ment has been employed to explain the abnormally large shielding of lithium in fluorenyllithium,[1] where the geometry of the coordination places the lithium atom in the region strongly shielded by ring currents. However, influence of $\sigma_E$ and $\sigma_w$ must also be important in this ionic system where the reaction field should be strong near the nucleus. It is interesting to note in this regard that the observed shifts bear a linear relationship to Kosower's solvent polarity parameter ($Z$) for the solvents acetonitrile, dimethyl sulfoxide, dimethylformamide, acetone, and pyridine[34] (the only nonhydroxylic solvents for which both types of data are available).

**Effect of Water on Li$^+$ Shifts in Acetonitrile.**—The data of Table II demonstrate that the chemical shift of lithium ion in acetonitrile is most sensitive to changes in concentration of added water when the mole ratio $n_{H_2O}/n_{Li^+}$ varies between 0.1 and about 20. Since the mole ratio $n_{CH_3CN}/n_{Li^+}$ is 220 in each of these solutions, some preference of Li$^+$ for water compared to acetonitrile in the solvation sphere is indicated. An alternative interpretation consistent with an overwhelming preference for water in the inner solvation sphere would attribute the continuing change in shift at higher water concentrations to the gradual change in the medium external to the inner solvation sphere and to its influence on the latter and ultimately on Li$^+$, primarily through $\sigma_E$.

**Effect of Salt Concentration.**—Table II displays the small effect on the lithium chemical shift of a fourfold change in the concentration of lithium perchlorate and bromide in acetonitrile. While the changes in shift are small, they are outside the limits of experimental error and indicate that the residual influence of the anion exists even at salt concentrations of about 0.05 to 0.23 $M$. As might be expected, the sensitivity of shift to changes in salt concentration is more than twice as great for lithium bromide as for the perchlorate salt.

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[34] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

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# Stoichiometry of the Reaction between Chromium(II) and the Chlorine Oxidants in Aqueous Perchloric Acid

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The stoichiometry of the reactions between excess chromium(II) and chlorate ion, chlorine dioxide, chlorite ion, hypochlorite ion, and chlorine in aqueous perchloric acid has been studied as a function of initial hydrogen ion and chloride ion concentration. In every case significant yields of the three possible chromium(III) products—$Cr(OH_2)_6^{3+}$, $(H_2O)_5CrCl^{2+}$, and a polynuclear chromium(III) species—were obtained. Extensive chlorine transfer to the chromium(III) was indicated by the large yields of $(H_2O)_5CrCl^{2+}$. An increase in both the hydrogen ion concentration and the initial chloride ion concentration increased the yields of the $(H_2O)_5CrCl^{2+}$ product. Increasing amounts of $Cr(OH_2)_6^{3+}$ were obtained with added chloride ion in the chlorate, chlorine dioxide, and chlorite reactions, but the yield was decreased in the hypochlorite and chlorine systems. Increasing yields of $Cr(OH_2)_6^{3+}$ were produced at higher hydrogen ion concentrations for all of the oxidizing agents except chlorine. Less polynuclear species was produced with all of the oxidizing agents if either the hydrogen ion or the initial chloride ion concentration was increased. At least one step in each of the reductions is inner-sphere since chlorine transfer to chromium is quite efficient. Reactive intermediates, in addition to known chlorine species, are involved, and the results are interpreted in terms of chromium–chlorine oxidant intermediates.

## Introduction

The products formed when chromium(II) perchlorate is oxidized in aqueous perchloric acid depends on the nature of the oxidizing agent. Ardon and Plane[1] have suggested that with a one-electron oxidizing agent, a mononuclear chromium(III) species, usually either $Cr(OH_2)_6^{3+}$ or $(H_2O)_5CrX^{2+}$ (where X is a ligand derived from the oxidizing agent), is formed. With two-electron oxidizing agents, however, they proposed the formation of a binuclear chromium(III) species

$$Cr(II) + 2e = Cr(IV) \qquad (1)$$

$$Cr(II) + Cr(IV) = \text{binuclear species} \qquad (2)$$

Kolaczkowski and Plane[2] have shown that, when chromium(II) is oxidized by oxygen, a binuclear species $[Cr(H_2O)_4OH]_2^{4+}$ is the predominant product after 1 hr, but Thompson and Connick[3] found that this is *not* the product first formed.

