Stoichiometry and Mechanism of the Chromium(II)–Peroxydisulfate Reaction[1a]

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Abstract: The rapid reaction ($k = 2.5 \times 10^4\ M^{-1}\ sec^{-1}$ at 25° and ionic strength 1.0) between chromium(II) and peroxydisulfate yields sulfatopentaaquochromium(III) and hexaaquochromium(III) ions. The ratio $[CrSO_4^+]/[Cr^{3+}]$ produced in the reaction is independent of perchloric acid concentration (0.02–1.2 *M*) and of the order of mixing and has the value 1.00 ± 0.05. When the reaction is carried out in the presence of added bromide ions, the yield of $CrSO_4^+$ is unchanged (50%), but the yield of Cr^{3+} decreases and $CrBr^{2+}$ becomes a significant reaction product. It is suggested that the reaction proceeds by a sequence of two one-electron steps. The first step (reaction of chromium(II) with peroxydisulfate) features an inner-sphere mechanism and produces $CrSO_4^+$ and a sulfate radical ion. The second step involves the reaction of chromium(II) with a sulfate radical ion and yields Cr^{3+} *via* a hydrogen-atom transfer or outer-sphere mechanism. Bromide ions compete with chromium(II) for sulfate radical ions: bromine atoms (or Br_2^-) are produced and subsequently react with chromium(II) to produce $CrBr^{2+}$.

Following the discovery[2] of the bridged activated complex, the dramatic decrease in substitution rate which occurs when chromium(II) is oxidized to chromium(III) has been exploited to obtain mechanistic information about reductions by chromium(II). In many instances, all that is needed to obtain the desired information is to identify the chromium(III) species formed as the primary products of the redox reactions. Significant mechanistic details, such as binuclear complex formation,[3,4] one- or two-electron transfer,[3,5,6] singly or doubly bridged transition states,[7,8] and adjacent or remote attacks,[9,10] have been established from relatively simple stoichiometric studies. One general feature that has emerged from these studies is that, when the oxidant contains an atom that can potentially act as a donor, the reduced form of the oxidant, or at least a part of it, is trapped in the coordination sphere of the primary chromium(III) product. This feature applies to ordinary, long-lived oxidants as well as to unstable, short-lived radicals such as bromine and iodine atoms,[3] $CHCl_2$ and $C_6H_5CH_2$ radicals.[11-13]

This fairly satisfactory state of affairs with respect to our understanding of some of the chemistry of the reducing agent chromium(II) has its counterpart in the case of the oxidizing agent peroxydisulfate. The chemistry of this oxidant has been systematized,[14,15] and one general feature that emerges from studies of oxidations by peroxydisulfate is the predominance of free-radical reactions involving the radical ion SO_4^-.

On the basis of the above information, we undertook a study of the chromium(II)–peroxydisulfate reaction and anticipated the following sequence of one-electron steps.

$$S_2O_8^{2-} + Cr^{2+} \longrightarrow CrSO_4^+ + SO_4^- \tag{1}$$

$$SO_4^- + Cr^{2+} \longrightarrow CrSO_4^+ \tag{2}$$

$$SO_4^- + H_2O \rightleftarrows HSO_4^- + OH \tag{3}$$

$$OH + Cr^{2+} \xrightarrow{H^+} Cr^{3+} + H_2O \tag{4}$$

By measuring the yield of $CrSO_4^+$ we hoped to obtain some information regarding the trapping of sulfate radical ions by chromium(II) and the radical interconversion reaction given by eq 3. As will be seen below, this predicted reaction scheme is only partially fulfilled.

