

lized from cyclohexane to give 2.8 g (59% yield) of yellow crystals of  $\gamma$ -triphenyltin  $\text{Et}_2\text{ATI}$ .

**$\gamma$ -Triphenylgermanium and  $\gamma$ -Triphenylsilicon  $\text{Et}_2\text{ATI}$ .**—These were prepared in a similar manner excepting that triphenylgermanium bromide and triphenylchlorosilane, respectively, were used in place of triphenyltin chloride.

**Ni(II) Chelates of  $\gamma$ -Triphenyltin(-silicon, -germanium)  $\text{Et}_2\text{ATI}$ .**—These chelates were prepared by the same procedure as detailed below for the germanium derivative.

A solution of 0.30 g (0.0012 mole) of hydrated nickel acetate in a mixture of 4 ml of water and 12 ml of ethanol was added dropwise to a stirred solution of 0.96 g (0.002 mole) of  $\gamma$ -triphenylgermanium  $\text{Et}_2\text{ATI}$  in 15 ml of benzene and 30 ml of ethanol. The reaction mixture was heated under reflux for 30 min and then cooled overnight at 0°. The solid obtained was recrystallized from cyclohexane to give 0.65 g (65% yield) of black crystals of the Ni(II) chelate of  $\gamma$ -triphenylgermanium  $\text{Et}_2\text{ATI}$ .

**Triphenyltin(IV)  $N,N'$ -Diethylaminotroponimineate.**—A solution of 1.76 g (0.01 mole) of  $\text{Et}_2\text{ATI}$  in 35 ml of ether was stirred at 0° while 6 ml of 1.6 *N*-butyllithium (0.01 mole) in hexane was added dropwise. It was then stirred at -80° with the dropwise addition of 3.86 g (0.01 mole) of triphenyltin chloride in 40 ml of ether. The reaction mixture was warmed to room temperature over a period of 1 hr and then held under reflux for

10 min. The reaction mixture was filtered and then concentrated. The yellow product that separated at 0° was recrystallized from ether to give 3.2 g (55% yield) of yellow crystals of triphenyltin(IV)  $N,N'$ -diethylaminotroponimineate.

This compound can be sublimed unchanged at 200° (0.5 mm), but it is extremely sensitive to moisture. By nmr it was shown that about two-thirds of the tin chelate in a  $\text{CDCl}_3$  solution was decomposed on simple filtration through a layer of cotton. Presumably, the action was from the small amount of water of hydration in the cotton.

**Triphenylgermanium(IV)[-silicon(IV)]  $N,N'$ -Diethylaminotroponimineates.**—In attempts to prepare the corresponding pentavalent germanium(IV) and silicon(IV) chelates by a similar procedure, crude products were obtained whose nmr spectra indicated the presence of the desired chelates. Data are given in Table II. Attempts to purify these germanium and silicon chelates by recrystallization were unsuccessful because of their instability. The silicon chelate appeared the less stable of the two.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
STATE UNIVERSITY OF NEW YORK, STONY BROOK, NEW YORK 11790

## Kinetics and Mechanism of the Chromium(II)-Catalyzed Substitution of Iodide Ion in the Iodopentaaquochromium(III) Ion by Water and by Fluoride, Chloride, and Bromide Ions<sup>1a,b</sup>

BY DAVID E. PENNINGTON AND ALBERT HAIM<sup>1c</sup>

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The substitution of iodide ion in the iodopentaaquochromium(III) ion by water is catalyzed by chromium(II). The catalyzed path obeys the rate law  $-\text{d}[\text{CrI}^{2+}]/\text{dt} = k_3[\text{Cr}^{2+}][\text{CrI}^{2+}]/[\text{H}^+]$ , with  $k_3 = 2.66 \times 10^{-2} \text{ sec}^{-1}$  at 25° and  $[\text{ClO}_4^-] = 2.0 \text{ M}$ . Chromium(II) also catalyzes the substitution of iodide by fluoride, chloride, and bromide ions. The dominant paths for these catalyzed reactions have the form  $-\text{d}[\text{CrI}^{2+}]/\text{dt} = k_X[\text{Cr}^{2+}][\text{CrI}^{2+}][\text{X}^-]$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ). At 25°,  $[\text{ClO}_4^-] = 2.0 \text{ M}$ , and  $[\text{HClO}_4] = 1.0 \text{ M}$ , the values of  $k_X$  are  $5.3 \times 10^4$ ,  $2.7 \times 10^2$ , and  $63 \text{ M}^{-2} \text{ sec}^{-1}$  for fluoride, chloride, and bromide ions, respectively. The mechanistic implications of these results are discussed. It is suggested that the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$  reaction proceeds *via* the transition state  $[\text{ICrOHCr}^{2+}]^\ddagger$ . Intermediates of the type  $\text{CrIX}^+$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) are postulated to account for the halide ion effects.

### Introduction

Following the discovery of the bridged activated complex in electron-transfer reactions,<sup>2</sup> many studies have been performed to elucidate the role of bridging ligands in such reactions.<sup>3</sup> More recently, the effects of nonbridging ligands directly bound to the oxidant have been examined systematically.<sup>4-7</sup> Extremely useful information regarding these effects has been obtained from

studies of the reductions of cobalt(III) and chromium(III) complexes by the hexaaquochromium(II) ion because, for these systems, it is possible to ascertain the nature of the bridging ligand and the positions (*cis* or *trans*) of the nonbridging ligands with respect to the bridge. It must be noted, however, that, for an inner-sphere mechanism involving a single bridging ligand, there are five additional coordinating positions on the reducing agent. Nonbridging ligand effects in these positions are difficult to evaluate because substitution lability of the reducing agent is necessary to make the bridged transition state readily accessible. Furthermore, it has been tacitly assumed that reductions by hexaaquochromium(II) ion that proceed *via* an inner-sphere mechanism may be rather insensitive to the replacement of perchlorate ion by other simple anions.

(1) (a) This work was supported by Grants GP-2001 and GP-6528 from the National Science Foundation; (b) abstracted in part from the Ph.D. dissertation of D. E. Pennington, the Pennsylvania State University, June 1967; (c) Fellow of the Alfred P. Sloan Foundation.

(2) H. Taube, H. Myers, and R. Rich, *J. Am. Chem. Soc.*, **76**, 4118 (1953).

(3) For a recent review see N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

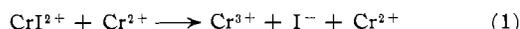
(4) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

(5) R. D. Cannon and J. E. Barley, *ibid.*, **88**, 1872 (1966).

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In connection with studies of the chromium(II)-catalyzed aqutation of the iodopentaquochromium(III) ion<sup>8</sup>



we have observed that fluoride, chloride, and bromide ions produce a dramatic increase in the rate of disappearance of  $\text{CrI}^{2+}$  and alter the reaction stoichiometry

$$\text{CrI}^{2+} + \text{Cr}^{2+} + \text{X}^- \longrightarrow \text{CrX}^{2+} + \text{Cr}^{2+} + \text{I}^- \quad (\text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-) \quad (2)$$

The effects of the halide ions on rate and stoichiometry are most reasonably accounted for on the basis of non-bridging ligand effects on chromium(II).

