peroxide 0.1 s after initiation of the reaction. It was found that the rate of loss of this ESR signal corresponded to the rate of loss of intermediate at 500 nm. It is important to note that the broad ESR peak due to the chromium(III) had completely disappeared when the sharp peak was monitored.

Variation in the ionic strength of the solutions failed to reveal any ionic strength dependency.

Mechanism and Discussion

A mechanism for this system must explain the following: (a) the short induction period, (b) the concentration dependencies for the gain of intermediate, (c) the variability of the maximum change in absorbance with hydrogen peroxide and base for fixed chromium concentration, (d) the first-order loss of intermediate, (e) the absence of an ESR signal due to chromium(III) after initiation of the reaction, and (f) the effect of ethylenediamine on the system.

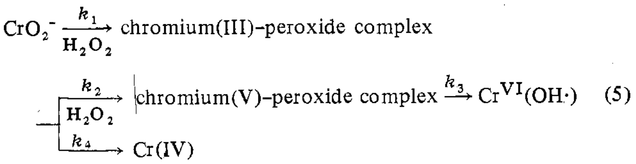
The mechanism of eq 2–4 can be envisioned as accounting for most of the observations. Only the species of interest are shown. The induction period is accounted for in this mechanism by having $k_1 < k_2$. Nevertheless, it cannot satisfactorily explain the variability of the peak height due to the fact that k_3 is so much smaller than k_2, thus decoupling the gain and loss steps.

$$CrO_2^- + H_2O_2 \xrightarrow{k_1} \text{chromium(III)–peroxide complex} \tag{2}$$

$$\text{chromium(III)–peroxide complex} + H_2O_2 \xrightarrow{k_2} \text{chromium(V)–peroxide complex [visible at 500 nm, ESR active]} \tag{3}$$

$$\text{chromium(V)–peroxide complex} \xrightarrow{k_3} Cr^{VI}(OH\cdot) \text{ [loss of intermediate]} \tag{4}$$

A modification of the above mechanism which will account for all of the experimental observations in a simple manner is the introduction of a branch. This can be presented schematically as in eq 5. In this mechanism only chromium(V) absorbs at 500 nm. The presence of the complex accounts for the short induction period. All protolytic reactions are assumed to be rapid.



$$CrO_2^- \xrightarrow[H_2O_2]{k_1} \text{chromium(III)–peroxide complex} \xrightarrow[H_2O_2]{k_2} \text{chromium(V)–peroxide complex} \xrightarrow{k_3} Cr^{VI}(OH\cdot) \quad \xrightarrow{k_4} Cr(IV) \tag{5}$$

The branching mechanism predicts that variation in the hydrogen peroxide concentration will directly influence the amount of chromium(V) produced relative to chromium(IV) with a concomitant effect on the absorbance at 500 nm. The ESR result is accounted for in that no chromium(III) should remain when the chromium(V) species has reached its maximum concentration. The effect of ethylenediamine on the system is easily explained by assuming that both chromium(IV) and chromium(V) absorb at 594 nm with similar absorptivities. The chelating agent, by occupying sites on the metal, inhibits the coordination of a second peroxide ligand thereby favoring the production of chromium(IV) at the expense of chromium(V). The result is a drastic reduction in the absorbance at 500 nm with only a minor effect at 594 nm. Kinetically indistinguishable reactions of the following type may be involved in this system

$$Cr(OH)_4^- \rightleftarrows Cr(OH)_3 + OH^- \tag{6}$$

$$Cr(OH)_3 + HO_2^- \rightarrow Cr(O_2H)(OH)_3^- \tag{7}$$

where $Cr(OH)_4^-$ is identified with CrO_2^- if $O^{2-} = 2OH^-$. Other workers[10,11] investigating systems where similar conditions prevailed have favored H_2O_2 as the reactive species. The concentration of H_2O_2 is determined by the equilibrium[12]

$$HO_2^- + H_2O \rightleftarrows H_2O_2 + OH^- \quad K_h = 4.44 \times 10^{-3} \tag{8}$$

with

$$[H_2O_2] = \frac{[H_2O_2]_T}{1 + [OH^-]_c/K_h} \tag{I}$$

where $[H_2O_2]_T$ is the total hydrogen peroxide concentration and $[OH^-]_c$ represents the hydroxide concentration after correction for base-consuming processes: conversion of $Cr(H_2O)_6^{3+}$ to CrO_2^- and neutralization of hydrogen peroxide functioning as a monoprotic acid. The product of reaction 4 is also an intermediate and not the final product since the rate at which the absorbance decreases at 500 nm is much more rapid than the rate of increase of absorbance at 374 nm, where CrO_4^{2-} absorbs.

