Inorganic Chemistry

A Tracer Study of the Chromium(II)–Chromium(VI) Reaction[1a,b]
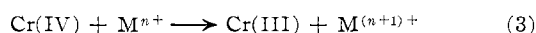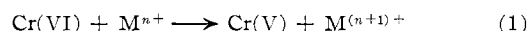
BY LOUIS S. HEGEDUS AND ALBERT HAIM[1c]

The reaction of chromium(II) with chromium(VI) in aqueous perchloric acid solutions produces hexaaquochromium(III) ion and a polymeric species, presumably $Cr_2(OH)_2^{4+}$. The ratio $[Cr^{3+}]/[Cr_2(OH)_2^{4+}]$ is approximately 2 and appears to be independent of the order of mixing of the reactants and of perchloric acid concentration from 0.010 to 1.0 M. When the reaction is carried out with radioactive chromium(VI), the radioactivity appears in both the Cr^{3+} and $Cr_2(OH)_2^{4+}$ fractions. Approximately 10 and 90% of the Cr^{3+} produced is derived from chromium(VI) and chromium(II), respectively. The results are compatible with the mechanism proposed by Ardon and Plane (a sequence of 1-equiv changes) if a small contribution of a 2-equiv change in the chromium(II)–chromium(V) reaction is included.
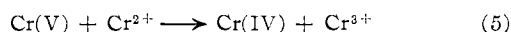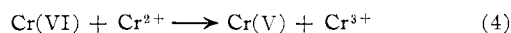
Introduction

The reaction of chromium(VI) with 1- and 2-equiv reducing agents has long been a favorite subject for mechanistic studies.[2–7] For 1-equiv oxidation–reduction reagents, the kinetic evidence indicates that the reduction of chromium(VI)[3–5] (or the oxidation of chromium(III)[8]) proceeds by a succession of 1-equiv steps and that the slow step often corresponds to the chromium(V)–chromium(IV) change.

$$Cr(VI) + M^{n+} \longrightarrow Cr(V) + M^{(n+1)+} \tag{1}$$

$$Cr(V) + M^{n+} \longrightarrow Cr(IV) + M^{(n+1)+} \tag{2}$$

$$Cr(IV) + M^{n+} \longrightarrow Cr(III) + M^{(n+1)+} \tag{3}$$

The interesting suggestion has been made[3,8] that the slowness of reaction 2 is associated with a change in coordination number from 4 in chromium(V) to 6 in chromium(IV).

For chromium(II) as the reducing agent, a sequence of 1-equiv steps has been proposed[9]

$$Cr(VI) + Cr^{2+} \longrightarrow Cr(V) + Cr^{3+} \tag{4}$$

$$Cr(V) + Cr^{2+} \longrightarrow Cr(IV) + Cr^{3+} \tag{5}$$

$$Cr(IV) + Cr^{2+} \longrightarrow Cr_2(OH)_2^{4+} \tag{6}$$

The mechanistic scheme for chromium(II)[9] (eq 4–6) is entirely analogous to that for other 1-equiv reducing agents[3–5] (eq 1–3) with the exception of the last step. When chromium(IV) reacts with a reducing agent such as iron(II), vanadium(IV), or neptunium(V) the hexaaquochromium(III) ion[10] is formed.[3–5] However, when chromium(IV) reacts with chromium(II), a binuclear species is produced.[9,11] Equations 4–6 account

nicely for the observed[9] stoichiometry of the chromium(II)–chromium(VI) reaction

$$3Cr^{2+} + Cr(VI) \longrightarrow 2Cr^{3+} + Cr_2(OH)_2^{4-} \tag{7}$$
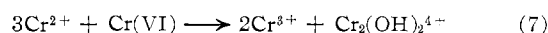
Furthermore, the mechanism is reasonable and consistent with the known chemistry of chromium in the oxidation states 2–6.

We have carried out a direct test of the proposed mechanism (eq 4–6) by labeling the chromium(VI) and examining the distribution of the labeled chromium between the products Cr^{3+} and $Cr_2(OH)_2^{4+}$. A meaningful tracer study can be carried out in this system because the chromium(II)–chromium(III)[12] and chromium(III)–chromium(VI)[13] exchange reactions are slow.