The chlorine-containing oxidizing agents can be reduced by both one- and two-electron paths, and Ardon and Plane[1] have shown that when chromium(II) is treated with these oxidizing agents, both mononuclear and polynuclear chromium(III) products are formed. Chlorine dioxide, chlorite ion, hypochlorite ion, and chlorine are possible intermediates in the reduction of

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[1] M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

[2] R. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

[3] G. Thompson, Ph.D. Thesis, University of California, Berkeley, Calif., 1964.

chlorate ion by chromium(II). A quantitative knowledge of the stoichiometry for all of these reactions should yield useful mechanistic inferences not only for the chlorate–chromium(II) reaction but also for the other chlorine oxidant–chromium(II) systems. This paper presents the results of a detailed investigation of the stoichiometry of the reaction[4] between chromium(II) and chlorine(V), chlorine(IV), chlorine(III), chlorine(I), and chlorine(0) as a function of initial hydrogen ion and chloride ion concentrations.

## Experimental Section

**Mixing Procedure for the Stoichiometry Runs.**—All of the reactions which involve the oxidation of chromium(II) by the chlorine oxidants are quite rapid.[5] Therefore, a fast mixing procedure which utilizes a spring-powered syringe[6] was employed in order to minimize any initial concentration gradients in the reaction mixture. Except for the chlorine–chromium(II) system,[7] two methods of mixing were employed. In one, oxidizing agent was injected into chromium(II) solution, and in the other chromium(II) was injected into the appropriate solution. All runs were made in triplicate under 1 atm of nitrogen. Chromium(II) was always present in approximately 15% excess over the amount required to reduce completely the oxidizing agent.

All solutions were cooled in melting ice and, except in the cases of solutions of volatile gases, purged of oxygen with prepurified nitrogen (Matheson, 99.996%). The reaction vessel was also flushed with nitrogen before addition of reactants. When chromium(II) was to be injected, chromium(II) solution from the storage vessel was stored under 1 atm of nitrogen in a small flask which was tightly stoppered with a serum cap. In the runs where sodium chloride was added, the calculated weights of carefully dried sodium chloride were initially present in the flask. The appropriate solution was drawn into the spring-powered 2-ml syringe which had been previously flushed with prepurified nitrogen. Fresh chromium(II) and chlorine oxidant solutions were used for each set of triplicate runs. In this manner, less than 5% of the chromium(II) was lost owing to air oxidation prior to initiation of the reaction, and reproducible amounts (±2%) of the chromium(II) were injected for each triplicate set.

The cell which contained one reactant was tightly stoppered with a rubber serum cap. Immediately prior to initiation of the reaction, a small hypodermic needle which was open to the atmosphere was inserted into the cap to relieve the increased pressure produced during injection. Actual mixing was effected by triggering the cocked syring after the hypodermic needle had been inserted nearly to the bottom of the cell through the serum cap. Three minutes after injection, prepurified oxygen (Southern Oxygen Co.) was bubbled through the reaction mixture for at least 4 min to oxidize completely the excess chromium(II) to nearly pure polynuclear species.[1,8] The solution was quantitatively transferred to a column of Dowex-50 cation-exchange resin in the acid form, and the three chromium(III) species were separated.

**Separation and Analyses of the Reaction Products.**—Ten-inch columns of Dowex-50 resin, 0.5 in. in diameter, were used to effect the separation of the chromium(III) species. Careful purification of the resin was found to be necessary. The purification involved thorough washing of the resin with 3*M* perchloric acid followed by rinsing with distilled water. The resin was vigorously stirred with 0.8 *M* sodium hydroxide at 70°, and dilute hydrogen peroxide added. The peroxide was allowed to react with the resin for 10 min in order to remove the reducing species which interfered with the polynuclear chromium(III) determination. Finally, the nearly white resin was rinsed with dilute acid and packed uniformly in the columns.

The reaction mixture which contained free chloride ion and the three chromium(III) species of different charge type was placed on the column. The free chloride ion was eluted from the column with distilled water, and the eluent was collected for analysis. The $(H_2O)_5CrCl^{2+}$ band (kelly green in color) was eluted to the bottom of the column with 0.7 *M* perchloric acid and quantitatively removed from the resin with 1 *M* perchloric acid. The violet $Cr(OH_2)_6^{3+}$ band was eluted to the bottom of the column and removed quantitatively with 3 *M* perchloric acid.