### Experimental Section

**Materials.**—Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate with amalgamated zinc and were stored in serum bottles under prepurified argon. The chromium(II) concentration was determined by reaction with an excess of iron(III), followed by titration of the iron(II) produced with a standard potassium dichromate solution.<sup>9</sup> The total chromium content was measured spectrophotometrically as  $\text{CrO}_4^{2-}$  after oxidation with alkaline peroxide.<sup>10</sup> The hydrogen ion concentrations of the chromium(II) solutions were determined by the procedure of King and Neptune<sup>11</sup> as modified by Thompson and Gordon.<sup>12</sup>

Sodium perchlorate and lithium perchlorate solutions were prepared by neutralization of standard perchloric acid solutions with anhydrous sodium carbonate and anhydrous lithium perchlorate, respectively.

Reagent grade sodium iodate was recrystallized from water and then dried at 110°.

All other chemicals were reagent grade. Triply distilled water was used to prepare all of the solutions.

The ion-exchange resin, Dowex 50W-X8 (50–100 mesh, H<sup>+</sup> form), was washed successively with 2 M hydrochloric acid, 1 M sodium hydroxide, 1 M sodium citrate, 2 M hydrochloric acid, and 2 M perchloric acid; the washings with the different reagents were interspaced by washings with water.

Solutions of iodopentaquochromium(III) ion were prepared following the method of Swaddle and King<sup>13</sup> (reaction of chromium(II) with an excess of triiodide ion) except for the following modifications. Sodium thiosulfate was used instead of sodium sulfite to reduce the excess triiodide ion. The ion-exchange resin and the solutions used to rinse the column and to elute the iodopentaquochromium(III) ion were maintained near 0°. The concentrated middle fraction of the eluent containing the  $\text{CrI}^{2+}$  ion was stored at -78°.

**Stoichiometric Measurements.**—The stoichiometry of the  $\text{CrI}^{2+}$ -Cr(II) reaction in the absence of anions other than perchlorate ion was determined by spectrophotometric observation of the reaction products in the 500–350-m $\mu$  region.

For the reaction in the presence of added halide ions, an ion-exchange separation procedure was used to determine the nature and concentration of the chromium(III) products. Reaction vessels were serum bottles covered with self-sealing rubber caps. All manipulations were performed under an atmosphere of prepurified argon. The desired volumes of  $\text{CrI}^{2+}$  solutions (containing 0.1–0.3 mmole of chromium) were added by means of calibrated hypodermic syringes with steel needles to the solutions containing the desired amounts of chromium(II), sodium perchlorate, perchloric acid, and sodium halide. After completion

of the reactions (approximately 30–60 min at room temperature), oxygen was admitted to oxidize the excess chromium(II). The resulting solution was diluted tenfold and then added to a Dowex 50W-X8 ion-exchange column. After the column was rinsed with 0.15 M perchloric acid, the chromium(III) product of charge +2 was eluted with 1.0 M perchloric acid. This fraction was examined spectrophotometrically from 700 to 350 m $\mu$ , and then the chromium content was determined. Since air oxidation of chromium(II) in the presence of halide ions produces small amounts of halogenopentaquochromium(III) ions, it was necessary to correct the yields of  $\text{CrX}^{2+}$  (X = F, Cl, Br) for the amounts produced by the air oxidation. The blank experiments were performed under conditions identical with those of the stoichiometric experiments, except that sodium iodide was used instead of the iodochromium(III) ion.

**Kinetic Measurements.**—Two different procedures were used to study the kinetics of the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$  reaction. In the first procedure,  $\text{CrI}^{2+}$  was generated *in situ* by the reaction of excess chromium(II) with iodine, which in turn was generated by the reaction of iodate ion with a slight excess of iodide ion. The desired amounts of sodium iodide, sodium perchlorate, and/or perchloric acid were added to a cylindrical spectrophotometric cell of appropriate length. The cell was covered with a self-sealing rubber cap, and oxygen was removed by means of a stream of prepurified argon. The cell was then placed in the thermostated ( $\pm 0.1^\circ$ ) cell compartment of a Cary 14 recording spectrophotometer. After temperature equilibration was reached, the desired amount of sodium iodate solution was added by means of a calibrated syringe, followed immediately by the desired amount of chromium(II). Under the experimental conditions, the  $\text{Cr}^{2+}$ - $\text{I}_2$  reaction is essentially complete within the time of mixing ( $k > 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ ), and therefore only the chromium(II)-catalyzed aqutation of  $\text{CrI}^{2+}$  was observed by following the decrease in absorbance with time at 475 m $\mu$ .

In the second procedure, the cell containing the desired quantities of chromium(II), sodium perchlorate, and/or perchloric acid was placed in the compartment of the spectrophotometer. After temperature equilibrium the desired amount of the  $\text{CrI}^{2+}$  purified by ion-exchange chromatography was added, and a recording of absorbance *vs.* time was obtained at 306 m $\mu$  (for  $[\text{CrI}^{2+}] \approx 10^{-5} \text{ M}$ ) or 475 m $\mu$  (for  $[\text{CrI}^{2+}] \approx 10^{-3} \text{ M}$ ).

The kinetic measurements in the presence of added halide ions were carried out with the  $\text{CrI}^{2+}$  purified by ion-exchange chromatography, and absorbance *vs.* time curves were obtained at 306 m $\mu$ . Since all reactions studied are catalyzed by chromium(II), pseudo-first-order rate constants  $k'$  were obtained from slopes of  $\log(D_t - D_\infty)$  *vs.* time, where  $D_t$  and  $D_\infty$  are the absorbances at time  $t$  and at the completion of the reaction (8–10 half-lives), respectively.

### Results

**The Chromium(II)-Catalyzed Aqutation of  $\text{CrI}^{2+}$ .**—The stoichiometry of this reaction (eq 1) was established by spectrophotometric observation of the reaction products in the wavelength range from 500 to 350 m $\mu$ . In this spectral region the molar absorptivities of chromium(II) are quite small (less than 0.2), whereas the hexaaquochromium(III) ion exhibits an absorption maximum at 408 m $\mu$  with molar absorptivity 15.6.<sup>14a</sup> The reaction mixtures contained  $5.0 \times 10^{-3} \text{ M CrI}^{2+}$ ,  $2.0 \times 10^{-2}$  to  $2.0 \times 10^{-1} \text{ M Cr}^{2+}$ , and  $2.0 \times 10^{-2}$  to  $5.0 \times 10^{-1} \text{ M H}^+$ . In all cases product solutions exhibited maxima at 408–410 m $\mu$  with molar absorptivities varying between 16 and 18. These values are significantly higher than the value of 15.6 expected for

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

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

(11) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

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

(13) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

(14) (a) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959);

(b) For example, 1% air oxidation of the chromium(II) in a solution  $5.0 \times 10^{-3} \text{ M Cr}^{2+}$  and  $2.0 \times 10^{-2} \text{ M Cr}^{2+}$  would yield a molar absorptivity of 16.4.

quantitative formation of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . However, small ( $\approx 1\%$  of the chromium(II)) amounts of air oxidation would result in substantial contributions to the absorbance at  $408 \text{ m}\mu$ ,<sup>14b</sup> and we conclude, therefore, that eq 1 describes the stoichiometry of the  $\text{Cr}(\text{II})$ - $\text{CrI}^{2+}$  reaction in perchlorate media.