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.[14] The total chromium content of the solution was measured spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.[15]

The preparation of chromium(VI) solutions containing the radioactive isotope Cr^{51} was accomplished in the following manner. Chromium metal (99.15% Cr, 0.004% Fe, 0.02% C, 0.023% S, 0.55% O, 0.030% H, 0.001% Na) was sealed in polyethylene tubing and irradiated in the nuclear reactor of The Pennsylvania State University. After irradiation the chromium metal was dissolved in 2 M hydrochloric acid. Conversion of the resulting chromium(III) to CrO_3 (as well as quantitative removal of chloride ion) was achieved by adding concentrated perchloric acid and fuming. Inactive potassium dichromate was added to reduce the radioactivity to a convenient level, and appropriate dilutions were made. The chromium(VI) content of the resulting solution was measured spectrophotometrically[15] before and

(1) (a) This work was supported in part by the National Science Foundation, Grant GP-2001; (b) abstracted in part from the B.S. thesis of L. S. Hegedus, The Pennsylvania State University, June 1965; (c) Fellow of the Alfred P. Sloan Foundation.

(2) For a review of the early work see F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1948).

(3) Reaction with iron(II): J. H. Espenson and E. L. King, *J. Am. Chem. Soc.*, **85**, 3328 (1963).

(4) Reaction with vanadium(IV): J. H. Espenson, *ibid.*, **86**, 5101 (1964).

(5) Reaction with neptunium(V): J. C. Sullivan, *ibid.*, **87**, 1495 (1965).

(6) Reaction with arsenic(III): J. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

(7) Reaction with sulfur(IV): G. P. Haight, Jr., E. Perchonock, F. Emmenegger, and G. Gordon, *J. Am. Chem. Soc.*, **87**, 3835 (1965).

(8) J. Y. P. Tong and E. L. King, *ibid.*, **82**, 3805 (1960).

(9) M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).

(10) For simplicity, coordinated water will not be shown explicitly. Thus, Cr^{3+} represents the hexaaquochromium(III) ion.

(11) Throughout this paper the polymeric species formed in the chromium(II)–chromium(VI) reaction is *assumed* to have the structure $Cr_2(OH)_2^{4+}$. This structure has been demonstrated for the dimer produced in the chromium(II)–oxygen reaction and in the first step of the hydrolytic polymerization of Cr^{3+}: R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964). However, P. Gütlich and G. Harbottle (private communication) indicate that the chromium(II)–oxygen and chromium(II)–chromium(VI) reactions produce, in addition to the dimer (presumably $Cr_2(OH)_2^{4+}$), small amounts of a "higher polymer."

(12) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(13) C. Altman and E. L. King, *ibid.*, **83**, 2825 (1961).

(14) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952, p 579.

(15) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

after oxidation with alkaline hydrogen peroxide. The excellent agreement between these measurements (better than 1%) showed the absence of any chromium(III) species in the radioactive chromium(VI) solutions.

Solutions containing radioactive hexaaquochromium(III) were obtained by reducing the radioactive chromium(VI) solutions with excess hydrogen peroxide in 1 M perchloric acid.[16] The excess hydrogen peroxide was destroyed by boiling the solution in the presence of activated charcoal.

Separation of Chromium(III) Species.—The separation of Cr^{3+} from $Cr_2(OH)_2^{4+}$ was accomplished by ion exchange with Dowex 50-X8 (50–100 mesh, H^+ form).[9] Hexaaquochromium-(III) was eluted with 2 M perchloric acid. The binuclear species $Cr_2(OH)_2^{4+}$ was removed from the resin by treatment with sodium hydroxide and hydrogen peroxide, a procedure that converts $Cr_2(OH)_2^{4+}$ into CrO_4^{2-}.

Experimental Procedure.—Reaction vessels were serum bottles covered with self-sealing rubber caps and containing Teflon-covered stirring bars. Solutions were added to the serum bottles by means of hypodermic syringes with steel needles under rapid stirring. This procedure was found satisfactory for the relatively high concentrations (>0.01 M) used in the present work. After completion of the reaction, Cr^{3+} and $Cr_2(OH)_2^{4+}$ were separated as described above, and the chromium content of the Cr^{3+} fraction was determined. For the tracer studies, in addition to the chromium analyses, 3-ml aliquots of the Cr^{3+} and $Cr_2(OH)_2^{4+}$ fractions and of the product mixture (prior to ion-exchange separation) were counted with a Hewlitt sodium iodide scintillation counter.