The total chromium content of the various solutions was determined by oxidizing the chromium(III) to chromium(VI) with ammonium persulfate in the presence of silver ion at 100°. The excess iron(II) present after the addition of carefully weighed ferrous ammonium sulfate was titrated with standard permanganate.[9] Chloride ion was removed from the $(H_2O)_5CrCl^{2+}$ solutions prior to analysis by heating in the presence of excess silver ion. The polynuclear chromium(III) was removed from the ion-exchange resin by oxidation to chromium(VI) with alkaline peroxide. The resin was separated by filtration and thoroughly washed with distilled water. The excess peroxide in the filtrate was decomposed by boiling, and the chromium(VI) content was determined as above. It was shown that quantitative removal of the polynuclear species from the resin was effected by this procedure.

In the experiments where no chloride ion was added to the reaction mixture initially, the chloride ion present in the eluent was estimated by comparing the turbidity of this solution with standard chloride solutions in the presence of equal amounts of excess silver nitrate. The accuracy of this determination was estimated to be ±0.002 mmole of chloride ion.[10]

**Preparation and Analysis of Reagents.**—The chromium(II) perchlorate solutions were prepared by reducing hexaaquochromium(III) perchlorate with lightly amalgamated zinc[11] and were stored under specially purified nitrogen in an all-glass, sealed vessel. Prepurified nitrogen, which had been further purged of oxygen by passage over hot copper wire and hot, finely divided metallic copper coated on diatomaceous earth,[12] was continually bubbled through two traps and finally through the stock chromium(II) solution. The traps contained chromium(II) solutions of approximately the same concentration as that in the main reservoir. The hexaaquochromium(III) perchlorate was prepared by reducing chromium(VI) oxide with a slight excess of formic acid in the presence of excess perchloric acid.[13]

The hydrogen ion concentration in the chromium(II) solution was determined by a modification of the procedure of King and Neptune.[14] The chromium(III) and zinc(II) were converted to the corresponding oxalate complexes by heating for several hours in the presence of a large excess of potassium oxalate. The free hydrogen ion concentration was then determined potentiometrically by titration with standard sodium hydroxide solution. Since the mononuclear chromium(III) species appeared to undergo

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(4) No attempt will be made to differentiate between the protonated and unprotonated chlorine-containing species. Thus, chlorine(III) refers to chlorite ion and chlorous acid, and chlorine(I) refers to hypochlorite ion and hypochlorous acid. The other species will be referred to as follows: chlorate ion as chlorine(V), dissolved chlorine dioxide as chlorine(IV), and dissolved chlorine as chlorine.

(5) With the exception of the reaction between perchlorate ion and chromium(II), several reports have shown that this reaction is extremely slow with respect to the time scale of the reactions reported. For example, see D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958), and B. Zabin and H. Taube, *Inorg. Chem.*, **3**, 963 (1964).

(6) R. C. Thompson and G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).

(7) It was not feasible to load chlorine solutions into the syringe because of the possible reaction between the halogen and the stainless steel syringe needle. In addition, the high volatility of the chlorine gas in solution causes considerable difficulty with the injection of reproducible amounts. When chromium(II) was injected, however, the needle was in contact with the chlorine solution for only a few seconds.

(8) When chloride ion was added to the reaction mixture, it was necessary to make a small correction for additional $(H_2O)_5CrCl^{2+}$ and $Cr(OH_2)_6^{3+}$ produced by the final air oxidation of the excess chromium(II).

(9) C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Vol. 1C, D. Van Nostrand Co., New York, N. Y., 1959, p 586.

(10) This amount corresponded to $\approx 3 \times 10^{-5}$ *M* chloride ion.

(11) J. Lingane and R. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

(12) F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).

(13) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2825 (1961).

(14) E. L. King and J. A. Neptune, *ibid.*, **77**, 3186 (1955).

complexation more rapidly than the polynuclear species, an aliquot of chromium(II) solution was added to a slight excess of bromine, and the excess bromine was removed from the resulting chromium(III) solution by boiling. No hydrogen ion was consumed by this procedure. The solution was then treated as above. For the actual stoichiometric experiments, the contribution of hydrogen ion from the chromium(II) solution to the total hydrogen ion concentration was less than 5%.