The solution to the linear first-order differential equation expressing the concentration of chromium(V) with time (for the formation step, neglecting the decouplied loss step) is

$$[Cr(V)] = \frac{k_2[H_2O_2][Cr(III)]_0}{k_2[H_2O_2] + k_4} - \frac{k_2[H_2O_2][Cr(III)]_0 e^{-k_1[H_2O_2]t}}{(k_2 - k_1)[H_2O_2] + k_4} + \frac{k_1k_2[H_2O_2]^2[Cr(III)]_0 e^{-(k_2[H_2O_2]+k_4)t}}{\{(k_2 - k_1)[H_2O_2] + k_4\}\{k_2[H_2O_2] + k_4\}} \tag{II}$$

and the maximum concentration (setting $t = \infty$ and neglecting the decoupled loss step) is

$$[Cr(V)]_{max} = \frac{k_2[H_2O_2][Cr(III)]_0}{k_2[H_2O_2] + k_4} \tag{III}$$

At the end of the first half-life, $t^{(1)}{}_{1/2}$, $[Cr(V)]_{1/2} = {}^1/_2[Cr(V)]_{max}$ and assuming

$$e^{-k_1[H_2O_2]t^{(1)}{}_{1/2}} >> \frac{k_1[H_2O_2]}{k_2[H_2O_2] + k_4} e^{-(k_2[H_2O_2]+k_4)t^{(1)}{}_{1/2}}$$

it can be shown from the appropriate combination of eq II and III that the observed rate constant for the first half-life, $k^{(1)}{}_{obsd}$, is

$$k^{(1)}{}_{obsd} = \frac{\ln 2}{t^{(1)}{}_{1/2}} = \frac{-k_1[H_2O_2]\ln 2}{\ln \frac{1}{2}\left\{1 - \frac{k_1[H_2O_2]}{k_2[H_2O_2] + k_4}\right\}} \tag{IV}$$

The validity of the assumption is shown by the agreement of the rate constants in column 5 with those of column 7 in Table I.

By similar reasoning, the observed rate constant for the second and subsequent half-lives, $k^{(2)}{}_{obsd}$, can be shown to be

$$k^{(2)}{}_{obsd} = \frac{\ln 2}{t^{(2)}{}_{1/2}} = k_1[H_2O_2] \tag{V}$$

The value of k_1 is thus experimentally accessible from the second half-life.

The quantity $[Cr(V)]_{max}$ can be related to the maximum absorbance at 500 nm through Beer's law ($\Delta A = \epsilon[Cr(V)]_{max}$)

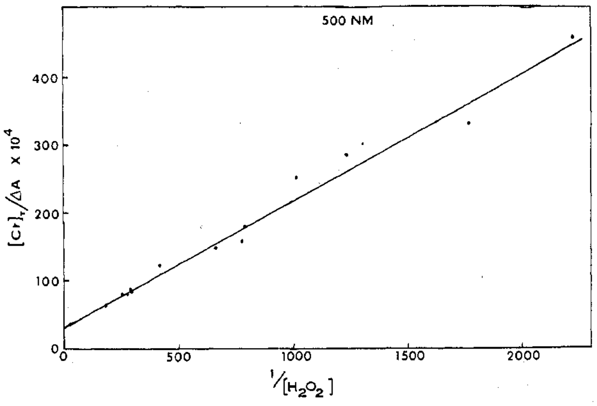


Figure 3. Least-squares plot of eq VI. Data from Tables I and II are employed. The reciprocal of the intercept yields ϵ 310. The ratio k_4/k_2 obtainable from the slope equals 0.0056.