In a previous communication<sup>8</sup> we demonstrated that the kinetics of reaction 1 conforms to the rate law

$$\frac{-d \ln [\text{CrI}^{2+}]}{dt} = k' = k_1 + \frac{k_2}{[\text{H}^+]} + k_3 \frac{[\text{Cr}^{2+}]}{[\text{H}^+]} \quad (3)$$

The rate coefficients  $k_1$  and  $k_2$  correspond to the spontaneous aquation of  $\text{CrI}^{2+}$  via  $[\text{H}^+]$ -independent and  $1/[\text{H}^+]$ -dependent paths, respectively.<sup>13</sup> In the earlier work,<sup>8</sup> carried out at  $[\text{ClO}_4^-] = 1.0 \text{ M}$ , it was found that  $k_3 = 2.2 \times 10^{-3} \text{ sec}^{-1}$  at  $25^\circ$ . It was also noted that although the data did not provide evidence for an additional path of the form  $k_4[\text{Cr}^{2+}]$ , a small contribution by such a path could not be ruled out.<sup>15</sup> Since an increase in ionic strength should enhance the contribution of the  $k_4$  path relative to the  $k_3$  path, as well as extend the range of hydrogen ion concentrations that can be used, additional measurements were carried out at  $[\text{ClO}_4^-] = 2.0 \text{ M}$  and are presented in Table I. These measurements were performed at  $475 \text{ m}\mu$  with concentrations of  $\text{CrI}^{2+}$  in the range  $3.9$ – $5.0 \times 10^{-3} \text{ M}$ . Under these conditions, the quality of the data is reasonably good, and duplicate experiments agree within 1–2%. The values of  $k_3$  in column 4 of Table I were calculated on the basis of eq 3 using the measured values of  $k'$  and the known<sup>13</sup> values of  $k_1$  and  $k_2$ . The contribution of the  $k_1$  and  $k_2$  terms to the over-all disappearance of  $\text{CrI}^{2+}$  is less than 5%, except at the lowest concentrations of hydrogen ion and chromium(II) ion where the correction is  $\approx 12\%$ . It is seen that the values of  $k_3$  remain reasonably constant when  $[\text{Cr}^{2+}]$  and  $[\text{H}^+]$  are varied by factors of 14 and 16, respectively, and we conclude that eq 3 provides a fairly accurate description of the kinetics of the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$  system in perchlorate media of varying acidity. It is noteworthy that the present data provide no evidence for the hydrogen ion independent term  $k_4$ . In order to put this conclusion on a more quantitative basis, the data of Table I were treated by a nonlinear least-squares program<sup>16</sup> under two different assumptions: (a) the value of  $k_4$  was arbitrarily set equal to zero, and the least-squares calculation yielded the value of  $k_3$ ; (b) the  $k_4$  term was included in the rate law and the least-squares calculations of  $k_3$  and  $k_4$  were carried out. Under assumption a,  $k_3 = (2.66 \pm 0.03) \times 10^{-2} \text{ sec}^{-1}$ , the average per cent deviation between calculated and observed values of  $k'$  is 2.8%, and the maximum deviation is 5.3%. Under assumption b,  $k_3 = (2.69 \pm 0.04) \times 10^{-2} \text{ sec}^{-1}$  and  $k_4 = (-3.69 \pm 4.47) \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ , the average per cent deviation is 2.6%, and the maximum deviation is 5.6%. It is apparent from these calculations that the inclusion of the  $k_4$  term in the

(15) The highest hydrogen concentration used in the earlier work<sup>8</sup> was  $0.506 \text{ M}$ , and the limit  $k_4 < 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  was established.

(16) The nonlinear least-squares program is described in Los Alamos Report LA2367 (March 4, 1980) and Addenda (Jan 14, 1963). A. H. is grateful to Dr. T. W. Newton for invaluable help with the program.

TABLE I  
KINETICS OF THE CHROMIUM(II)-CATALYZED  
AQUATION OF THE IODOPENTAQUOCHROMIUM(III) ION<sup>a</sup>

$[\text{H}^+], \text{M}$	$[\text{Cr}^{2+}], \text{M}$	$10^3 k', \text{sec}^{-1}$	$10^3 k_3, \text{sec}^{-1}$
0.099	0.0100	3.21, 3.20	2.76, 2.75
0.100	0.0420	12.0	2.76
0.151	0.0906	17.2	2.83 <sup>b</sup>
0.152	0.0301	5.53, 5.66	2.65, 2.71
0.317	0.0652	5.50, 5.57	2.58, 2.62
0.400	0.0906	5.89	2.53 <sup>b</sup>
1.53	0.141	2.54	2.65 <sup>b</sup>
1.61	0.121	2.03	2.56 <sup>b</sup>
1.62	0.100	1.80	2.74 <sup>b</sup>
0.081	0.0241	8.25	2.60 <sup>b,c</sup>
1.20	0.0241	0.52	2.55 <sup>b,c</sup>
0.072	0.045	23.7	3.7 <sup>d</sup>
0.125	0.045	13.4	3.6 <sup>d</sup>
0.607	0.123	7.4	3.5 <sup>d</sup>

<sup>a</sup> Measurements at  $475 \text{ m}\mu$  with  $\text{CrI}^{2+}$  ( $3.9$ – $5.0 \times 10^{-3} \text{ M}$ ) prepared *in situ* by the reaction of iodine with excess chromium(II) except where noted; temperature  $25^\circ$ , except where noted;  $[\text{ClO}_4^-] = 2.0 \text{ M}$ , maintained with sodium perchlorate, except where noted. <sup>b</sup>  $\text{CrI}^{2+}$  purified by ion-exchange chromatography. <sup>c</sup>  $[\text{ClO}_4^-] = 2.0 \text{ M}$  maintained with lithium perchlorate. <sup>d</sup> Measurements at  $30^\circ$  and  $[\text{ClO}_4^-] = 1.0 \text{ M}$ .

rate law is not justified, and we conclude that  $k_4 < 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ .

In arriving at this conclusion it has been tacitly assumed that medium effects (*e.g.*, replacement of perchloric acid by sodium perchlorate) are unimportant. However, as pointed out by Newton and Baker,<sup>17</sup> a single term in an empirical hydrogen ion dependence may be the result of fortuitous cancellation of an actual path by a medium effect. In order to test this possibility, two measurements (*cf.* entries 10 and 11 of Table I) were carried out with lithium perchlorate instead of sodium perchlorate as the background electrolyte. Although the values of  $k_3$  for these measurements appear to be slightly smaller (*ca.* 5%) than the values obtained in sodium perchlorate media, the difference is sufficiently small to justify the assumption that medium effects are unimportant in this reaction.<sup>18–19</sup>

Included in Table I are measurements at  $30^\circ$  with  $[\text{ClO}_4^-] = 1.0 \text{ M}$ . From these and earlier<sup>8</sup> measurements at  $15$  and  $25^\circ$ , we compute the following activation parameters for the rate coefficient  $k_3$ :  $\Delta H^\ddagger = 16 \text{ kcal/mole}$  and  $\Delta S^\ddagger = -11 \text{ eu}$ .

**The Chromium(II)-Catalyzed Substitutions of Iodide Ion in  $\text{CrI}^{2+}$  by Fluoride, Chloride, and Bromide Ions.**—The results of the experiments performed to establish the stoichiometries of the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$ - $\text{X}^-$  reactions

(17) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

(18) Actually the relative insensitivity of the rate coefficient  $k_3$  to the nature of the cations in solution is not unexpected since the reaction under consideration involves positively charged species.

(19) Very extensive series of kinetic measurements of reaction 1 were performed at  $306 \text{ m}\mu$  with concentrations of  $\text{CrI}^{2+}$  (purified by ion-exchange chromatography) in the range  $5$ – $7 \times 10^{-3} \text{ M}$ . Under these conditions the results were distressingly erratic. The values of  $k_3$  measured at  $306 \text{ m}\mu$  were consistently higher (20–50%) than those measured at  $475 \text{ m}\mu$ . The source of difficulty was finally traced to the formidable rate increase caused by chloride ion impurities ( $10^{-4}$ – $10^{-3} \text{ M}$ ) in the reactant solutions. Since the rate enhancement caused by chloride ion is accompanied by its consumption (see eq 2), the effect is quite noticeable when low  $\text{CrI}^{2+}$  concentrations ( $5 \times 10^{-3} \text{ M}$ ) are used (measurements at  $306 \text{ m}\mu$ ), but becomes negligible when high  $\text{CrI}^{2+}$  concentrations ( $5 \times 10^{-2} \text{ M}$ ) are used (measurements at  $475 \text{ m}\mu$ ). The results presented in Table I are, as far as we can ascertain, relatively free from effects of chloride ion impurities.

(X = F, Cl, Br) are presented in Table II. The experimental conditions were chosen to minimize the contributions of the  $k_2$  and  $k_3$  paths (high hydrogen ion concentration) and maximize the contribution of the  $k_X$  path (high halide ion concentration). Under the conditions used the contribution of the halide ion dependent path (see eq 5 below) amounts to at least 98% of the total disappearance of  $\text{CrI}^{2+}$ . One source of difficulty in these experiments is the incorporation of halide ion into the coordination sphere of the chromium(III) product when the excess chromium(II) is oxidized by oxygen. Blank experiments were performed to correct for the amount of  $\text{CrX}^{2+}$  produced in this manner, and the blank correction was minimized by using relatively high  $\text{CrI}^{2+}$  concentrations and low  $\text{Cr}^{2+}$  concentrations.<sup>20</sup>

TABLE II  
STOICHIOMETRIES OF THE CHROMIUM(II)-CATALYZED  
SUBSTITUTIONS OF IODIDE ION IN  $\text{CrI}^{2+}$  BY FLUORIDE,  
CHLORIDE, AND BROMIDE IONS<sup>a</sup>

Halide ion	$\text{CrI}^{2+}$ initially present, mmole	$\text{CrX}^{2+}$ recovered, mmole	$\text{CrX}^{2+}$ in blank, mmole	% $\text{CrX}^{2+b}$
F <sup>-</sup>	0.354	0.324, 0.310	0.015	87, 84
Cl <sup>-</sup>	0.354	0.384, 0.359	0.014	104, 97
Br <sup>-</sup>	0.354	0.381	0.012	104
	0.532	0.524	0.012	96

<sup>a</sup> Measurements at 25°;  $[\text{HClO}_4] = 1.90 M$ ;  $[\text{Cl}^-] = [\text{Br}^-] = [\text{HF}] = 0.10 M$ ;  $[\text{Cr}^{2+}] = 0.0059 M$ ; total reaction volume, 16 ml. <sup>b</sup> Per cent of  $\text{CrI}^{2+}$  converted to  $\text{CrX}^{2+}$ , corrected for blank.

For chloride and bromide ions, the yields of the corresponding halogenopentaquochromium(III) complexes are essentially quantitative (*cf.* column 5 of Table II), and we conclude that these reactions proceed according to the stoichiometry given by eq 2. For fluoride ion, however, the yield of  $\text{CrF}^{2+}$  is substantially lower than 100%. In this case the defect from 100% is caused by the subsequent chromium(II)-catalyzed addition of fluoride ion to the  $\text{CrF}^{2+}$  formed initially in reaction 2



The occurrence of reaction 4 was demonstrated in separate experiments whereby  $\text{CrF}^{2+}$  was allowed to react with fluoride ion in the presence of chromium(II) for a period of time equal to that used in the stoichiometric experiments. For example, a solution of initial composition  $[\text{CrF}^{2+}] = 6.13 \times 10^{-3} M$ ,  $[\text{H}^+] = 0.63 M$ ,  $[\text{HF}] = 0.100 M$ , and  $[\text{Cr}^{2+}] = 6.0 \times 10^{-3} M$  yielded after 30 min 9.1%  $\text{CrF}_2^+$  of unknown isomeric composition. We conclude, therefore, that the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$ - $\text{F}^-$  reaction also produces  $\text{CrF}^{2+}$  quantitatively and that the lower yields observed correspond to the follow-up reaction, eq 4.