The zinc(II) concentration of the chromium(II) solutions was determined by means of ion-exchange techniques. Aliquots of the air-oxidized chromium(II) solutions were passed through a column of Dowex-50 resin in the hydrogen ion form, and the eluted acid was titrated with standard sodium hydroxide solution. Corrections were made for the initial hydrogen ion concentration, the hydrogen ion released by the air-oxidized chromium(II), and the hydrogen ion consumed during air oxidation of the chromium(II).

The problem of accurately dispensing aliquots of solutions of a volatile gas was circumvented by preparing the chlorine dioxide directly in either a stoppered cell into which chromium(II) solution was to be injected or a stoppered flask which was to be used as a reservoir for filling the syringe. In either case a cold solution of sodium chlorite was added to a cold solution which contained a stoichiometrically equivalent amount of sodium hypochlorite and excess acid.[15] In this manner only small quantities (less than 3%) of chlorate ion were produced. In addition, chloride ion was a product only to the extent of half the concentration of the chlorine dioxide produced. The concentration of the chlorine dioxide was determined iodometrically by injecting aliquots from the reservoir into acidic sodium iodide solution or by injecting sodium iodide solution into the chlorine dioxide directly.

Analytical reagent grade sodium chlorite (99.1%) was dissolved in distilled water, and the solutions were analyzed iodometically. The solutions were stored at melting-ice temperature at pH $\approx 7$ in order to minimize any disproportionation of the sodium chlorite.[16] As an additional precaution, fresh sodium chlorite solutions were prepared for each set of triplicate runs. When chromium(II) was to be injected, it was necessary to add acid to the sodium chlorite solution in the cell to adjust the hydrogen ion concentration. This was accomplished for the 0.55 *M* acid runs by rapidly injecting the acid into the sodium chlorite solution just prior to initiation of the reaction without any immediate formation of chlorine dioxide.[16]

Hypochlorous acid solutions were prepared by standard techniques.[17] Solutions were stored as basic sodium hypochlorite in the dark at 0° and were stable for several weeks.

The chlorine solutions were prepared by allowing stoichiometric quantities of acidified sodium chloride and sodium hypochlorite in to react a stoppered cell. The resulting oxidizing power was determined iodometrically.

In a typical experiment, 0.620 ml of cold, oxygen-free 0.605 *N* sodium chlorate was injected into 6.10 ml of 0.070 *M* chromium(II) perchlorate in 0.606 *M* perchloric acid. After mixing, the initial concentrations were 0.550 *M* perchloric acid, 0.0558 *N* chlorate, and 0.0635 *M* chromium(II). Three minutes later the excess chromium(II) was oxidized by bubbling oxygen through the reaction mixture, and the products were separated and analyzed. In all of the experiments, where chloride ion was added initially, it was added to the chromium(II) solution immediately prior to mixing to ensure complete equilibration and to minimize any reaction with the chlorine-containing oxidizing agent.

In 0.55 *M* acid and low chloride ion runs, the ionic strengths were essentially constant and varied only with the zinc concentration in the chromium(II) solution and with the very small amounts of sodium chloride added. The ionic strength was somewhat higher, however, in the high chloride and high acid experiments.

## Results

The results of the detailed study of the stoichiometry of the reaction between chromium(II) and sodium chlorate, chlorine dioxide, sodium chlorite, sodium hypochlorite, and chlorine in aqueous perchloric acid are listed in Table I. Whenever it was feasible experimentally, the reactions were studied as a function of initial hydrogen ion and chloride ion concentration. In every reaction each of the three possible chromium(III) products was produced in significant yield. The entries in Table I represent the average value of three identical experiments, and the average deviation for each triplicate set was always less than 2%. In all experiments there was an excess of chromium(II) present, so that complete reduction of the oxidizing agent occurred.

