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Chloratopentaaquochromium(III) Ion. Synthesis, Aquation, and Reduction by Chromium(II)

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Received October 15, 1974 AIC40717+

The chloratopentaaquochromium(III) ion is produced in good yield via the chromium(VI) oxidation of chlorous acid and can be isolated in solution by ion-exchange techniques. The activation parameters for the aquation of the complex ion are $\Delta H^* = 21.8 \pm 0.1$ kcal/mol and $\Delta S^* = -5.1 \pm 0.1$ cal mol^{-1} deg^{-1}. These values are nearly identical with those previously reported for the nitratopentaaquochromium(III) ion. The stoichiometry of the reduction of chloratochromium(III) by chromium(II) in 0.55 *M* $HClO_4$ at 25° is $6Cr^{2+} + (H_2O)_5Cr(ClO_3)^{2+} = (H_2O)_5CrCl^{2+} + 1.41(H_2O)_6Cr^{3+} + 2.30Cr(OH)_2Cr^{4+}$. The empirical rate law for this reaction is $-d[(H_2O)_5Cr(ClO_3)^{2+}]/dt = k[Cr^{2+}][(H_2O)_5Cr(ClO_3)^{2+}]$ over the $[H^+]$ range 0.32–1.79 *M*. Values of $\Delta H^* = 8.1 \pm 0.6$ kcal/mol and $\Delta S^* = -31 \pm 2$ cal mol^{-1} deg^{-1} were determined. Chromium-51 tracer experiments indicate that the chromium(III) originally in the complex ion is predominantly found in the higher charged chromium(III) product. A partial reaction scheme is proposed for the reduction of the chlorato-chromium(III) ion by chromium(II), based on the present results and those obtained earlier in the Cr(II)–Cl(V) reaction.

Introduction

The elucidation of reaction schemes for multiequivalent oxidation–reduction reactions that proceed in many steps is a very challenging problem.[1] Kinetic data provide only limited information about the rate-determining step, which frequently is only the first step in the overall reaction.[2] Occasionally, variable product distributions and tracer studies provide additional insight. The chromous reduction of chlorate ion is an example of a system where a variety of experimental approaches were viable.[3,4] The basic conclusion was that oxychlorine complexes of chromium(III) were produced as intermediates which were unstable to rapid further attack by chromium(II). An attractive test of this hypothesis would involve the preparation of chromium(III)–oxychlorine complex ions and the investigation of their reduction by chromium(II). Unfortunately, in our hands the synthesis of any of these complexes has been difficult. Recently, we have succeeded in isolating solutions of the chloratopentaaquochromium(III) ion. This communication presents stoichiometric, kinetic, and chromium-51 tracer results for the chromium(II) reduction of this complex ion, in addition to its synthesis and aquation kinetics.