The kinetic measurements for the chromium(II)-catalyzed substitution of iodide ion in  $\text{CrI}^{2+}$  by bro-

midate ion at 25° and  $[\text{ClO}_4^-] = 2.0 M$  are presented in Table III. In interpreting these results, the contributions of the spontaneous aquation ( $k_1$  and  $k_2$  paths) and the chromium(II)-catalyzed aquation ( $k_3$  path) cannot be neglected. However, the experimental conditions are such that the sum of the  $k_1$ ,  $k_2$ , and  $k_3$  paths contributes less than 20% to the disappearance of  $\text{CrI}^{2+}$ , except at the lowest hydrogen ion concentration where the contribution is 33%. The results of Table III were initially treated on the basis of the equation (X = Br)

$$\frac{-d \ln [\text{CrI}^{2+}]}{dt} = k' = k_1 + \frac{k_2}{[\text{H}^+]} + \frac{k_3[\text{Cr}^{2+}]}{[\text{H}^+]} + k_X[\text{Cr}^{2+}][\text{X}^-] \quad (5)$$

The values of  $k'$ , the observed pseudo-first-order rate coefficients, are given in column 5. The values of  $k_{\text{Br}}$ , listed in column 6, were calculated from the measured values of  $k'$ , the known values of  $k_1$ ,  $k_2$ , and  $k_3$ , and the appropriate concentrations. The majority of the experiments in Table III were carried out by using sodium perchlorate and perchloric acid as background electrolytes. In experiments 1-6 the hydrogen ion concentration was maintained constant, and the concentrations of bromide and chromium(II) ions were varied. Under these conditions, it is seen that the values of  $k_{\text{Br}}$  remain reasonably constant, and we conclude that eq 5 provides an appropriate description of the kinetics of the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$ - $\text{Br}^-$  system at constant acidity. In experiments 7-13 the concentrations of bromide and chromium(II) ion were maintained constant, and the hydrogen ion concentration was varied. Under these conditions, there is a distinct trend toward increasing  $k_{\text{Br}}$  with increasing acidity. This result is quite surprising because, for a system such as the present one, there are no plausible locations in the reactant species for bringing a hydrogen ion into the transition state. The question naturally arises as to whether the increase in rate with increasing acidity corresponds to an actual hydrogen ion dependent path or to a medium effect. In an attempt to obtain some information regarding the possible magnitude of medium effects in the present system, the last three experiments of Table III were carried out with lithium perchlorate as a background electrolyte. It is seen that the increase in rate with increasing acidity is less pronounced for solutions containing  $\text{Li}^+$  than for solutions containing  $\text{Na}^+$ . The dependence of  $k_{\text{Br}}$  upon  $[\text{H}^+]$  for either  $\text{Li}^+$  or  $\text{Na}^+$  is adequately represented by  $k_{\text{Br}}^0(1 + a[\text{H}^+])$ . Using the nonlinear least-squares computer program it is found that  $k_{\text{Br}}^0 = 49.7 \pm 0.9 M^{-2} \text{sec}^{-1}$  and  $a = 0.25 \pm 0.02 M^{-1}$  for  $\text{Na}^+$ ;  $k_{\text{Br}}^0 = 58.4 \pm 0.9 M^{-2} \text{sec}^{-1}$  and  $a = 0.12 \pm 0.01 M^{-1}$  for  $\text{Li}^+$ . For reactions between positive ions, changes in rate of 0-20% are observed when  $\text{Na}^+$  is substituted by  $\text{Li}^+$ .<sup>17</sup> Therefore the value of 17% observed in the present system seems quite reasonable, especially when it is recognized that the reaction involves two positive ions and a negative ion. A further increase in rate of 24% is observed when  $\text{Li}^+$  is substituted by  $\text{H}^+$ . In view of the differ-

(20) A detailed study of the products formed by air oxidation of chromium(II) in the presence of iodide ion and either chloride, bromide, or fluoride ions was not undertaken; however, it appears that both  $\text{CrI}^{2+}$  and  $\text{CrX}^{2+}$  (X = F, Cl, Br) are formed.

TABLE III  
KINETICS OF THE CHROMIUM(II)-CATALYZED SUBSTITUTION  
OF IODIDE ION IN  $\text{CrI}^{2+}$  BY BROMIDE ION<sup>c</sup>

Expt no.	$[\text{H}^+]$ , $M$	$[\text{Br}^-]$ , $M \times 10^2$	$[\text{Cr}^{2+}]$ , $M \times 10^2$	$10^3 k'$ , $\text{sec}^{-1}$	$k_{\text{Br}}$ , $M^{-2}$ $\text{sec}^{-1}$
1	1.04	0.625	1.72	7.26	62.1
2	1.04	0.625	5.17	22.2, 23.5	64.4, 68.4
3	1.04	0.625	10.0	41.7, 44.2	62.3, 66.3
4	1.04	2.00	1.72	21.9, 22.1	62.0, 62.5
5	1.04	6.00	1.72	64.2, 64.5	61.6, 61.9
6	1.04	10.0	1.72	107, 109	62.2, 63.3
7	0.155	0.625	1.72	8.90	52.1
8	0.155	0.625	1.80	9.14, 9.29	50.7, 51.9
9	0.303	0.625	1.80	7.37, 7.71	50.0, 52.8
10	0.550	0.625	1.80	7.56	58.1
11	0.750	0.625	1.80	7.22, 7.33	57.2, 58.2
12	1.94	0.625	1.80	8.31, 8.63	70.8, 73.5
13	1.95	0.625	1.80	8.45	72.2
14	0.155	0.625	1.80	9.89, 10.1	57.4, 59.2 <sup>b</sup>
15	0.550	0.625	1.80	8.23	64.2 <sup>b</sup>
16	1.04	0.625	1.80	7.94, 8.04	65.4, 66.2 <sup>b</sup>

<sup>a</sup> Sodium perchlorate as background electrolyte, except where noted;  $[\text{CrI}^{2+}] = 4-8 \times 10^{-3} M$ ;  $[\text{ClO}_4^-] = 2.0 M$ ; measurements at 25°. <sup>b</sup> Lithium perchlorate as background electrolyte.

ence between  $\text{Na}^+$  and  $\text{Li}^+$ , the observed increase in rate when either  $\text{Li}^+$  or  $\text{Na}^+$  is substituted by  $\text{H}^+$  could be consistent with a medium effect. However, we must admit that the possibility of an actual hydrogen ion dependent path cannot be ruled out on the basis of these comparisons. In any event, the variation of  $k_{\text{Br}}$  with  $[\text{H}^+]$ , although relatively important if interpreted as a medium effect, is sufficiently small to justify the conclusion that the dominant path in the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$ - $\text{Br}^-$  reaction is hydrogen ion independent.