Experimental Section

Materials. Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate with amalgamated zinc. The chromium(II) concentration was determined by reaction with excess iron(III), followed by titration of the iron(II) produced with a standard potassium dichromate solution.[16] The total chromium content was estimated spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.[17]

Solutions containing the ion $CrSO_4^+$ were obtained by four different procedures: (1) dissolution of commercially available $Cr_2(SO_4)_3 \cdot xH_2O$; (2) reduction of potassium dichromate by sulfur dioxide; (3) oxidation of chromium(II) by iron(III) in 0.1 *M* sulfuric acid; (4) oxidation of chromium(II) by peroxydisulfate. In each case the ion $CrSO_4^+$ was isolated by the ion-exchange procedure described below and examined spectrophotometrically in the 700–300-nm region. The spectra of the $CrSO_4^+$ solutions obtained by the four different procedures were identical within experimental error. The absorption maxima occurred at 586 and 417 nm with molar absorptivities 19.1 ± 0.1 and 18.9 ± 0.1, respectively. Our values are in good agreement with those previously reported by Finholt, *et al.*[18] (19.0 and 18.8 at 587 and 417 nm, respectively).

Separation of Chromium(III) Species. The separations of $CrSO_4^+$, $CrBr^{2+}$, and Cr^{3+} were accomplished by ion-exchange chromatography with Dowex 50W-X8 (50–100 mesh, H^+ form). These ions were eluted with 0.15, 1.0, and 2.0 *M* perchloric acid, respectively.

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(1) (a) This work was supported by the National Science Foundation, Grants GP-2001 and GP-6528; (b) Fellow of the Alfred P. Sloan Foundation, 1965–1968.

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Table I. Stoichiometry of the Chromium(II)–Peroxydisulfate Reaction (25°, $[Cr^{2+}] = 0.0274\text{–}0.0416\ M$, $[S_2O_8^{2-}] = 0.0137\text{–}0.0208\ M$)[a]

Expt	Conditions[b]	R[c]	No. of measurements
1	A, $[HClO_4] = 0.020\ M$	0.99 ± 0.07	8
2	B, $[HClO_4] = 0.020\ M$	1.00 ± 0.07	4
3	A, $[HClO_4] = 0.14\ M$	1.03	1
4	B, $[HClO_4] = 0.14\ M$	0.98	1
5	A, $[HClO_4] = 1.2\ M$	0.95 ± 0.02	2
6	B, $[HClO_4] = 1.2\ M$	0.97 ± 0.01	2
7	C, $[HClO_4] = 0.10\ M$	1.02 ± 0.02	2
8	A, $[HClO_4] = 1.0\ M$, $[HSO_4^-] = 0.027\ M$	1.00 ± 0.09	6
9	B, $[HClO_4] = 1.0\ M$, $[HSO_4^-] = 0.027\ M$	1.02 ± 0.05	4
10	D, $[HClO_4] = 0.10\ M$	0.94 ± 0.01	2

[a] These are initial concentrations calculated by assuming that reaction did not occur. Unless otherwise noted, 5 ml of chromium(II) or peroxydisulfate solution was added to 15 ml of a solution containing the stoichiometric amount of the other reagent. [b] A, chromium(II) added to peroxydisulfate; B, peroxydisulfate added to chromium(II); C, 5 ml of peroxydisulfate added to 1 ml of 1.25 *M* chromium(II), 0.6 *M* perchloric acid; D, equal volumes of 0.098 *M* chromium(II) and 0.0497 *M* peroxydisulfate mixed in the rapid flow apparatus. [c] Defined as $[CrSO_4^+]/[Cr^{3+}]$ produced in the reaction.

Experimental Procedure. Reaction vessels were serum bottles covered with self-sealing rubber caps and containing Teflon-covered stirring bars. All the desired reagents except the chromium(II) or the peroxydisulfate (depending on the order of mixing) were added to the serum bottle under prepurified nitrogen or argon. The last reagent was added to the serum bottle by means of a hypodermic syringe (usually 5 ml) while the solution in the bottle was rapidly stirred. After completion of the reaction, the chromium(III) products were separated as described above and examined spectrophotometrically in the 700–300-nm region on a Cary 14 recording spectrophotometer. The chromium content of each fraction was estimated spectrophotometrically as CrO_4^{2-}. It must be noted that, at the electrolyte concentrations used in the present work, the $CrSO_4^+$ fraction was incompletely retained in the ion-exchange column. Therefore, the solution that passed directly through the column was combined with the fraction eluted with 0.15 *M* $HClO_4$ in order to measure the yield of $CrSO_4^+$.