Experimental Section

Preparation of the Chloratopentaaquochromium(III) Ion. Direct synthetic methods, similar to those used in the preparation of nitratochromium(III) ion,[5,6] were unsuccessful for the chlorato complex due to decomposition of chlorate ion and oxidation of chromium(III) to chromium(VI). However, the reaction of Cr(VI) with excess Cl(III) in acidic solution produces the chlorato complex in good yield (ca. 80% based on the initial Cr(VI)). In a typical preparation, 1.2 g of $NaClO_2$ (13 mmol) dissolved in 10 ml of cold water was added with stirring to a solution containing 0.3 g of $Na_2Cr_2O_7 \cdot 2H_2O$ (2 mmol of Cr(VI)) in 10 ml of cold 4 *M* $HClO_4$.[7] The reaction is rapid, much more so than the disproportionation of chlorous acid under these conditions.[8] The reaction solution was placed on 40 ml of Dowex 50WX8 resin in a jacketed column maintained at 2°. ClO_2, Cl^-, $HClO_2$, ClO_3^-, and any unreacted $HCrO_4^-$ were rinsed with 0.05 *M* $HClO_4$, and the dark green chlorato complex was separated from the $Cr(H_2O)_6^{3+}$ with 2 *M* $HClO_4$. The center portion of the green band typically yielded 40 ml of 0.025 *M* chlorato complex in 1.6 *M* $HClO_4$ and 0.4 *M* $NaClO_4$. The cold eluent was either used immediately or stored in Dry Ice for up to 1 week without detectable decomposition. The total chromium content of the solution was determined as chromate ion in alkaline solution at 3750 Å.[9] The "oxidizing power" toward acidic iron(II) was determined by allowing an aliquot of the eluent to react with a known excess of ferrous ammonium sulfate in a stoppered container and subsequent titration of the remaining iron(II) with standardized permanganate. Iron(II) slowly, but quantitatively, reduces chlorate to chloride ion; the reaction with the green eluent is even slower. A value of 5.94 ± 0.06 was obtained for the ratio *R* = (millimoles of Fe(II) consumed)/(millimoles of Cr). This compares well to a calculated value of 6.00 for $(H_2O)_5Cr(ClO_3)^{2+}$. The experimental value is the average of 42 independent preparations and assays over the course of this study. The same value was obtained if a portion of the chlorato complex was allowed to aquate completely, and the chromium(III) aquation product was identified as $Cr(H_2O)_6^{3+}$, exclusively. *R* was invariant in the following alternative experiments: (a) collection of the entire dark green band, (b) an additional ion-exchange separation (at 2°) of a partially aquated complex solution, and (c) a 24-hr elution with 0.5 *M* $HClO_4$ on a long column at 0°. Experiment c led to a modified procedure in which solutions of the complex were isolated free of sodium perchlorate; the band was slowly developed with 0.5 *M* $HClO_4$ on a long column before elution with 2 *M* $HClO_4$. The slight defect of *R* from a value of 6.00 may be real and due to trace contamination by another oxychlorine–chromium(III) complex. Spectral scans of the chlorato complex solutions always indicated the growth of chlorine dioxide (<1% of the complex concentration) over several hours at room temperature.

Kinetics of the Aquation of Chloratopentaaquochromium(III). Solutions of the chlorato complex were prepared as described above. It was not until later in this study that solutions free of sodium perchlorate were obtained; consequently, most of the experiments utilized sodium perchlorate to maintain a constant ionic strength. Mixed $HClO_4$–$NaClO_4$ solutions were used in the elution procedure to obtain samples of the chlorato complex at the desired $[H^+]$. The aquation experiments were initiated by addition of a freshly prepared complex solution at 0° to a darkened, jacketed reaction vessel maintained at the desired temperature (usually $23.6 \pm 0.1°$) by rapidly circulating water from a constant-temperature bath. Approximately 2 min was required for thermal equilibration; this time is very short relative to the aquation rate. At suitable times aliquots were removed and placed on short columns of Dowex 50WX8 resin at 0°, and the free ClO_3^- was rapidly rinsed from hexaaquochromium(III) and chloratochromium(III) with ice-cold 0.01 *M* $HClO_4$. Times were recorded immediately after addition of the aliquot to the cold column; the elution procedure required ca. 15 min. The free ClO_3^- was determined by the titrimetric procedure described above. The $[ClO_3^-]$–time data (8–10 points per experiment) were analyzed by a least-squares adjustment to the integrated form of the rate expression

$$d[ClO_3^-]/dt = -d[(H_2O)_5Cr(ClO_3)^{2+}]dt = k'[(H_2O)_5Cr(ClO_3)^{2+}] \qquad (1)$$

Stoichiometry of the Chromium(II) Reduction of Chloratopentaaquochromium(III), Chlorate Ion, and Chlorine Dioxide. Chromium(II) perchlorate solutions were prepared by reduction of hexaaquochromium(III) perchlorate with lightly amalgamated zinc in an inert atmosphere. The preparation of chlorine dioxide solutions has been described previously.[10] The mixing of reactants was accomplished in 3 msec with a Durrum stopped-flow instrument. In the chlorine dioxide experiments assays were made by similar mixing of the ClO_2 with a known excess of iron(II), followed by back-titration with standard permanganate. The chloropentaaquochromium(III) and hexaaquochromium(III) were separated from the polynuclear chromium(III) product by ion-exchange procedures after air oxidation of any excess chromium(II) in the spent reaction mixture.[3] In experiments with stoichiometric excesses of chlorate ion, the final oxidant concentration was determined by the titrimetric procedure described above.