Results

The results of the stoichiometric experiments for the chromium(VI)–chromium(II) reaction are summarized in Table I. Visual observation indicated that, at the concentrations used, the reaction appears to be complete within the time of mixing, and, therefore, changing the order of mixing appreciably changes the concentrations of the reactants. As seen from the values listed in column 3 of Table I, R, the ratio of Cr^{3+} to $Cr_2(OH)_2^{4+}$ produced in the reaction, is close to the value 2.0 predicted on the basis of eq 7 and appears to be independent of the order of mixing and of acidity in the range 0.010–1.0 M perchloric acid.

TABLE I

STOICHIOMETRY OF THE CHROMIUM(II)–CHROMIUM(VI) REACTION
(25°, [Cr(VI)] = 0.0122 M,[a] [Cr(II)] = 0.0366 M[a])

$[H^+]$, M[b]	Order of mixing	R[c]	No. of expt
0.010	d	1.9 ± 0.2	2
0.10	d	1.96	1
1.0	d	2.2 ± 0.2	5
0.010	e	1.8 ± 0.2	4
0.10	e	1.90	1
1.0	e	1.9 ± 0.2	6

[a] Initial concentration calculated assuming that reaction did not occur. [b] Final concentration calculated from added $[H^+]$ and $[H^+]$ consumed in the reaction. [c] Ratio $[Cr^{3+}]/[Cr_2(OH)_2^{4+}]$ produced in the reaction. [d] Chromium(II) added to chromium(VI). [e] Chromium(VI) added to chromium(II).

The results of the tracer experiments are summarized in Table II. In all of these experiments the radioactivity was originally present in the chromium(VI) reactant. After reaction the radioactivity was found to be present in both the Cr^{3+} and $Cr_2(OH)_2^{4+}$ products.

(16) Separate experiments[1b] showed that polymeric species are not produced under these conditions.

As seen from the values listed in column 4 of Table II, approximately 10% of the Cr^{3+} produced in the reaction originates in the chromium(VI) reactant, while the remaining 90% originates in the chromium(II) reactant. For the $Cr_2(OH)_2^{4+}$ product, about 40 and 60% of the chromium originate in the chromium(VI) and chromium(II), respectively.[17]

TABLE II

TRACER STUDY OF THE CHROMIUM(II)–CHROMIUM(VI) REACTION
(25°, [Cr(VI)] = 0.0111 M,[a] [Cr(II)] = 0.0333 M[a])

$[H^+]$, M[b]	Order of mixing	R[c]	% Cr* as Cr^{3+}[d]	% Cr* as $Cr_2(OH)_2^{4+}$[e]
0.010	f	1.85	9.6	40.3
1.0	f	1.84, 1.87	10.2, 8.3	39.8, 37.8
0.010	g	2.12	10.2	36.8
1.0	g	2.12	10.5	41.1

[a] Initial concentration calculated assuming that rection did not occur. [b] Final concentration calculated from added $[H^+]$ and $[H^+]$ consumed in the reaction. [c] Ratio $[Cr^{3+}]/[Cr_2(OH)_2^{4+}]$ produced in the reaction. [d] Per cent of the chromium in the Cr^{3+} product that originated in the chromium(VI). Value expected on the basis of eq 4–6 is zero. [e] Per cent of the chromium in the $Cr_2(OH)_2^{4+}$ product that originated in the chromium(VI). Value expected on the basis of eq 4–6 is 50. [f] Chromium(VI) added to chromium(II). [g] Chromium(II) added to chromium(VI).