Kinetic measurements and some of the stoichiometric measurements were carried out in a rapid-flow apparatus of the type described by Dulz and Sutin.[19]

Results

The oxidation–reduction stoichiometry of the chromium(II)–peroxydisulfate reaction was determined by mixing various nonstoichiometric amounts of the reactants and measuring the amount of the reactant in excess remaining at the completion of the reaction. In duplicate measurements, 5.00 ml of a 0.215 *M* chromium(II) perchlorate solution was added to 0.812 mmole of potassium peroxydisulfate dissolved in 15 ml of water. The excess of peroxydisulfate was estimated by adding an excess of potassium iodide, followed by titration of the iodine produced with a standard sodium thiosulfate solution. It was found that 0.495 and 0.497 mole of peroxydisulfate were used up per mole of chromium(II). In a second set of duplicate measurements, 5.00 ml of a 0.215 *M* chromium(II) perchlorate solution was added to 0.143 mmole of potassium peroxydisulfate dissolved in 15 ml of water. The excess of chromium(II) was estimated by addition of an excess of iron(III), followed by titration of the iron(II) produced with a standard potassium dichromate solution. It was found that 2.03 and 2.04 moles of chromium(II) were used up per mole of peroxydisulfate. These results show that the redox stoichiometry of the chromium(II)–peroxydisulfate reaction is accurately represented by

$$2Cr(II) + S_2O_8^{2-} = 2Cr(III) + 2SO_4^{2-} \qquad (5)$$

In eq 5 we have not specified the identity of the chromium(III) species produced. By means of the ion-exchange separation procedure, followed by spectrophotometric identification of the separated fractions, it was established that, when ClO_4^-, SO_4^{2-}, and HSO_4^- are the only anions present, $CrSO_4^+$ and Cr^{3+} account for 95–99% of the chromium(II) reacted. It is noteworthy that dimeric or higher polymeric chromium(III) species are not produced in the reaction,[20] and the significance of this observation will be discussed below.

A substantial number of experiments were performed in order to establish the yields of $CrSO_4^+$ and Cr^{3+}. The results, summarized in Table I, are expressed in terms of *R*, the ratio $[CrSO_4^+]/[Cr^{3+}]$ produced in the reaction. The values of *R* are calculated from the expression $a/(b - a)$, where a = millimoles of $CrSO_4^+$ collected, and b = millimoles of Cr^{2+} reacted.[21] Since the chromium(II)–peroxydisulfate reaction is quite rapid ($k = 2.5 \times 10^4\ M^{-1}\ sec^{-1}$), changing the order of mixing appreciably changes the concentration of the reactants. As seen in column 3 of Table I, *R* is close to the value 1.0 and appears to be independent of the order of mixing. Even when the initial chromium(II) concentration is as high as 1.25 *M* (*cf.* expt 7), the yield of $CrSO_4^+$ is 50%. Equal amounts of $CrSO_4^+$ and Cr^{3+} are also produced when mixing is accomplished in the fast-flow apparatus (*cf.* expt 10). *R* is also independent of the hydrogen ion concentration (0.02 to 1.2 *M*)[22] and of added bisulfate ion (0.027 *M*). The latter result was somewhat disappointing to us, since we hoped to obtain some information about the sulfate radical ion–hydroxyl radical interconversion reaction (eq 3) by studying the possible dependence of *R* upon bisulfate ion concentration.

Since we anticipated that the chromium(II)–peroxy-

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(19) G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

(20) Usually the per cent recovery of $CrSO_4^+$ and Cr^{3+} was 96–98%. The lack of quantitative recovery does *not*, however, indicate that small amounts of polymeric species are produced. In our experience, a quantitative recovery of Cr^{3+} from Dowex 50X-8 resin requires prolonged washing of the resin with very large volumes of 2 *M* perchloric acid.

(21) We believe that this calculation of *R* is more meaningful than the alternate calculation $R = a/c$, where c = millimoles of Cr^{3+} collected. Because of incomplete recovery,[20] $c = f(b - a)$, where f, the fraction of chromium(II) reacted that was collected as $CrSO_4^+$ or Cr^{3+}, varied between 0.95 and 0.99.