Kinetic Study of the Chloratopentaaquochromium(III)–Chromium(II) Reaction. The kinetic experiments were monitored spectrophotometrically with a Zeiss PMQ-II instrument equipped with a thermostated (±0.1°) sample compartment. A magnetic stirring device ensured rapid mixing ($\leq$1 sec) of the reactants. Available oxygen was minimized by continuously flushing the entire sample compartment with tank CO_2 and the reaction cuvette with CO_2 that had passed through a chromium(II) bubbler. Blank experiments indicated that chromium(II) (0.05–0.10 *M*) could be maintained in the cuvette for ca. 10 min without detectable air oxidation, a time period sufficient for completion of the chloratochromium(III)–chromium(II) reaction under the experimental conditions employed. Both the disappearance of chromium(II) and the appearance of the chromium(III) products were monitored (at 7190 and 4800 Å, respectively). A number of small corrections were applied to the absorbance values obtained during the reaction. The absorbance due to the small amount of dimeric chromium(III) introduced with the chromium(II) was determined in blank experiments. The 7190-Å data were corrected for absorbance due to chloratochromium(III) (ϵ 0.40 M^{-1} cm^{-1}) and the chromium(III) products (ϵ 1.10–1.22 M^{-1} cm^{-1}, depending on the hydrogen ion concentration). ϵ 4.75 M^{-1} cm^{-1} was determined for chromium(II) at this wavelength. The 4800-Å data were corrected for chloratochromium(III) absorbance (ϵ 5.15 M^{-1} cm^{-1}); chromium(II) is transparent. In each experiment the chromium(II) concentration at infinite time was determined spectrally at 7190 Å by injection of a known excess of hexaaquoiron(III) (ϵ 0.105 M^{-1} cm^{-1} for iron(III) and 0.219 M^{-1} cm^{-1} for iron(II)), and $[Cr(II)]_0$ was calculated by summing this result with the known initial normality of chloratochromium(III). This procedure was necessary since rather large but only approximately known volumes (0.9–1.9 ml) of chromium(II) were injected. An important assumption was made in the analysis of the kinetic data, namely, that *the distribution of the various chromium(III) products of the reaction is constant throughout an experiment.* The kinetic results support this assumption (*vide infra*). Also, the same supposition was successfully made in the closely related chlorine(V)–chromium(II) system.[4] The corrected absorbance–time data (20–30 points per experiment) were analyzed by a least-squares adjustment to the integrated form of the rate expression

$$-d[(H_2O)_5Cr(ClO_3)^{2+}]/dt = -(1/6)d[Cr^{2+}]/dt = k[Cr^{2+}][(H_2O)_5Cr(ClO_3)^{2+}] \qquad (2)$$

Chromium-51 Tracer Study of the Chloratopentaaquochromium(III)–Chromium(II) Reaction. The ^{51}Cr was obtained from the Amersham/Searle Corp. as a chromium(III) chloride solution in hydrochloric acid. A γ-ray spectrum established the radiochemical purity of the tracer. The activity was lowered by dilution with nonradioactive chromium(III), and chromium trioxide was separated after fuming in perchloric acid.[11] Tagged chloratochromium(III) solutions were prepared via the *Cr(VI)–Cl(III) reaction as described above. $(H_2O)_6{}^*Cr^{3+}$ solutions were obtained by reduction of $^*CrO_3$ with H_2O_2 and ion-exchange separation from the polynuclear chromium(III) by-product. $^*Cr^{2+}$ solutions were prepared by reduction of $(H_2O)_6{}^*Cr^{3+}$ over a granulated zinc–mercury pool in an inert atmosphere. The reactants were mixed rapidly at 0° in the absence of oxygen. After complete reaction any excess chromium(II) was air oxidized. The chlorochromium(III) (along with excess chloratochromium(III) in some experiments) and hexaaquochromium(III) products were separated and the solutions were concentrated. In some experiments the polynuclear chromium(III) product was removed from the resin by repeated treatment with hot basic peroxide solution and subsequent filtration. Chromium assays and scintillation counting were performed on all the fractions collected. Total recovery of the chromium was $\geq$98%; total recovery of the activity ranged from 96 to 104%.