Table IV. Rate Constants for the Proposed Mechanism

$k_1 = (5.3 \pm 1.0) \times 10^3\ M^{-1}\ s^{-1}$ $k_3 = 0.11 \pm 0.02\ s^{-1}$
$k_2 = 2.0 \times 10^4\ M^{-1}\ s^{-1}$ $k_4 = 1.1 \times 10^2\ s^{-1}$

assuming unit path length. Substitution of the absorbance for $[Cr(V)]_{max}$ in eq III followed by rearrangement yields

$$\frac{\epsilon [Cr(III)]_0}{\Delta A} = 1 + \frac{k_4}{k_2 [H_2O_2]} \qquad (VI)$$

A plot of $[Cr(III)]_0/\Delta A$ vs. $[H_2O_2]^{-1}$ should be linear with a slope of $k_4/k_2\epsilon$ and an intercept of ϵ^{-1}. The least-squares plot is shown in Figure 3. The linearity of this plot not only supports the branching mechanism but also shows the first-order hydrogen peroxide dependence for the formation of chromium(V). The slope of this plot provides the ratio $k_4/k_2 = 0.0056$.

Computer simulation of the formation step at 500 nm utilizing eq II facilitated the determination of best values for k_2 and k_4 which are shown in Table IV along with the k_1 and k_3 values. The rate constants in column 7 of Table I were calculated using eq IV and the values for k_2 and k_4 previously determined through computer simulation. These calculated rate constants are in good agreement with the experimental values in column 5 of the same table.

The assignment of a chromium(V) species as the intermediate absorbing at 500 nm is made on the basis of the ESR results. Chromium(V) in solution is known to give a very narrow ESR line.[13] Wiberg and Schafer,[5] in their study of the oxidation of isopropyl alcohol by chromic acid in 97% acetic acid, obtained an ESR spectrum consisting of one well-defined peak with g value of 1.9805 which they assigned to a chromium(V) species. In the present study, the peak had a line width of 2.5 G and a g value of 1.977. In addition, Wiberg and Schafer spectrophotometrically monitored an intermediate which absorbed at 510 nm and decayed at the same rate as the ESR peak. Referring once again to the present study, the intermediate observed at 500 nm decayed at the same rate as the ESR peak and is therefore identified as a chromium(V) species.

The possibility of species other than chromium(V) giving rise to an ESR signal has been considered. Chromium(IV) as the source of the peak is not likely. An ESR study of chromium(IV) in a solid showed a loss of signal due to line broadening above liquid nitrogen temperature.[14] This leaves the question of the contribution of hydroperoxyl and hydroxyl free radicals. The observed peak cannot be due to $HO_2\cdot$, which has a line width of 27 G.[15] The OH· radical is very short-lived in basic media and ESR spectra previously assigned to the species are now thought to be associated with metal–hydroxyl radical complexes.[16,17] While a chromium–hydroxyl radical complex as the source of the sharp ESR peak cannot be definitely ruled out, the similarity of our spectral data (visible and ESR) with those of Wiberg and Schafer taken together with the observation that all previously reported metal–hydroxyl radical complexes have g values above 2.01 tends to strengthen the case for chromium(V) as the intermediate.[18,19] Although the hydroperoxyl and hydroxyl free radical concentrations may be too low to detect by ESR, their presence is nevertheless inferred from the observation of a small amount of O_2 evolution measured by gas buret. The mechanism of O_2 evolution in alkaline hydrogen peroxide solution has been studied by others.[20]

With the intermediate identified as a chromium(V) species on the basis of ESR evidence, the assumption of the product of the other pathway as a chromium(IV) species bears examination. Ardon and Plane,[3] on the basis of product analysis, speculated that hydrogen peroxide could act as a 1- or 2-equiv oxidant in reacting with chromium(II) in acid media to give monomeric and dimeric chromium(III). If the product of the other pathway in this study is identified as chromium(IV), then the oxidation of chromium(III) by hydrogen peroxide is similarly proposed to go by parallel one- and two-electron pathways. It should be noted that kinetic evidence for the path complex → chromium(V) does not allow for the direct conversion of chromium(IV) to chromium(V) since this would change the mathematics of eq VI which gave a linear plot. It follows from this that chromium(IV) must be consumed in a 2-equiv change.

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Registry No. $Cr(OH_2)_6^{3+}$, 14873-01-9; H_2O_2, 7722-84-1; en, 107-15-3.

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