In Table I, these results are listed in terms of mole per cent of chromium(III) found in each of the products relative to the equivalent amount of oxidizing agent consumed where mole per cent values for the $Cr(OH_2)_6^{3+}$ and the $(H_2O)_5CrCl^{2+}$ species were calculated directly. The amount of chloride ion added, if any, in each experiment is indicated by the *z* value, where *z* = millimoles of chloride ion added/millimoles of chloride ion derivable from the oxidizing agent.

The order of mixing the reactants affected the corresponding values in Table I only slightly,[18] *except* in the case of chlorine dioxide. The second set of the latter reactions [where chromium(II) was injected into chlorine dioxide] was repeated by using different initial concentrations of reactants and yielded essentially identical results.

The difficulty in mixing in this case is possibly due to the fact that a solution of a soluble gas was used rather than that of an ionic species. It should be mentioned that all of these reactions appeared to be "instantaneous" visually, except for the chlorate reaction in which the deep green color developed for several seconds.

The results of analyses for free chloride ion in the distilled water eluent from the ion-exchange separation of the reaction products and the $(H_2O)_5CrCl^{2+}$ formed are equal to the amount of chloride ion derivable from the chlorine oxidant. The agreement is usually within the limits of detection (±0.002 mmole). This result substantiates the indirect calculation used to determine the amounts of polynuclear species produced in the reactions.

Most of the chlorine from the oxidizing agent appears in the coordination sphere of the $(H_2O)_5CrCl^{2+}$ product. The efficiency of this chlorine transfer for $ClO_3^-$, $ClO_2$, $ClO_2^-$, $OCl^-$, and $Cl_2$ in 2.60 *M* $HClO_4$ is 93, 84, 97, 88, and 75%, respectively, and 89, 77, 84, 57, and 68%, respectively, in 0.55 *M* $HClO_4$.

The addition of even small amounts of chloride ion to the reaction mixture has a marked effect on the stoichiometry. The amount of $(H_2O)_5CrCl^{2+}$ formed increases in the presence of chloride ion in all the re-

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[15] H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).

[16] G. Gordon and R. G. Kieffer, unpublished data, 1965.

[17] G. H. Cady, *Inorg. Syn.*, **5**, 160 (1957).

[18] The apparent scatter in the data for the hypochlorite runs where chloride ion was added is due to the different *z* values.

Table I

Mole Per Cent Chromium(III) Found in the Products of the Various Chromium(II)–Chlorine Oxidant Reactions

| Species | 0.550 *M* $HClO_4$ | 2.60 *M* $HClO_4$ | 0.550 *M* $HClO_4$ | | |
|---|---|---|---|---|---|
| $ClO_3^-$ added to Cr(II) | | | | | |
| | | | $z = 1.04$[e] | $z = 10.4$ | $z = 321$ |
| Chloro[a] | 15.2[d] | 15.9 | 18.3 | 24.6 | 36.0 |
| Hexaaquo[b] | 22.4 | 30.5 | 33.5 | 38.4 | 40.7 |
| Polynuclear[c] | 62.4 | 53.6 | 48.2 | 37.0 | 23.3 |
| Cr(II) added to $ClO_3^-$ | | | | | |
| | | | $z = 0.980$ | $z = 9.77$ | |
| Chloro | 14.7 | 15.3 | 18.2 | 26.0 | |
| Hexaaquo | 22.4 | 27.2 | 33.7 | 39.3 | |
| Polynuclear | 62.9 | 57.5 | 48.1 | 34.7 | |
| $ClO_2$ added to Cr(II) | | | | | |
| | $z = 0.560$ | $z = 0.560$ | $z = 1.69$ | $z = 11.9$ | |
| Chloro | 31.8 | 31.0 | 39.2 | 48.4 | |
| Hexaaquo | 33.3 | 33.6 | 34.4 | 40.5 | |
| Polynuclear | 34.9 | 35.4 | 26.4 | 11.1 | |
| Cr(II) added to $ClO_2$ | | | | | |
| | $z = 0.560$ | $z = 0.560$ | $z = 1.56$ | $z = 10.6$ | |
| Chloro | 24.1 | 26.1 | 27.2 | 33.8 | |
| Hexaaquo | 24.6 | 33.2 | 28.9 | 31.5 | |
| Polynuclear | 51.3 | 40.7 | 43.9 | 34.7 | |
| $ClO_2^-$ added to Cr(II) | | | | | |
| | | | $z = 0.960$ | $z = 9.44$ | |
| Chloro | 21.7 | 24.4 | 27.3 | 34.0 | |
| Hexaaquo | 42.8 | 53.5 | 46.8 | 48.4 | |
| Polynuclear | 35.5 | 22.1 | 26.9 | 17.6 | |
| Cr(II) added to $ClO_2^-$ | | | | | |
| | | | $z = 0.980$ | $z = 9.61$ | |
| Chloro | 20.9 | | 27.2 | 35.6 | |
| Hexaaquo | 45.0 | | 51.0 | 50.5 | |
| Polynuclear | 34.1 | | 21.8 | 13.9 | |
| $OCl^-$ added to Cr(II) | | | | | |
| | | | $z = 0.970$ | $z = 9.71$ | |
| Chloro | 29.5 | 44.7 | 39.8 | 61.7 | |
| Hexaaquo | 33.3 | 42.7 | 29.5 | 24.6 | |
| Polynuclear | 37.2 | 12.6 | 30.7 | 13.7 | |
| Cr(II) added to $OCl^-$ | | | | | |
| | | | $z = 0.510$ | $z = 4.71$ | |
| Chloro | 27.3 | 43.4 | 33.8 | 52.7 | |
| Hexaaquo | 32.1 | 41.1 | 33.5 | 25.6 | |
| Polynuclear | 40.6 | 15.5 | 32.7 | 21.7 | |
| Cr(II) added to $Cl_2$[f] | | | | | |
| | | | $z = 0.500$ | $z = 4.59$ | |
| Chloro | 67.7 | 74.5 | 72.0 | 78.2 | |
| Hexaaquo | 22.9 | 19.5 | 20.4 | 17.8 | |
| Polynuclear | 9.9 | 6.0 | 7.6 | 4.0 | |