Results and Discussion

Preparation and Aquation of Chloratopentaaquochromium(III). The yield of chloratochromium(III) was 81 ± 1% with a $[HClO_2]_0/[Cr(VI)]_0$ ratio of $\geq$6 in 2 *M* $HClO_4$ and was unaffected by the initial presence of ClO_2 at a concentration half that of the chromium(VI). The yield is appreciably lower with a reactant concentration ratio of 2.3; in this case approximately 36% of the chromium(VI) does not react. The rate of the Cr(VI)–Cl(III) reaction is considerably faster than the disproportionation of chlorous acid under the experimental conditions. For example, the half-life is <2 sec at 25° with $[Cr(VI)]_0$ = 0.18 *M*, $[HClO_2]_0$ = 0.080 *M*, and $[HClO_4]$ = 2.0 *M*. Under the same conditions, the half-life for the disproportionation of chlorous acid is ca. 18 min.[8] These observations provide the basis for the following tentative conclusions. (1) Intermediates produced in the disproportionation of chlorous acid, such as Cl_2O_2, are unimportant in the production of the chloratochromium(III) complex. (2) The two simplest mechanistic steps to form the complex are (a) an inner-sphere, 1-equiv oxidation of chlorine dioxide by chromium(IV) and (b) an inner-sphere, 2-equiv oxidation of chlorous acid by chromium(V). Step b seems more likely, since the initial presence of chlorine dioxide did not affect the yield of chloratochromium(III). The production of the chromium(V) intermediate could result from the reaction Cr(VI) + Cl(III) = Cr(V) + Cl(IV). Chromium(VI) and chlorine(IV) react very slowly, if at all, under the experimental conditions. It is interesting to note that we find no detectable nitratochromium(III) product in the chromium(VI) oxidation of nitrous acid.

Table I. First-Order Rate Constants for the Aquation of the Chloratopentaaquochromium(III) Ion[a]

$[HClO_4]$, *M*	$10^5k'$, sec^{-1}	$[HClO_4]$, *M*	$10^5k'$, sec^{-1}	$[HClO_4]$, *M*	$10^5k'$, sec^{-1}
1.54	4.35_4	0.211	5.01_0	2.06[d]	4.06_5
1.37	4.37_6	0.183	5.29_7	0.602[d]	4.07_4
0.771	4.56_3	1.65[b]	1.84_5	0.189[d]	4.13_3
0.448	4.75_2	1.60[c]	8.63_0		

[a] $[Complex]_0$ = (1.41–2.50) × 10^{-2} *M*; *T* = 23.55° and *I* = 2.0 *M* ($NaClO_4$), unless otherwise indicated. [b] At 17.0°. [c] At 29.0°. [d] Ionic strength at 2.0 *M* with $LiClO_4$.

The spectrum of chloratochromium(III) is very similar to that of hexaaquochromium(III) in the visible region but differs substantially in the ultraviolet region. Molar absorptivities (M^{-1} cm^{-1}) at 5° are 14.0 (maximum, 5870 Å), 17.6 (maximum, 4130 Å), 2.0 (2600 Å), and 33.9 (2300 Å). Nitratochromium(III) was concluded to be a monodentate complex;[6] we presume the same for chloratochromium(III).

The aquation kinetic results are summarized in Table I. The first-order behavior was obeyed for 3 half-lives, with standard deviations in k' of 0.6–2.0%. In $NaClO_4$ solutions a minor path inverse in hydrogen ion concentration is apparently operative: $k' = k_0 + k_1/[H^+]$, where k_0 = (4.29 ± 0.06) × 10^{-5} sec^{-1} and k_1 = (1.75 ± 0.20) × 10^{-6} M^{-1} sec^{-1} at 25°. Similar results are reported for the aquation of nitratopentaaquochromium(III) when $LiClO_4$ is used to maintain constant ionic strength.[5,6] In the present system, however, the aquation rate is essentially hydrogen ion independent in $LiClO_4$ solutions. There may be a "conjugate-base" path as is found in the nitrato,[5,6] chloro,[12] bromo,[13] iodo,[12] and thiocyanato[14] systems, but we are unable to detect it over the limited and rather high hydrogen ion concentration range employed. It is interesting to note that no contribution from pathways involving protonation of chloratochromium(III) is observed, as is anticipated from the lack of basicity of the chlorate ion in water.