(22) However, at high chromium(II) concentration, low hydrogen ion concentration, and very slow addition of peroxydisulfate to chromium(II), the yield of $CrSO_4^+$ is appreciably less than 50%. For example, slow addition (15 min) of 5 ml of 0.0868 *M* peroxydisulfate to 1 ml of 0.868 *M* chromium(II) in 0.02 *M* perchloric acid results in yields of $CrSO_4^+$ of 35 and 36% (duplicate experiments). The decrease in the yield is caused by the chromium(II)-catalyzed dissociation of $CrSO_4^+$, a reaction which becomes important only at low $[H^+]$ and high $[Cr^{2+}]$: D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, 88, 3450 (1966).

disulfate reaction would feature some free-radical chemistry, experiments were carried out with bromide ion added as a potential scavenger. The results are summarized in Table II. In the presence of bromide ion, three chromium(III) species, namely $CrSO_4^+$, $CrBr^{2+}$ and Cr^{3+}, are produced. Values of R and Q, the ratios $[CrSO_4^+]/([CrBr^{2+}] + [Cr^{3+}])$ and $[CrBr^{2+}]/[Cr^{3+}]$ produced in the reaction, are presented in columns 4 and 5, respectively. It is seen that the yield of $CrSO_4^+$ (as measured by R) is unaffected by the addition of bromide ion, but that the yield of Cr^{3+} decreases, and $CrBr^{2+}$ becomes a significant reaction product. The yield of $CrBr^{2+}$ (as measured by Q) appears to increase with increasing bromide ion concentration (*cf.* expt 1–3) and decreasing chromium(II) concentration (*cf.* expt 4–7). It is seen (*cf.* expt 8) that chloride ion also decreases the yield of Cr^{3+} but leaves that of $CrSO_4^+$ essentially unaffected. The effect of chloride ion, however, is smaller than that of bromide ion (*cf.* expt 7 and 8).

Table II. Stoichiometry of the Chromium(II)–Peroxydisulfate Reaction in the Presence of Added Bromide Ion (25°, $[HClO_4]$ = 0.10 M)[a]

Expt	$[Cr^{2+}]$, M	$[Br^-]$, M	R^b	Q^c
1	0.0542	0.050	0.92 ± 0.02	1.32 ± 0.02
2	0.0542	0.25	0.98 ± 0.01	2.16 ± 0.04
3	0.0542	0.50	1.05 ± 0.03	2.85 ± 0.10
4	0.00880	0.10	0.89 ± 0.02	4.38 ± 0.05
5	0.0220	0.10	0.93 ± 0.02	2.84 ± 0.02
6	0.0440	0.10	0.91 ± 0.02	1.66 ± 0.02
7	0.0455	0.10	1.06 ± 0.02	1.70 ± 0.03
8	0.0455	0.10[d]	0.95 ± 0.02	1.10 ± 0.02[e]

[a] 5 ml of a solution containing the stoichiometric amount of peroxydisulfate added to 20 ml of a solution with the concentrations of chromium(II) and bromide ion specified in columns 2 and 3, respectively. [b] Defined as the ratio $[CrSO_4^+]/([Cr^{3+}] + [CrBr^{2+}])$ produced in the reaction. Average of two measurements. [c] Defined as the ratio $[CrBr^{2+}]/[Cr^{3+}]$ produced in the reaction. Average of two measurements. [d] Chloride ion was used instead of bromide ion. [e] Defined as the ratio $[CrCl^{2+}]/[Cr^{3+}]$ produced in the reaction.

A cursory examination of the kinetics of the chromium(II)–peroxydisulfate reaction was carried out in the rapid-flow apparatus. At 25°, $[Cr^{2+}] = 4.0 \times 10^{-3}$ M, $[S_2O_8^{2-}] = 2.0 \times 10^{-4}$ M, $[HClO_4] = 0.10$ M, and ionic strength 1.0 M adjusted with sodium perchlorate, the second-order rate constant (derived from the transmittance changes at 240 nm for six repetitive measurements) was $(2.5 \pm 0.3) \times 10^4$ M^{-1} sec^{-1}. Under the same conditions, except for the replacement of 0.20 M sodium perchlorate by 0.20 M sodium bromide, the second-order rate constant was $(2.5 \pm 0.3) \times 10^4$ M^{-1} sec^{-1}. A comparison of the rate constants measured in the absence and in the presence of bromide ion shows that this ion has no detectable effect on the reaction rate. This result is remarkable in view of the profound effect of bromide ion on the reaction stoichiometry (see Table II). The significance of this observation will be discussed below.