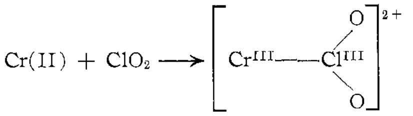
[a] Chloro refers to $(H_2O)_5CrCl^{2+}$. [b] Hexaaquo refers to $Cr(OH_2)_6^{3+}$. [c] Polynuclear refers to the polynuclear chromium(III) product. The entries are the differences between the milliequivalents of the oxidizing agent added and the sum of the chloro and hexaaquo species. [d] Entries = (arithmetic mean of triplicate experiments/milliequivalents of oxidizing agent added) × 100. [e] $z$ = millimoles of chloride ion added/millimoles of chloride ion derivable from oxidizing agent. [f] The various amounts of the halogen species may have changed somewhat in the last set of experiments owing to the various equilibria which involve chlorine in aqueous solution. Based on equilibrium data [see G. Zimmerman and F. Strong, *J. Am. Chem. Soc.*, **79**, 2063 (1957)], the relative amounts of $Cl_2$, HOCl, and $Cl_3^-$ which would be present in last set of experiments are: 86, 14, and <0.1% in the absence of chloride; 96, 4, and <0.3% in 0.06 *M* NaCl; and 97, 0.5, and 2.2% in 0.55 *M* NaCl.

actions studied[19] and in yields several orders of magnitude greater than that predicted from either statistical or equilibrium considerations. The amount of $Cr(OH_2)_6^{3+}$ similarly increases if chloride ion is added to the chlorate, chlorine dioxide, and chlorite systems. This effect is most marked in the chlorate–chromium(II) reaction. However, if hypochlorite ion or chlorine is the oxidizing agent, the yield of $Cr(OH_2)_6^{3+}$ is decreased. The amount of polynuclear chromium(III) species is decreased if chloride ion is present in the reaction mixture for all the systems studied.

The stoichiometry of the reactions was also sensitive to the hydrogen ion concentration. The amount of polynuclear species produced decreases as the hydrogen ion concentration is increased. This effect is greatest in the hypochlorite reaction but is appreciable for all of the oxidizing agents. However, large amounts of $Cr(OH_2)_6^{3+}$ were produced with an increase in the hydrogen ion concentration in each case, except chlorine. As was noted earlier, higher yields of $(H_2O)_5CrCl^{2+}$ product are generally obtained at higher acidities.