The kinetic measurements for the chromium(II)-catalyzed substitution of iodide ion in  $\text{CrI}^{2+}$  by chloride ion at 25° and  $[\text{ClO}_4^-] = 2.0 M$  are presented in Table IV. The results are entirely analogous to those obtained for the corresponding reaction of bromide ion and were treated on the basis of eq 5 ( $X = \text{Cl}$ ). Since the reaction with chloride ion is faster than that with bromide ion, the contribution of the  $k_1$ ,  $k_2$ , and  $k_3$  terms was less than 10% in all cases. In experiments 1-13 the hydrogen ion concentration was maintained constant, and the concentrations of chloride and chromium(II) ions were varied by factors of 100 and 15, respectively. Under these conditions, the values of  $k_{\text{Cl}}$  remain reasonably constant, and we conclude that the chloride ion dependent reaction is first order in  $[\text{Cl}^-]$  and first order in  $[\text{Cr}^{2+}]$ , as indicated by eq 5. In experiments 14-16 the hydrogen ion concentration was varied, and there is a discernible trend toward increasing rate with increasing acidity. The data are not sufficiently extensive to establish the functional dependence of  $k_{\text{Cl}}$  upon  $[\text{H}^+]$ ; however, it would appear that a dependence higher than first order obtains. As was the case with the bromide system, we cannot ascertain whether we are dealing with a chemical or a medium effect. In any event, the effect of  $[\text{H}^+]$  on  $k_{\text{Cl}}$  is moderate (in going from  $[\text{H}^+] = 0.153 M$  to  $[\text{H}^+] = 1.96 M$ , the rate increases by 30%) and we conclude that the dominant reaction path in the

TABLE IV  
KINETICS OF THE CHROMIUM(II)-CATALYZED SUBSTITUTION  
OF IODIDE ION IN  $\text{CrI}^{2+}$  BY CHLORIDE ION<sup>a</sup>

Expt no.	$[\text{H}^+]$ , $M$	$[\text{Cl}^-]$ , $M \times 10^2$	$[\text{Cr}^{2+}]$ , $M \times 10^2$	$10^3 k'$ , $\text{sec}^{-1}$	$10^{-2} k_{\text{Cl}}$ , $M^{-2}$ $\text{sec}^{-1}$
1	1.03	0.100	0.994	3.47	3.10
2	1.04	0.100	2.58	7.66	2.63
3	1.04	0.100	3.10	9.84	2.87
4	1.04	0.100	4.97	16.9	3.11
5	1.04	0.100	5.17	14.0, 15.7	2.44, 2.77
6	1.03	0.100	10.3	31.5, 31.7	2.87, 2.89
7	1.03	1.00	0.622	17.2, 17.4	2.72, 2.75
8	1.04	1.00	3.11	82.6, 86.1	2.62, 2.74
9	1.03	2.00	0.622	29.2, 29.4	2.32, 2.34
10	1.03	5.00	0.622	79.1, 83.0	2.54, 2.66
11	1.04	7.50	0.607	129, 137	2.84, 3.01
12	1.03	10.0	0.622	171	2.75
13	1.04	10.0	0.607	172, 174	2.83, 2.87
14	0.153	1.00	1.72	46.9, 47.4	2.53, 2.56
15	0.301	1.00	1.72	44.9, 46.7	2.57, 2.62
16	1.96	1.00	1.72	58.5	3.39

<sup>a</sup> Measurements at 25°;  $[\text{ClO}_4^-] = 2.0 M$ ;  $[\text{CrI}^{2+}] = 6.0-10 \times 10^{-4} M$ .

$\text{CrI}^{2+}$ - $\text{Cr}^{2+}$ - $\text{Cl}^-$  system is independent of hydrogen ion concentration.

The kinetic measurements for the chromium(II)-catalyzed substitution of iodide ion in  $\text{CrI}^{2+}$  by fluoride ion at 25° and  $[\text{ClO}_4^-] = 2.0 M$  are presented in Table V. Since HF is the dominant fluoride-containing

TABLE V  
KINETICS OF THE CHROMIUM(II)-CATALYZED SUBSTITUTION OF  
IODIDE ION IN  $\text{CrI}^{2+}$  BY FLUORIDE ION

Expt no.	$[\text{H}^+]$ , $M$	$[\text{HF}]$ , $M \times 10^2$	$[\text{Cr}^{2+}]$ , $M \times 10^2$	$10^3 k'$ , $\text{sec}^{-1}$	$k_{\text{HF}}$ , $M^{-1}$ $\text{sec}^{-1}$
1	1.02	0.200	4.82	5.80	46.6
2	1.02	1.00	1.04	4.67, 4.80	41.9, 43.3
3	1.02	1.60	1.04	7.82, 7.82	45.5, 45.5
4	1.02	2.66	1.21	14.3, 14.3	44.1, 44.1
5	1.00	4.00	1.21	16.3, 16.9, 17.1, 18.5	33.7, 34.5, 34.9, 38.2
6	0.106	0.102	1.04	6.52, 6.53	36.2, 36.2
7	0.204	0.200	1.04	6.34, 6.52	48.0, 49.5
8	0.202	0.200	2.41	12.9, 12.9	39.0, 39.0
9	0.200	0.400	2.41	21.0, 21.4	36.6, 37.1
10	0.400	0.400	2.41	9.93, 10.1	34.1, 34.6
11	0.693	0.700	2.41	10.5	38.8
12	0.990	1.00	2.41	11.4, 11.6	44.0, 44.5

<sup>a</sup> Measurements at 25°;  $[\text{ClO}_4^-] = 2.0 M$ ;  $[\text{CrI}^{2+}] = 5-10 \times 10^{-3} M$ .

species at the hydrogen ion concentrations used, the kinetic measurements were treated on the basis of the equation

$$\frac{-d \ln [\text{CrI}^{2+}]}{dt} = k' = k_1 + \frac{k_2}{[\text{H}^+]} + \frac{k_3 [\text{Cr}^{2+}]}{[\text{H}^+]} + k_{\text{HF}} \frac{[\text{Cr}^{2+}][\text{HF}]}{[\text{H}^+]} \quad (6)$$

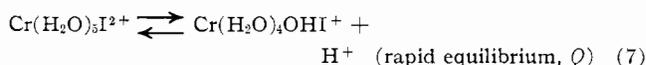
Under the experimental conditions used in the measurements of Table V, the contribution of the  $k_1$ ,  $k_2$ , and  $k_3$  paths was less than 20% except for the runs at the lowest acidity where the contribution was 45%. In experiments 1-5 the hydrogen ion concentration was maintained constant, and the concentrations of chromium(II) and hydrofluoric acid were varied. Although the

values of  $k_{\text{HF}}$  scatter considerably, the results suffice to show that the reaction is first order in  $[\text{HF}]$ . In experiments 6–8 and 10–12, the values of  $[\text{HF}]$  and  $[\text{H}^+]$  were varied by a factor of about 10, but the ratio  $[\text{HF}]/[\text{H}^+]$  (and therefore the fluoride ion concentration) was maintained approximately constant. Again considerable scatter is observed, but the relative consistency of the  $k_{\text{HF}}$  values indicates that the reaction is principally first order in  $[\text{HF}]$  and inversely proportional to  $[\text{H}^+]$ . There appears to be a trend toward increasing rate with increasing acidity, suggesting perhaps a modest (about 20% at 1 M  $[\text{H}^+]$ ) contribution of a term of the form  $k_{\text{HF}}[\text{Cr}^{2+}][\text{HF}]$ . The cause of the scatter in the results is unknown. Various sources of reagents and different preparations were used in the measurements. One obvious difficulty is attack of the spectrophotometric cells by hydrofluoric acid. In view of the limited quality of the data, all we can conclude at the present time is that the principal path for the  $\text{Cr}^{2+}$ – $\text{CrI}^{2+}$ – $\text{F}^-$  reaction is described by the  $k_{\text{HF}}$  term of eq 6.