Discussion

Since the chromium(II)–peroxydisulfate reaction does not yield binuclear chromium(III) species, it is reasonable to assume that the reaction involves a sequence of two one-electron steps.[5] We suggest that the first step in the sequence proceeds according to the inner-sphere reaction represented by eq 1. The formation

$$S_2O_8^{2-} + Cr^{2+} \longrightarrow CrSO_4^+ + SO_4^- \qquad (1)$$

of $CrSO_4^+$ as the primary product of the oxidation of chromium(II) conforms to previous findings regarding the efficient trapping of the oxidant (or part of it) in the coordination sphere of the newly formed chromium(III) product. Moreover, in common with other redox activations of peroxydisulfate,[14] the generation of a sulfate radical ion as the one-electron reduction product of peroxydisulfate is indicated in eq 1. Entirely analogous initiation steps have been previously proposed for the chromium(II) reductions of organic peroxides.[23,24] Furthermore, since one of the oxygen atoms of the hexaaquochromium(III) ion produced in the chromium(II)–hydrogen peroxide reaction originates in the peroxide oxygen, it was suggested that the initial inner-sphere one-electron step produces $CrOH^{2+}$ and a hydroxyl radical.[25] It is noteworthy that eq 1 is also formally analogous to the chromium(II) reduction of organic halides,[11–13] where halopentaaquochromium(III) ions and organic radicals are produced in the initial one-electron inner-sphere step.

If we accept the suggestion that the initial step in the peroxydisulfate–chromium(II) reaction is given by eq 1 (we will return to the adequacy of this suggestion later), the question arises as to the fate of the sulfate radical ion generated in this step. In the absence of anions other than perchlorate, the sulfate radical ion can in principle react with chromium(II) or with water. In trying to distinguish between these possibilities, it should be recognized that the stoichiometric results (equal amounts of $CrSO_4^+$ and Cr^{3+} are produced in the reaction) require that only hexaaquochromium(III) ion be produced in the second step of the reaction. Therefore, if the sulfate radical ion reacts with chromium(II), we must conclude that hexaaquochromium(III) (and *not* $CrSO_4^+$ as anticipated in eq 2) is produced in this step (eq 6).

$$Cr^{2+} + SO_4^- \longrightarrow Cr^{3+} + SO_4^{2-} \qquad (6)$$

Alternatively, if the sulfate radical ion were converted to the hydroxyl radical by reaction with water (eq 3), then the production of hexaaquochromium(III) would be assigned to the subsequent reaction of the hydroxyl radical with chromium(II) (eq 4).[26]

$$SO_4^- + H_2O \longrightarrow HSO_4^- + OH \qquad (3)$$

$$Cr^{2+} + OH \xrightarrow{H^+} Cr^{3+} + H_2O \qquad (4)$$

It must be noted that the question of the identity of the active intermediate in redox activations of peroxydisulfate has been considered several times.[14,27] The

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(23) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, 30, 1134 (1965).

(24) J. K. Kochi, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 207 (1966).

(25) L. B. Anderson and R. A. Plane, *Inorg. Chem.*, 3, 1470 (1964).

(26) It must be noted that at this point no mechanistic significance is to be assigned to eq 4 and 6. These equations merely indicate the stoichiometric production of hexaaquochromium(III) by reaction of sulfate radical ions or hydroxyl radicals with chromium(II). Detailed mechanisms to be considered for reaction 6 are: (1) outer-sphere electron transfer; (2) hydrogen-atom transfer from one of the water molecules in the coordination sphere of chromium(II) to the sulfate radical ion. For reaction 4, either an inner-sphere, outer-sphere, or hydrogen-atom-transfer mechanism would lead to the formation of hexaaquochromium(III).