Values of ΔH^* = 21.8 ± 0.1 kcal/mol and ΔS^* = −5.1 ± 0.1 cal mol^{-1} deg^{-1} were calculated from the temperature-dependence data. These values are almost identical with those obtained for the hydrogen ion independent path in the aquation of nitratochromium(III), where ΔH^* = 21.6 kcal/mol and ΔS^* = −5.1 ± 0.2 cal mol^{-1} deg^{-1}. This agreement of activation parameters suggests that the mode of bonding in chloratochromium(III) is through the chlorate oxygen, rather than

Table II. Stoichiometry of the Cr^{2+} Reduction of $(H_2O)_5Cr(ClO_3)^{2+}$, ClO_3^-, and ClO_2[a]

Oxidant	$[HClO_4]$, *M*	% $(H_2O)_5$-$CrCl^{2+}$	% $(H_2O)_6Cr^{3+}$
$(H_2O)_5Cr(ClO_3)^{2+}$	0.55	16.0 ± 0.1	23.5 ± 0.1
	2.6	16.4 ± 0.2	28.6 ± 0.1
ClO_3^-	0.55	17.2 ± 0.2	24.4 ± 0.6
	2.6	17.8 ± 0.4	34.4 ± 0.6
ClO_2	0.55	21.9 ± 1.6	18.4 ± 0.6
	2.6	22.2 ± 0.1	28.5 ± 0.6

[a] $T = 25°$, $[Cr(II)]_0 = 0.05$–0.10 *M*, and $[\text{oxidant}] = 0.006$–0.030 *M*. Reactions carried out with stopped-flow mixing. % product reported = (mmol of product)(100)/($n \times \Delta$ mmol of oxidant), where $n = 6$ for $(H_2O)_5Cr(ClO_3)^{2+}$ and ClO_3^-, and $n = 5$ for ClO_2. The remaining Cr(III) product is a higher charged species, presumably $Cr(OH)_2Cr^{4+}$.[16]

through the chlorine.[15] This result is probably anticipated, but it should be remembered that the synthesis involves a specific kinetic path in a redox reaction rather than an equilibration method. It is unfortunate that a structural determination has not been made, primarily as a result of our inability to prepare crystals of chloratochromium(III).

Stoichiometry of the Chromium(II) Reduction of Chloratopentaaquochromium(III). Stoichiometric results for the reduction of chloratochromium(III), chlorate ion, and chlorine dioxide with (usually) excess chromous ion are summarized in Table II. The chromium(II)–chlorine(V) data were redetermined at 25° with stopped-flow mixing for comparative purposes; the results agree fairly well with earlier values at 0° and with slower mixing (% $(H_2O)_5CrCl^{2+}$ = 15.0 and 15.6 and % $(H_2O)_6Cr^{3+}$ = 22.4 and 28.9 at 0.55 and 2.6 *M* $HClO_4$, respectively).[3] The chromium(II)–chlorine(IV) stoichiometry was redetermined for two additional reasons. The earlier work utilized reaction mixtures containing an appreciable chloride ion concentration and the results were not reproducible.[3] The gross stoichiometries in 0.55 *M* $HClO_4$ can be summarized as in eq 3–5.[16] All the reactions exhibit essentially quantitative

$$6Cr^{2+} + (H_2O)_5Cr(ClO_3)^{2+} = (H_2O)_5CrCl^{2+} + 1.41(H_2O)_6Cr^{3+} + 2.30Cr(OH)_2Cr^{4+} \tag{3}$$

$$6Cr^{2+} + ClO_3^- = (H_2O)_5CrCl^{2+} + 1.46(H_2O)_6Cr^{3+} + 1.77Cr(OH)_2Cr^{4+} \tag{4}$$

$$5Cr^{2+} + ClO_2 = (H_2O)_5CrCl^{2+} + 0.92(H_2O)_6Cr^{3+} + 1.54Cr(OH)_2Cr^{4+} \tag{5}$$

trapping of the oxidant chlorine as chloride ion in the coordination sphere of the chlorochromium(III) product. Reactions 3 and 4 yield very similar amounts of the monomeric products, but speculation on this result is premature since the fate of the chromium(III) in the chlorato complex in reaction 3 is not divulged by the stoichiometry data. The data in Table II are sufficient to preclude the reaction schemes

$$Cr^{2+} + (H_2O)_5Cr(ClO_3)^{2+} = Cr^{2+} + (H_2O)_6Cr^{3+} + ClO_3^- \tag{6}$$

followed by

$$6Cr^{2+} + ClO_3^- = \text{products}$$

$$Cr^{2+} + (H_2O)_5Cr(ClO_3)^{2+} = Cr(OH)_2Cr^{4+} + ClO_2 \tag{7a}$$

or

$$Cr^{2+} + (H_2O)_5Cr(ClO_3)^{2+} = 2(H_2O)_6Cr^{3+} + ClO_2 \tag{7b}$$

both followed by

$$5Cr^{2+} + ClO_2 = \text{products}$$

The expected amount of hexaaquochromium(III) for reaction 3 would be 2.46, 0.92, and 2.92 for eq 6, 7a, and 7b, respectively.