## Discussion

The extensive transfer of chlorine to the coordination sphere of the chromium(III) suggests considerable attack at the chlorine center of the oxidizing agent by the chromium(II) *via* an inner-sphere mechanism. If a one-electron transfer were concomitant with this attack, the interesting possibility of an intermediate consisting of a complex between the partially reduced species and the substitution inert chromium(III) occurs. Such an intermediate, however, would be unstable with respect to further reduction by the excess chromium(II) present. The possibility of intermediates of this type complicates any correlation to be drawn from the data in Table I. For example, if in the reaction between chromium(II) and chlorine dioxide the first step is



(3)

the stoichiometry for the ensuing reduction of the intermediate might be quite different than that for the corresponding reaction

$$4Cr(II) + ClO_2^- \longrightarrow \text{products} \qquad (4)$$

Intermediates such as the one proposed in reaction 3 render a test of Ardon and Plane's[1] hypothesis very difficult in these systems. In addition, the possibility of either one- or two-electron transfers exists which

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(19) The absence of any $(H_2O)_4CrCl_2^+$ product is assumed since all of the chloride ions produced in the reaction were accounted for in the $(H_2O)_5CrCl^{2+}$ species and the free chloride ion analysis and also since none were observed in the ion-exchange separation of the products. However, this does not preclude the possible initial formation of the dichloro species. Taube and Myers [*J. Am. Chem. Soc.*, **76**, 2103 (1954)] have shown that the aquation of the dichlorotetraaquochromium(III) species to the chloropentaaquochromium(III) species as catalyzed by chromium(II) is rapid (half-life ≈ 10 sec). Thus, in the presence of the excess chromium(II), any $(H_2O)_4CrCl_2^+$ product would be expected to be converted to $(H_2O)_5CrCl^{2+}$ *via* the chromium(II)-catalyzed path.

further complicates the detailed interpretation of the stoichiometry.

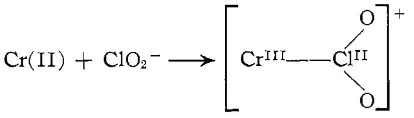
To illustrate this point, in the reaction between chromium(II) and chlorite ion, the rate-determining step could correspond to two-electron transfer

$$\mathrm{Cr(II)} + \mathrm{ClO_2^-} \longrightarrow \mathrm{Cr(IV)} + \mathrm{Cl(I)} \qquad (5)$$

followed by

$$\mathrm{Cr(II)} + \mathrm{Cr(IV)} \longrightarrow \text{binuclear species} \qquad (6)$$

However, reactions 5 and 6 would result in at least a 50% yield of polynuclear chromium(III) species.[20] That considerably less than 50% of this product is formed in this reaction can be seen from the data in Table I. If, instead, a path involving one-electron attack by chromium(II) on chlorite ion were important



(7)

the observed 35% yield of polynuclear species could still be consistent with Ardon and Plane's[1] scheme.

The decreasing yield of polynuclear chromium(III) product with increasing hydrogen ion concentration is in agreement with the results obtained in the hypochlorite–iron(II) reaction.[21] In the latter system the polynuclear product is tentatively identified as $(\mathrm{FeOH})_2^{4+}$. Sutin and co-workers suggest that this dinuclear species is formed from $[\mathrm{Fe}<^{\mathrm{OH}}_{\mathrm{Cl}}>\mathrm{Fe}]^{4+}$ which would tend to form the dihydroxy bridges at low acidities, while at high acidities it might dissociate into mononuclear products. A similar hydrolysis for the corresponding chromium(III) dimer $[\mathrm{Cr}<^{\mathrm{OH}}_{\mathrm{Cl}}>\mathrm{Cr}]^{4+}$ would account for both the decreasing yield of polynuclear species and the increasing yield of $\mathrm{Cr(OH_2)_6^{3+}}$ with increasing acidity. It is not clear, however, that the chromium(III) species could form the dihydroxy bridges in 0.55 *M* perchloric acid. In fact, the large yield of $\mathrm{(H_2O)_5CrCl^{2+}}$ would appear to preclude the formation of significant quantities of this dimer in the chlorate, chlorine dioxide, and chlorite reactions since the formation of the dihydroxy-bridged species from the dimer would not produce the chlorochromium(III) product. It should be mentioned that $[\mathrm{Cr}<^{\mathrm{OH}}_{\mathrm{Cl}}>\mathrm{Cr}]^{4+}$ or $[\mathrm{Cr}<^{\mathrm{OH}}_{\mathrm{OH}}>\mathrm{Cr}]^{4+}$ could be formed by means of two one-electron attacks by chromium(II) on the oxidizing agent and not necessarily by a single two-electron transfer.