Several blank experiments, in which nonradioactive chromium(VI) was reduced by nonradioactive chromium(II) in the presence of radioactive Cr^{3+}, were performed to test for any exchange between Cr^{3+} and the various chromium species present or generated during the chromium(II)–chromium(VI) reaction. The procedure followed was that described for the tracer experiments, except that an amount of radioactive Cr^{3+} equal to ~25% of the chromium(II) and chromium-(VI) used was added before reaction. The perchloric acid concentration was 1.0 M and the order of mixing of reactants was changed. After ion-exchange separation it was found that no radioactive chromium had been incorporated in the $Cr_2(OH)_2^{4+}$ fraction, showing the absence of exchange between Cr^{3+} and other chromium species.[18] These results further indicate that ion-exchange separations of Cr^{3+} from $Cr_2(OH)_2^{4+}$ were complete, since any retention of Cr^{3+} on the resin would have resulted in some radioactivity in the $Cr_2(OH)_2^{4+}$ fraction.[19]

Discussion

Although the observed stoichiometry of the chromium(II)–chromium(VI) reaction conforms reasonably well to the mechanism represented by eq 4–6, this

(17) The results of the tracer studies can be expressed in various manners. For example, of the radioactive chromium originally present as chromium-(VI), about 20% appears in the Cr^{3+} fraction, while about 80% appears in the $Cr_2(OH)_2^{4+}$ fraction. Alternatively, since 25% (on an atom basis) of the total chromium produced originates in the chromium(VI), the distribution is about 5 and 20% for the Cr^{3+} and $Cr_2(OH)_2^{4+}$ fractions, respectively.

(18) Substantially the same results have been obtained by P. Gütlich and G. Harbottle, *Radiochim. Acta*, **5**, 70 (1966).

(19) However, the separation of $Cr_2(OH)_2^{4+}$ from the resin was not always complete. Note in Table II that the sum of the values in columns 4 and 5 is in some instances less than the value 50% predicted for total recovery.

mechanism is, in part, in variance with the results of the tracer studies. According to eq 4–6, all of the Cr^{3+} product originates in the chromium(II) reactant, while the $Cr_2(OH)_2^{4+}$ produced derives one atom each from chromium(II) and chromium(VI). The tracer studies show that, although this prediction is fulfilled to a large extent, a small ($\sim10\%$) but significant portion of the Cr^{3+} product originates in the chromium(VI). The blank experiments mentioned above show that the radioactivity found in the Cr^{3+} fraction is not the result of exchange between Cr^{3+} and any other chromium species present or formed during the reaction. Therefore, it must be concluded that at some stage in the reaction chromium(VI) or a chromium species derived from chromium(VI) is the precursor of a portion of the Cr^{3+} produced. Since a 3-equiv reduction of chromium(VI) would seem unlikely, we will restrict our attention to the oxidation states 5 and 4 as possible precursors of the Cr^{3+} produced. The following 1-equiv reductions of chromium(IV), previously used to account for some of the features of the chromium(III)–chromium(VI) exchange,[13] could conceivably produce Cr^{3+}.

$$Cr(V) + {}^*Cr(IV) \longrightarrow Cr(VI) + {}^*Cr^{3+} \quad (8)[20]$$

$$Cr(IV) + Cr(IV) \longrightarrow Cr(V) + Cr^{3+} \quad (9)$$
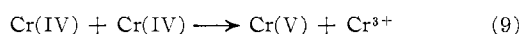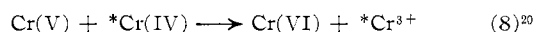
However, since the occurrence of reactions 8 or 9 prevents the chromium(IV) from forming $Cr_2(OH)_2^{4+}$, a mechanism which includes reactions 8 or 9 in addition to reactions 4–6 would result in a ratio $[Cr^{3+}]/[Cr_2(OH)_2^{4+}]$ larger than 2.[21] Furthermore, since reactions 8 and 9 involve intermediates at steady-state concentrations, it does not appear reasonable to suppose that chromium(V) (eq 8) or chromium(IV) (eq 9) can compete effectively with chromium(II) (eq 6), especially when these intermediates are generated in a system containing an appreciable concentration of chromium(II) (chromium(VI) added to chromium(II)). On these grounds, we are inclined to disregard reactions 8 or 9 as possible sources of radioactive Cr^{3+}.