Table III. Kinetic Results for the Chloratopentaaquochromium(III)–Chromium(II) Reaction[a]

$10^2[Cr^{2+}]_0$, *M*	10^3[complex]$_0$, *M*	$[HClO_4]$, *M*	k,[b] M^{-1} sec^{-1}
6.31	7.83	1.79	0.405 ± 0.012
6.24	7.78	1.72	0.427
6.62	9.17	1.74	0.441 ± 0.017[c]
8.30	11.2	1.62	0.429 ± 0.006
6.09	7.83	0.762	0.461 ± 0.019[c]
6.38	7.83	0.737	0.506 ± 0.016
6.10	7.78	0.652	0.525 ± 0.004
6.06	7.78	0.339	0.524 ± 0.002
6.07	7.78	0.339	0.514 ± 0.004[c]
9.21	13.8	0.506	0.285 ± 0.001[d]
5.37	7.74	0.320	0.292 ± 0.001[d]
6.19	6.77	0.332	0.201 ± 0.006[e]
5.66	6.77	1.69	0.558 ± 0.004[f]
5.36	6.77	1.69	0.830 ± 0.030[g]

[a] $T = 2.0°$, $I = 2.1$ *M* ($LiClO_4$), and λ 4800 Å unless otherwise indicated. [b] Uncertainties are average deviations of duplicate experiments. [c] λ 7190 Å. [d] $I = 1.07$ *M*. [e] $I = 0.69$ *M*. [f] $T = 7.9°$. [g] $T = 14.5°$.

Kinetics of the Chloratopentaaquochromium(III)–Chromium(II) Reaction. A number of corrections were necessary in the analysis of the kinetic data, in addition to the assumption that the product distribution was constant throughout the reaction. Nevertheless, the fit to the integrated form of rate law 2 was acceptable, with standard deviations of 1–2% through 2 half-lives. Values of the second-order rate parameter k are summarized in Table III. Similar values of k were obtained by monitoring the disappearance of chromium(II) or the appearance of the chromium(III) products. There is apparently a minor path with an inverse hydrogen dependence, but the major reaction path is in accord with the net activation process

$$Cr^{2+} + (H_2O)_5Cr(ClO_3)^{2+} = [Cr \cdot ClO_3 \cdot Cr^{4+}]^* \tag{8}$$

where the composition (with the usual uncertainty in hydration) but not necessarily the structure of the activated complex is implied. Values of $\Delta H^* = 8.1 \pm 0.6$ kcal/mol and $\Delta S^* = -31 \pm 2$ cal mol^{-1} deg^{-1} were calculated from the temperature-dependence data.

The major activation process for the reduction of chlorate ion by chromous ion is

$$Cr^{2+} + ClO_3^- + H^+ = [Cr \cdot ClO_3 \cdot H^{2+}]^* \tag{9}$$

Values of $\Delta H^* = 11.2 \pm 0.1$ kcal/mol and $\Delta S^* = -17.0 \pm 0.4$ cal mol^{-1} deg^{-1} have been reported.[4] Formally, the activated complexes in (8) and (9) differ by the substitution of H^+ for Cr^{3+}. A similar difference occurs in the reduction of Cr(III)·Pu(V) by Pu(III)[17,18] and Cr(III)·Np(V) by Np(III)[19] relative to the "analogous" reduction of Pu(V) by Pu(III)[18,20] and of Np(V) by Np(III),[21] respectively. It was concluded that in these reactions chromium(III) is more effective than hydrogen ion in promoting reduction. However, this analysis was simplified by the probable bond breaking at the actinide–oxygen bond on reduction. In contrast, process 9 has been suggested to produce a chromium(III)–oxychlorine complex which is unstable to further rapid reduction by chromium(II). The stoichiometric and chromium-51 tracer results (vide infra) suggest that an intermediate is produced as a consequence of process 8 in which *two* chromium(III) bonds to the oxychlorine species are present. Thus, it is not clear whether bond breaking occurs in the first step of the reduction of either ClO_3^- or $(H_2O)_5Cr(ClO_3)^{2+}$ by chromous ion. Process 8 has a more favorable activation enthalpy but a less favorable activation entropy than process 9, a result that is not inconsistent with the above discussion.