(27) R. Woods, I. M. Kolthoff, and E. J. Meehan, *J. Am. Chem. Soc.*, 86, 1698 (1964).

problem arises because sulfate radical ions generated by the thermal or photolytic decomposition of peroxydisulfate are known to undergo the radical interconversion reaction given by eq 3.[14] However, these studies are carried out in the absence of any added oxidizable substrates, and these conditions obviously favor the radical-exchange reaction. In the presence of oxidizable substrates, on the other hand, it has been established, on the basis of chemical competition studies,[14,27,28] that the reactive intermediate produced in the redox activation of peroxydisulfate by iron(II) is the sulfate radical ion. Therefore, these studies show that various substrates compete favorably with water for the sulfate radical ion. In fact, it has been recently stated that reaction 3 is probably slow and occurs only in the absence of scavengers for sulfate radical ions.[29] In order to put this conclusion on a more quantitative basis, we have carried out some approximate calculations of the rate constant for reaction 3.

In a study of the chain reaction between hydrogen peroxide and peroxydisulfate, Tsao and Wilmarth[30] reported that one of the terms in the rate law was half-order in peroxydisulfate and independent of hydrogen peroxide. According to the proposed interpretation, the rate coefficient for that term is $k_d/k_1k_3^2$, where k_d is the rate constant for recombination of sulfate radical ions, k_1 is the rate constant for the decomposition of peroxydisulfate, and k_3 is the rate constant for reaction 3. Using the reported values of k_d[31] and k_1,[30] we obtain the result $k_3 \sim 6 \times 10^2$ sec^{-1}. A second calculation can be made by using the estimated equilibrium constant for reaction 3[14] and the reported[32] rate constant for the reverse reaction. This calculation yields $k_3 \sim 8 \times 10^3$ sec^{-1}. A third estimate of k_3 can be obtained by recognizing that iron(II) at a concentration of 5×10^{-5} *M* competes favorably with water for the sulfate radical ion generated in the iron(II)–peroxydisulfate reaction.[27] Since the rate constant for the iron(II)–sulfate radical ion reaction has been reported[32] as 10^9 M^{-1} sec^{-1}, we conclude that $k_3 < 5 \times 10^5$ sec^{-1}. Finally, it has been reported that the disappearance of sulfate radical ions generated in the flash photolysis of peroxydisulfate[31] proceeds by a second-order recombination reaction (eq 7).

$$SO_4^- + SO_4^- \longrightarrow S_2O_8^{2-} \qquad (7)$$

The concentration of sulfate radical ions produced during the flash was $\sim 5 \times 10^{-5}$ *M*. Assuming that under these conditions a 10% contribution of the first-order disappearance by eq 3 could not be detected, we arrive at the limit $k_3 < 2 \times 10^3$ sec^{-1}. In view of the approximate nature of the calculations above, we can estimate that the rate constant for reaction 3 is of the order of 10^3–10^4 sec^{-1}.

Once the rate constant for reaction 3 has been estimated, a distinction between the two schemes outlined above (eq 6 or eq 3 and 4) could be achieved if the rate constant for reaction 6 were known. Unfortunately, no measurements have been reported for this reaction. Nevertheless, a distinction can be made by examining the implications of the bromide ion competition studies for each of the two mechanisms (*cf.* Chart I).