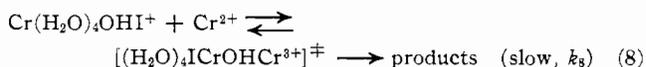
### Discussion

**The Chromium(II)-Catalyzed Aquation of  $\text{CrI}^{2+}$ .**—Electron-transfer reactions between chromium(II) ion and complexes of the type  $\text{CrX}^{2+}$ , where  $\text{X}^-$  is a suitable bridging ligand ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ ),<sup>21–23</sup> have been known for many years to proceed predominantly *via* bridged transition states  $[\text{CrXC}r^{4+}]^\ddagger$ . Under the experimental conditions used to measure the rates of these reactions (relatively low  $[\text{Cr}^{2+}]$  and relatively high  $[\text{H}^+]$ ), ligand transfer accompanies electron transfer, and the rate of exchange is independent of hydrogen ion concentration. However, it has become increasingly apparent in the past year<sup>7,8,24</sup> that this is not the only accessible pathway for transferring an electron for chromium(II) to  $\text{CrX}^{2+}$ . In a previous communication,<sup>8</sup> we demonstrated the increased lability of halogenopentaquo-chromium(III) complexes in the presence of relatively high chromium(II) concentrations and relatively low hydrogen ion concentrations. Under these conditions, net aquation according to eq 1 can be detected quite readily. The rate of reaction 1 ( $k_3$  path in eq 3) is first order in  $[\text{Cr}^{2+}]$ , first order in  $[\text{CrI}^{2+}]$ , and inversely proportional to  $[\text{H}^+]$ . We conclude, therefore, that the composition of the transition state is  $[\text{Cr}_2\text{IOH}^{3+}]^\ddagger$ . In view of the stoichiometric results (net loss of iodide ion from the coordination sphere of chromium(III)), we also conclude that iodide ion is *not* utilized as a bridging group in the reaction. Whether the hydroxide ion is bound to  $\text{Cr}^{2+}$ , to  $\text{CrI}^{2+}$ , or to both ions in the transition state cannot be ascertained from the present results. However, it is noteworthy that inverse hydrogen ion dependences are featured in reactions that proceed by a hydroxide ion bridged activated complex, but do not obtain in outer-sphere reactions,<sup>25–29</sup> and it has been suggested<sup>27</sup> that

aquohydroxy comparisons may be useful to distinguish between inner- and outer-sphere mechanisms. Consequently, it is reasonable to ascribe the dependence of the  $k_3$  path upon  $1/[\text{H}^+]$  to hydrolysis of  $\text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}$



followed by the rate-determining, hydroxide-bridged reaction



An entirely analogous mechanism has been previously proposed for the chromium(II)-catalyzed aquation of  $\text{CrCl}^{2+}$ <sup>24</sup> and the iron(II)-catalyzed aquation of  $\text{FeCl}^{2+}$ .<sup>30</sup>

In Table VI we summarize the results obtained for a series of chromium(II)–chromium(III) reactions that proceed according to a rate law of the form  $k_3[\text{Cr}^{2+}][\text{CrX}^{n+}]/[\text{H}^+]$ . Assuming that the mechanism represented by eq 7 and 8 obtains, the observed rate coefficient  $k_3$  equals  $Qk_8$ . Values of  $Q$  are known only for  $\text{X} = \text{H}_2\text{O}$  and  $\text{Cl}^-$ . The values for the remaining ligands can be reasonably well approximated as follows:  $Q$  for  $\text{NH}_3 \approx Q$  for  $\text{H}_2\text{O}$ ;  $Q$  for  $\text{I}^-$  and  $\text{Br}^- \approx Q$  for  $\text{Cl}^-$ . The values of  $k_8$  calculated on the basis of these assumptions are presented in column 6 of Table VI. The appreciable variation in  $k_8$  with the

TABLE VI  
COMPARISON OF CHROMIUM(II)-CATALYZED AQUATIONS OF  $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{n+}$  COMPLEXES

X	$k_3$ , sec <sup>-1</sup> <sup>a</sup>	$\Delta H^\ddagger$ , kcal/ mole	$\Delta S^\ddagger$ , eu	$10^3 Q$ , M <sup>b</sup>	$k_8$ , M <sup>-1</sup> sec <sup>-1</sup> <sup>c</sup>	Ref
NH <sub>3</sub>	$5.9 \times 10^{-5}$	21.6	-5.6	(10)	$\approx 7 \times 10^{-1}$	d
H <sub>2</sub> O	$1.0 \times 10^{-4}$	21	-2	10	$\approx 1 \times 10^0$	e
Cl <sup>-</sup>	$2.6 \times 10^{-4}$	21.6	-2	$\approx 0.7$	$\approx 4 \times 10^1$	f
Br <sup>-</sup>	$\approx 2 \times 10^{-3}$	...	...	(0.7)	$\approx 3 \times 10^2$	g
I <sup>-</sup>	$2.68 \times 10^{-2}$	16.2	-11	(0.7)	$\approx 4 \times 10^3$	This work

<sup>a</sup> Defined by the rate term  $k_3[\text{Cr}^{2+}][\text{CrX}^{n+}]/[\text{H}^+]$ . Values at 25°. <sup>b</sup> Defined as  $[\text{Cr}(\text{H}_2\text{O})_4\text{OHX}^{(n-1)+}][\text{H}^+]/[\text{Cr}(\text{H}_2\text{O})_5\text{X}^{n+}]$ . <sup>c</sup> Rate constant for hydroxide-bridged reaction of  $\text{Cr}(\text{H}_2\text{O})_4\text{OHX}^{(n-1)+} + \text{Cr}^{2+}$ . <sup>d</sup> Reference 32. <sup>e</sup> M. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954). <sup>f</sup> Reference 24. <sup>g</sup> Reference 8.

nature of group X suggests that substantial nonbridging-ligand effects are operative in these electron-transfer reactions. Whether these effects are localized in *cis* or *trans* positions with respect to the hydroxide bridge cannot be ascertained from the present data. On purely statistical grounds, the species *cis*- $\text{CrOHX}^{(n-1)+}$  are expected to be four times as abundant as the corresponding *trans* isomers. However, there is no necessary correlation between abundance and reactivity, and in view of the substantial effects previously found<sup>4,6,7</sup>

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(21) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

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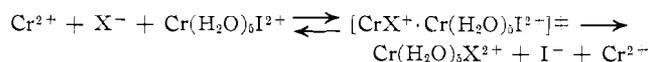
for *trans* ligands, it is tempting to ascribe the increase in rate along the series  $\text{Cr}(\text{H}_2\text{O})_4\text{XOH}^{n+}$  ( $\text{X} = \text{H}_2\text{O}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) to an increasing *trans* effect of group  $\text{X}$ . It is noteworthy that the observed reactivity order is that expected on the basis of Orgel's theory:<sup>31</sup> as the crystal field strength of the group *trans* to the bridging ligand decreases, the energy of the  $d_{z^2}$  orbital accepting the electron decreases, and the rate increases. If this rationalization is accepted, the value of  $k_s$  for  $\text{CrNH}_3(\text{H}_2\text{O})_4\text{OH}^{2+}$  would appear, at first glance, to be abnormally high. However, as noted previously,<sup>32</sup> since  $\text{NH}_3$  has a stronger crystal field than  $\text{H}_2\text{O}$ , the *cis* isomer (which has water *trans* to the hydroxide group) may well be more reactive than the *trans* isomer (which has ammonia *trans* to the hydroxide).