There is a marked effect of ionic strength on k in the present system. The effect is more pronounced than was observed in the chromium(II)–chlorine(V) system and is not unexpected in view of the larger ΔZ^2 for the present reaction and the extended form of the Debye–Hückel equation.

Chromium-51 Tracer Results for the Chloratopentaaquo-

Table IV. Chromium-51 Tracer Results for the $(H_2O)_5Cr(ClO_3)^{2+}$–Cr^{2+} Reaction[a]

[Complex]$_0$, M	$[Cr^{2+}]_0$, M	Source of activity	% *Cr in $(H_2O)_5CrCl^{2+}$ [b]	% *Cr in $(H_2O)_6Cr^{3+}$ [b]	% *Cr in $Cr(OH)_2Cr^{4+}$ [b]
0.0257	0.102	Cr^{2+}	(13.2)	91.2 (26.1)	(60.7)
0.0256	0.0731	Cr^{2+}	(13.5)	89.0 (20.1)	77.8 (66.3)
0.0203	0.123	Cr^{2+}	92.8 (15.4)	90.0 (20.4)	75.3 (64.2)
0.0233	0.150	Cr^{2+}	94.4 (15.0)	95.9 (25.6)	(59.4)
0.0313	0.0868	Complex	(35.6)	6.9 (4.5)	23.6 (59.9)
0.0214	0.112	Complex	(2.3)	3.9 (5.0)	20.1 (92.8)
0.0186	0.167	Complex	0.2 (0.2)	2.1 (3.7)	12.5 (96.1)

[a] Conditions: 0° and 2 M $HClO_4$. [b] First entry: (100)(mmol of *Cr in fraction)/(mmol of Cr in fraction). Second entry (in parentheses): (100)(mmol of *Cr in fraction)/(Σ*Cr in all fractions).

chromium(III)–Chromium(II) Reaction. The results of chromium-51 tracer experiments are summarized in Table IV. The interpretation of these data is not obvious and is further complicated by the reaction

$$^*Cr^{2+} + CrCl^{2+} = Cr^{2+} + {}^*CrCl^{2+} \qquad (10)$$

The rate constant[22] for reaction 10 is ca. 8 M^{-1} sec^{-1} in 1 M $HClO_4$ at 0°, and thus this potential scrambling reaction must be considered. Possible scrambling via reaction 6 will be ignored on the basis of the stoichiometry data. The isotopic exchange reaction between chromium(II) and hexaaquochromium(III) is much too slow to be of significance.[23]

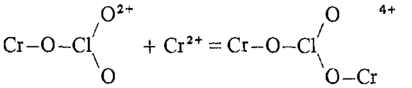
When the activity is introduced with the chromium(II), nearly all the chlorochromium(III) and hexaaquochromium(III) products derive their chromium from the reductant and *not* from the chromium(III) originally bound to the chlorate ion. The isotopic dilution occurs primarily in the higher charged chromium(III) product. Potential problems from reaction 10 are probably not important for the following reasons. First, the results were insensitive to whether excess complex or chromous ion were present. Second, were the initial chlorochromium(III) product derived from the unenriched chromium originally in the complex, equilibrium considerations would not allow >90% final enrichment in this product. This is especially true in the third experiment where nearly stoichiometric amounts of reactants were initially present. A third consideration is that the spectrum and aquation kinetic results for the chlorato complex suggest that the chlorate is oxygen bonded to the chromium(III). If this is correct, it is very difficult to visualize the chromium(III) becoming bonded to the chlorine during the reduction of the complex by chromium(II).

The same conclusions hold when the data for reactions in which the tracer was introduced in the complex are scrutinized. Nearly all the activity appears in the "dimer" product, and near background levels are observed in the monomeric chromium(III) fractions. The last experiment in which no complex remained after reaction (and therefore was not eluted along with the chlorochromium(III)) is particularly persuasive.

The agreement of the results irrespective of the source of the activity is satisfying when the considerable experimental manipulations are considered. A blank experiment in which unenriched chromium(II) and chloratochromium(III) reacted in the presence of tagged hexaaquochromium(III) showed no final activity in either the chlorochromium(III) or "dimeric" chromium(III) products. Finally, the percent activity in the monomeric products when the chromium(II) is tagged agrees rather well with the stoichiometry results presented in Table II.