Chart I

Mechanism A

$$S_2O_8^{2-} + Cr^{2+} \longrightarrow CrSO_4^+ + SO_4^- \qquad (1)$$

$$SO_4^- + Cr^{2+} \longrightarrow Cr^{3+} + SO_4^{2-} \qquad (6)$$

$$SO_4^- + Br^- \longrightarrow SO_4^{2-} + Br\ (\text{or } Br_2^-) \qquad (8)$$

$$Cr^{2+} + Br\ (\text{or } Br_2^-) \longrightarrow CrBr^{2+} \qquad (9)$$

Mechanism B

$$S_2O_8^{2-} + Cr^{2+} \longrightarrow CrSO_4^+ + SO_4^- \qquad (1)$$

$$SO_4^- + H_2O \longrightarrow HSO_4^- + OH \qquad (3)$$

$$Cr^{2+} + OH \xrightarrow{H^+} Cr^{3+} + H_2O \qquad (4)$$

$$OH + Br^- \longrightarrow OH^- + Br\ (\text{or } Br_2^-) \qquad (10)$$

$$Cr^{2+} + Br\ (\text{or } Br_2^-) \longrightarrow CrBr^{2+} \qquad (9)$$

Since the addition of bromide ion does not alter the yield of $CrSO_4^+$, but decreases that of Cr^{3+}, it is apparent that bromide ion affects only the step that leads to the production of Cr^{3+}. On the basis of the mechanism represented by eq 1 and 6, the bromide ion effect on the stoichiometry indicates that the sulfate radical ion produced in the initial step is diverted from the normal reaction sequence: competition between bromide ions and chromium(II) for sulfate radical ions (eq 6 and 8) is operative, and the bromine atoms (or Br_2^-) generated in eq 8 react with chromium(II) to form $CrBr^{2+}$ (eq 9). On the basis of the mechanism represented by eq 1, 3, and 4, the bromide ion effect is interpreted as the result of competition of bromide ion and chromium(II) for the hydroxyl radical (eq 10 and 4). The observed dependence of the yield of $CrBr^{2+}$ on the concentrations of bromide ion and chromium(II) (see Table II) is consistent with either interpretation. However, it must be noted that mechanism B contains the implicit assumption that bromide ion is ineffective in competing with water for sulfate radical ions. The adequacy of this assumption can be tested by comparing the rate constants for reactions 3 and 8.

The rate constant for reaction 8 can be calculated from the competition ratio measured[33] for reactions 8 and 11 and the absolute rate constant[32] for reaction 11.

$$Fe^{2+} + SO_4^- \longrightarrow Fe^{3+} + SO_4^{2-} \qquad (11)$$

The calculation yields the value 4×10^8 M^{-1} sec^{-1}, to be compared with the value 10^3–10^4 sec^{-1} for reaction 3. It is seen that, even at 0.050 *M* bromide ion concentration, reaction 3 contributes less than 1% to the disappearance of sulfate radical ions. Therefore, since bromide ions effectively suppress the production of hydroxyl radicals, the assumption implicit in mechanism B is invalid, and we can rule out eq 3, 4, and 10 when bromide ion is present. In particular, it is clear that the reaction of chromium(II) with hydroxyl radicals (eq 4) cannot be invoked to account for the formation of hexaaquochromium(III) in the presence of bromide ion. However, since appreciable amounts of

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(30) M. S. Tsao and W. K. Wilmarth, *Discussions Faraday Soc.*, **29**, 137 (1960).

(31) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 71, 2511 (1967).

(32) E. Heckel, A. Henglein, and G. Beck, *Ber. Bunsenges. Physik. Chem.*, **70**, 149 (1966).

(33) I. M. Kolthoff, A. I. Medalia, and H. P. Raaen, *J. Am. Chem. Soc.*, 73, 1733 (1951).

hexaaquochromium(III) are formed under these conditions, we must conclude that the sulfate radical ion–chromium(II) reaction produces hexaaquochromium(III), and hence that mechanism A is operative.[34]

The latter conclusion requires that chromium(II) compete effectively with bromide ions for the sulfate radical ions. Since hexaaquochromium(III) is formed even at 0.50 *M* bromide ion concentration, we estimate the rate constant for reaction 6 to be $\sim 10^{10}\ M^{-1}\ \text{sec}^{-1}$. This value appears to be reasonable[35] when compared with the value $10^9\ M^{-1}\ \text{sec}^{-1}$ for reaction 11, since, as far as we can ascertain, reductions by chromium(II) are invariably faster than reductions by iron(II). To be sure, it might be argued that with an oxidant as reactive as the sulfate radical ion, the rate discrimination between chromium(II) and iron(II) might be quite small. This may indeed be the case, but a reversal in reactivities would appear to be unreasonable.