Turning to chromium(V) as the possible precursor of Cr^{3+}, it must be realized that a 2-equiv reduction is necessary, and therefore possible reactions are

$$^*Cr(V) + Cr(IV) \longrightarrow {}^*Cr^{3+} + Cr(VI) \quad (10)[20]$$

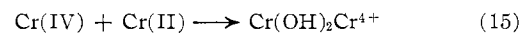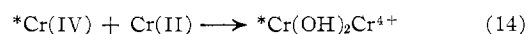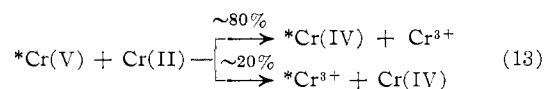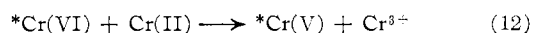$$^*Cr(V) + Cr(II) \longrightarrow {}^*Cr^{3+} + Cr(IV) \quad (11)[20]$$
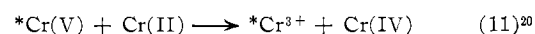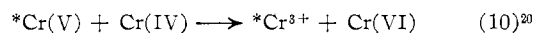
It is noteworthy that eq 10 and 11 are identical with eq 8 and 5, respectively, in terms of reactants and products, but that they differ in the number of equivalents transferred. Equations 10 and 11 represent a 2-equiv

(20) The asterisks in eq 8, 10, and 11 do not represent radioactive species. They are simply used as a label to identify the origin of Cr^{3+} produced.

(21) Although when chromium(II) is added to chromium(VI) in 1.0 M perchloric acid the value of R appears to be somewhat larger than 2, a value of about 3 would be necessary to account for the tracer results on the basis of eq 4–6 and eq 8 or 9.

change, while eq 8 and 5 involve a 1-equiv change. The objections raised above to eq 8 and 9 also apply to eq 10, which may therefore be ruled out. Equation 11, on the other hand, appears to provide the simplest explanation for the appearance of some radioactivity in the Cr^{3+} fraction. When chromium(II) and chromium(V) react, a 1-equiv change yields a Cr^{3+} derived from chromium(II) (eq 5), while a 2-equiv change yields a Cr^{3+} derived from chromium(V) (eq 11). The thermodynamics of the reaction is, of course, independent of whether a 1- or 2-equiv change occurs, and on kinetic grounds it is perhaps not unexpected that the 1-equiv change is favored over the two-electron change by the factor of about 4 required by the tracer studies.

The suggested mechanism, identical with that proposed by Ardon and Plane,[9] except for a small contribution of the 2-equiv change in the reaction between chromium(V) and chromium(II), can therefore be represented as[22]

$$^*Cr(VI) + Cr(II) \longrightarrow {}^*Cr(V) + Cr^{3+} \quad (12)$$

$$^*Cr(V) + Cr(II) \xrightarrow{\begin{subarray}{l}\sim80\%\\ \\ \sim20\%\end{subarray}} \begin{array}{l} {}^*Cr(IV) + Cr^{3+} \\ {}^*Cr^{3+} + Cr(IV)\end{array} \quad (13)$$

$$^*Cr(IV) + Cr(II) \longrightarrow {}^*Cr(OH)_2Cr^{4+} \quad (14)$$

$$Cr(IV) + Cr(II) \longrightarrow Cr(OH)_2Cr^{4+} \quad (15)$$

Equation 12 differs from the analogous reactions of iron(II), vanadium(IV), and neptunium(V) in that the reverse of eq 12 is an unimportant reaction of chromium(V) relative to its subsequent reduction by chromium(II). This is demonstrated by the lack of incorporation of radioactivity in $Cr_2(OH)_2^{4+}$ when the chromium(II)–chromium(VI) reaction is carried out in the presence of radioactive Cr^{3+}. (The reverse of reaction 12 followed by reactions 13–15 would have produced radioactive $Cr_2(OH)_2^{4+}$.) It is noteworthy that the critical step in determining the distribution of radioactivity between the products is related to the reduction of chromium(V), a step which presumably involves a major change in the chromium coordination sphere.[3,8,18]

Finally, it must be noted that more complicated mechanisms involving binuclear intermediates could be devised to account for the stoichiometric and tracer results.[1b] However, in view of the limited experimental evidence available, it does not seem profitable to discuss the relative merits of such other mechanisms.

(22) In eq 12–15 the asterisks designate radioactive species.