There are several paths by which added chloride ion could dramatically affect the observed stoichiometry. In one, the added chloride could react with one or more of the possible chlorine-containing intermediates. The only reactions which are rapid enough to be competitive with the chromium(II) reactions are the hypochlorite–chloride reaction to produce chlorine[22] and the formation of trichloride ion from chlorine and chloride ion.[22] The effect of the shift in these equilibria

$$\mathrm{H^+} + \mathrm{Cl^-} + \mathrm{HOCl} \rightleftharpoons \mathrm{Cl_2} + \mathrm{H_2O} \qquad (8)$$

$$\mathrm{Cl_2} + \mathrm{Cl^-} \rightleftharpoons \mathrm{Cl_3^-} \qquad (9)$$

by the addition of initial chloride ion can be seen from the hypochlorite and chlorine data shown in Table I. It would appear that the over-all effect results in an increased yield of $\mathrm{(H_2O)_5CrCl^{2+}}$ and a decreased yield of polynuclear and $\mathrm{Cr(OH_2)_6^{3+}}$ species.

Another possible mechanism could involve the chloride ion as a nonbridging ligand in either an outer-sphere or an inner-sphere reaction, or both. However, chloride ion in the role of a nonbridging ligand usually has a very small effect on the rate of oxidation–reduction reactions.[23,24] This fact is quite important since the equilibrium constant for the formation of $\mathrm{(H_2O)_5CrCl^+}$ is small.[25] Thus, it seems improbable that significant amounts of $\mathrm{(H_2O)_5CrCl^{2+}}$ are produced in these reactions by a path in which chloride ion is a nonbridging ligand.

The added chloride ion also could act as a bridging ligand *via* the $\mathrm{(H_2O)_5CrCl^+}$ species and consequently result in the formation of the $\mathrm{(H_2O)_5CrCl^{2+}}$ product. However, the small concentration of this chromium(II) complex would require a markedly catalyzed rate compared to that of the uncomplexed chromium(II) if such a path is to be of significance.

It might well be expected, however, that a chloro complex of the postulated chromium(IV) intermediate would be formed in solutions containing added chloride ion. The subsequent reaction between the excess chromium(II) and this complex might result in the formation of $\mathrm{(H_2O)_5CrCl^{2+}}$ product rather than the polynuclear species since the chloride analysis data preclude the formation of significant yields of a polynuclear species in which chloride ion is incorporated into the coordination sphere of the chromium(III) in these reactions.

The chlorate, chlorine dioxide, and chlorite reactions with chromium(II) may be further complicated by reactions which would involve the oxidation of chlorite ion by hypochlorite ion or chlorine

$$2\mathrm{HClO_2} + \mathrm{HClO} \longrightarrow 2\mathrm{ClO_2} + \mathrm{Cl^-} + \mathrm{H_2O} + \mathrm{H^+} \qquad (10)$$

$$\mathrm{HClO} + \mathrm{ClO_2^-} \longrightarrow \mathrm{ClO_3^-} + \mathrm{Cl^-} + \mathrm{H^+} \qquad (11)$$

$$2\mathrm{HClO_2} + \mathrm{Cl_2} \longrightarrow 2\mathrm{ClO_2} + 2\mathrm{Cl^-} + 2\mathrm{H^+} \qquad (12)$$

Gordon and Emmenegger[26] have shown that reactions 10–12 are quite rapid under the conditions of the stoichiometry experiments reported in this paper. If the rates are competitive with the corresponding re-

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[20] This is true even if the rest of the reaction produced no polynuclear species, which is unlikely. The assumption that the chromium(IV) would react completely with the excess chromium(II) to form only polynuclear species under the conditions of these experiments[1] is implicit in this argument. The same observations, however, could alternatively be explained by assuming that the yield of polynuclear species in reaction 6 is considerably less than 100%.

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