At this point, we must return to the assumption that eq 1 describes the stoichiometry of the first reaction in the two-step sequence. Since two products are formed in equal yields, it is pertinent to inquire about the order of formation of these products. So far, we have assumed that $CrSO_4^+$ is produced in the first step and Cr^{3+} in the second step. However, the alternate reaction scheme in which the formation of the two products occurs in the reverse sequence (eq 12 and 2) is equally consistent with the results in Table I.

$$S_2O_8^{2-} + Cr^{2+} \longrightarrow Cr^{3+} + SO_4^- + SO_4^{2-} \qquad (12)$$

$$Cr^{2+} + SO_4^- \longrightarrow CrSO_4^+ \qquad (2)$$

We reject this alternate interpretation because it is incompatible with the results obtained in the presence of added bromide ion. In order to explain the bromide ion effect on the stoichiometry according to this scheme, it is necessary to assume that bromide ions increase the rate of initiation *via* an additional bromide ion dependent path which results in the production of $CrBr^{2+}$.[36] The kinetic results clearly preclude such an additional path since the reaction rate is unaffected by addition of bromide ion.

The present evidence is insufficient to distinguish between an outer-sphere (eq 13) and a hydrogen-atom transfer mechanism (eq 14) for reaction 6. In this

$$Cr(OH_2)_6^{2+} + SO_4^- \longrightarrow Cr(OH_2)_6^{2+} + SO_4^{2-} \qquad (13)$$

$$Cr(OH_2)_6^{2+} + SO_4^- \longrightarrow Cr(OH_2)_5OH^{2+} + HSO_4^- \qquad (14)$$

context, reference should be made to a hydrogen-abstraction reaction (eq 15) suggested recently[37] to

$$Co(NH_3)_5OH_2^{3+} + OH \longrightarrow Co(NH_3)_5OH^{3+} + H_2O \qquad (15)$$

account for hydrogen isotope effects observed in the oxidation of coordinated ammonia by radicals produced during the thermal decomposition of peroxydisulfate. The formal similarity between reactions 14 and 15 is noteworthy.

A surprising aspect of the proposed reaction mechanism (eq 1 and 6) is that the oxidation of chromium(II) by the sulfate radical ion, an oxidant which can potentially enter the coordination sphere of chromium, does not proceed *via* an inner mechanism. This situation is, as far as we can ascertain, exceptional. It may be that, since substitution of water on chromium(II) is extremely rapid[38] ($>8 \times 10^9\ \text{sec}^{-1}$), most oxidants with potential bridging ligands have an opportunity to penetrate the coordination sphere of chromium(II). The very reactive sulfate radical ion, on the other hand, does not wait for substitution, and an outer-sphere or a hydrogen-atom transfer mechanism becomes operative. In the related vanadium(II) system, it has been suggested[39] that oxidations of vanadium(II) that proceed at a rate faster than water substitution are of the outer-sphere type.

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(34) Although mechanism A accounts for the qualitative trends in *Q* as a function of bromide ion and chromium(II) concentrations, it does not seem possible to relate quantitatively the data in Table II to mechanism A. First, it must be noted that, for a reaction as rapid as the present one, the mixing procedure is inadequate when competition between two substrates for a reactive intermediate is featured. Second, since a stoichiometric amount of peroxydisulfate is added to the mixture of chromium(II) and bromide ion, integration of the expression $d[CrBr^{2+}]/d[Cr^{3+}] = k_9[Cr^{2+}][Br]/k_6[Cr^{2+}][SO_4^-]$ is inappropriate.

(35) Although the fastest chromium(II) reductions measured by flow methods proceed with rate constants of the order of $10^7\ M^{-1}\ \text{sec}^{-1}$, the rate constant for the permanganate–chromium(II) reaction, measured by pulse radiolysis techniques, is $3.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$: J. H. Baxendale, J. P. Keene, and D. Stott in "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press Inc., New York N. Y., 1965, p 107.

(36) In fact, a second assumption is necessary, namely that bromide ion is completely ineffective in competing with chromium(II) for the sulfate radical ion. This assumption is incompatible with the rate constants for reactions 8 and 2, even if reaction 2 proceeds at a diffusion controlled rate.

(37) D. D. Thusius and H. Taube, *J. Phys. Chem.*, 71, 3845 (1967).

(38) C. W. Merideth and R. E. Connick, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, No. M106.

(39) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).