Concluding Remarks

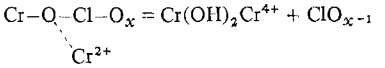
A consideration of all the data allows some meaningful speculation as to the reaction paths operative in the reduction of chloratochromium(III) by chromium(II). The initial chromium(II) attack probably occurs in an inner-sphere manner, presumably at a chlorate oxygen *not* bonded to chromium(III)



$$Cr{-}O{-}Cl\begin{matrix}\diagup O^{2+}\\ \diagdown O\end{matrix} + Cr^{2+} = Cr{-}O{-}Cl\begin{matrix}\diagup O\\ \diagdown O{-}Cr\end{matrix}^{4+} \qquad (11)$$

An outer-sphere attack should result in reactions 6 or 7b, and these are inconsistent with the stoichiometry results.[24] An inner-sphere attack at the bonded oxygen should require a scheme similar to eq 7a.

The subsequent fate of the intermediate proposed in reaction 11 is unknown except for two considerations. First, there must be an efficient inner-sphere, 1-equiv attack at some point at the chlorine, since essentially quantitative yields of chlorochromium(III) are observed. Previous data suggest that this attack could occur at almost any stage.[3] Second, the ultimate incorporation of the chromium(III) originally present in the chlorato complex into the "dimeric" product is required by the chromium-51 tracer experiments. An attractive possibility is that at some state in the reduction reaction 12 occurs. This



$$\underset{\diagdown Cr^{2+}}{Cr{-}O{-}Cl{-}O_x} = Cr(OH)_2Cr^{4+} + ClO_{x-1} \qquad (12)$$

type of reaction eliminates the awkward necessity for a 2-equiv oxidation of chromium(II) to form chromium(IV) [followed by Cr(II) + Cr(IV) = dimer],[25] coupled with a chromium(II)–complex chromium(III) exchange reaction at some stage. Reaction 12 may be generally applicable to oxy anion oxidations of chromous ion in which a "dimeric" product results, provided a prior formation of a chromium(III)-bonded intermediate occurs. The present system provides an ideal test case in that the source of the chromium(III) produced is distinguishable through tracer studies.

The tracer results allow analysis of the stoichiometry summarized in reactions 3 and 4. Since the complex chromium(III) is not appreciably incorporated into the monomeric products, the observed stoichiometries are remarkably similar. The above discussion requires different intermediates to be produced in the two reactions, and it is surprising but perhaps fortuitous that analogous product distributions result.

It is not known whether chromium–oxygen or chlorine–oxygen bond breaking is dominant in the aquation reaction. Further, it has been suggested that coordinated nitrate ion labilizes the other ligands in the coordination sphere of chromium(III).[26] A similar feature may occur in chloratochromium(III). We are currently testing these points by means of oxygen-18 tracer experiments.

Registry No. $(H_2O)_5Cr(ClO_3)^{2+}$, 54566-83-5; ClO_3^-, 14866-68-3; ClO_2, 10049-04-4; Cr^{2+}, 22541-79-3; $HClO_2$, 13898-47-0; $Cr_2O_7^{2-}$, 13907-47-6.

References and Notes

(1) Many examples can be found in the following references, to cite a few: (a) D. Benson, "Mechanisms of Inorganic Reactions in Solution", McGraw-Hill, London, 1968; (b) J. O. Edwards, "Inorganic Reaction Mechanisms", W. A. Benjamin, New York, N.Y., 1965; (c) T. A. Turney, "Oxidation Mechanisms", Butterworths, London, 1965; (d) J. Halpern, *Q. Rev. Chem. Soc.*, **15**, 207 (1961); (e) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry", Prentice-Hall, New York, N.Y., 1946.

(2) But not always—for example, see R. M. Noyes, R. J. Field, and R. C. Thompson, *J. Am. Chem. Soc.*, **93**, 7315 (1971).

(3) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557 (1966).

(4) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 562 (1966).

(5) T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

(6) M. Ardon and N. Sutin, *Inorg. Chem.*, **6**, 2268 (1967).

(7) Under these conditions the Cr(VI) exists in several forms, primarily H_2CrO_4, $HCrO_4^-$, and $Cr_2O_7^{2-}$. See (a) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953); (b) J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964).