Although the correlation between the reactivity of  $\text{Cr}(\text{H}_2\text{O})_4\text{XOH}^{n+}$  and the crystal field strength of  $\text{X}$  provides a satisfactory rationalization of the observed trends, other factors are undoubtedly important in governing the relative reaction rates.<sup>4</sup> Moreover, it is noteworthy that the increase in rate of electron transfer in going from  $\text{Cl}^-$  to  $\text{Br}^-$  to  $\text{I}^-$  parallels the increasing thermodynamic instability of the reactants. Interestingly, in the chromium(II)-catalyzed formation of chromium(III) complexes from  $\text{Cr}^{3+}$  and free ligands<sup>33</sup> (formally the reverse of reaction 1), the rate increases as the stability of the chromium(III) product increases.

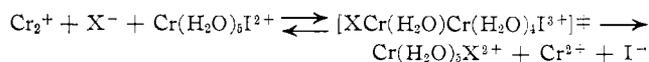
**The Chromium(II)-Catalyzed Substitution of Iodide Ion in  $\text{CrI}^{2+}$  by Fluoride, Chloride, and Bromide Ions.**—Halide ions affect both the rate and the stoichiometry of the  $\text{CrI}^{2+}$ - $\text{Cr}^{2+}$  reaction. The paths described by the rate terms  $k_X[\text{Cr}^{2+}][\text{CrI}^{2+}][\text{X}^-]$  ( $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ) and  $k_{\text{HF}}[\text{Cr}^{2+}][\text{CrI}^{2+}][\text{HF}]/[\text{H}^+]$  result, as indicated by eq 2, in quantitative formation of the corresponding halogenpentaquo chromium(III) complexes. This observation seems remarkable to us, especially in view of the thermodynamic instability (with the exception of  $\text{CrF}^{2+}$  at low  $[\text{H}^+]$ ) of the chromium(III) products under the conditions of the experiments. The kinetic results for  $\text{Cl}^-$  and  $\text{Br}^-$  establish that the principal transition state has the composition  $[\text{Cr}_2\text{IX}^{3+}]^\ddagger$ . For  $\text{F}^-$ , the interpretation of the  $k_{\text{HF}}$  term is ambiguous because a proton could be removed from either  $\text{CrI}^{2+}$ ,  $\text{Cr}^{2+}$ , or  $\text{HF}$ . Since an inverse hydrogen ion dependence is not observed for  $\text{Cl}^-$  and  $\text{Br}^-$ , it is reasonable to recast the  $k_{\text{HF}}$  term in the form  $k_{\text{F}}[\text{CrI}^{2+}][\text{Cr}^{2+}][\text{F}^-]$ , where  $k_{\text{F}} = k_{\text{HF}}/K_{\text{HF}}$  ( $K_{\text{HF}}$  is the dissociation constant of  $\text{HF}$ ). The stoichiometric results (production of  $\text{CrF}^{2+}$ ,  $\text{CrCl}^{2+}$ , and  $\text{CrBr}^{2+}$ ) show that the added halide ion makes a bond to a chromium(II) ion which is in the process of losing an electron. Consequently, the transition state is formulated as  $[\text{CrI}^{2+}\cdot\text{CrX}^+]^\ddagger$ .

Additional mechanistic information is not provided by the present results. Nevertheless, in order to obtain some understanding of the role of the ligand  $\text{X}^-$  in promoting the electron transfer, it is important to formulate some plausible geometries for the transition

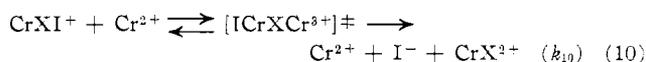
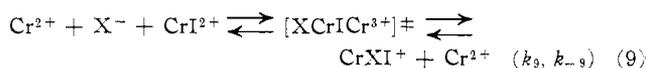
state  $[\text{CrI}^{2+}\cdot\text{CrX}^+]^\ddagger$ . Two distinct situations can be visualized: (a) The halide ion makes bonds *only* to chromium(II) in the transition state; such a transition state would obtain either in an outer-sphere mechanism, mechanism A



or in a water-bridged mechanism, mechanism B



(b) The halide ion makes bonds to both chromium(II) and the chromium(III) in the transition state; this mechanism implies prior formation of the mixed species  $\text{CrXI}^+$ , either in an equilibrium step or at steady state, mechanism C



The forward reaction in eq 9 represents an inner-sphere reaction with transfer of iodide ion from chromium(III) to chromium(II), with the added provision that the halide ion  $\text{X}^-$  also be bound to chromium(II) in the transition state. The reverse reaction in eq 9 and the forward reaction in eq 10 represent the chromium(II)-catalyzed dissociation of the postulated species  $\text{CrXI}^+$ . These reactions are entirely analogous to the previously studied chromium(II)-catalyzed dissociations of  $\text{CrF}_2^{2+}$ ,<sup>22</sup>  $\text{Cr}(\text{N}_3)_2^{2+}$ ,<sup>34</sup> and  $\text{CrCl}_2^+$ .<sup>35, 36</sup> The reverse reaction in eq 9 and the forward reaction in eq 10 differ in the position of attack by chromium(II): attack at  $\text{I}^-$  forms  $\text{CrI}^{2+}$  and does not lead to a net reaction, whereas attack at  $\text{X}^-$  produces  $\text{CrX}^{2+}$ , the observed reaction product. It must be noted that the present kinetic results do not necessitate the inclusion of chromium(II) in eq 9. The rapid formation of  $\text{CrXI}^+$  from  $\text{CrI}^{2+}$  and  $\text{X}^-$  would be equally consistent with the observed rate law. However, the rapid formation of  $\text{CrXI}^+$  in the absence of chromium(II) is extremely unlikely, especially in view of the kinetic and stoichiometric results on the spontaneous aquation of  $\text{CrI}^{2+}$  in the presence of chloride ion.<sup>37, 38</sup> The mechanism represented by eq 9 and 10 is entirely analogous to the one previously proposed by Taube and King<sup>39</sup> to account for the remarkable observation on the chromium(II)-catalyzed exchange of chlorine atoms between  $\text{CrCl}^{2+}$  and free chloride ion.

As already indicated, the experimental evidence available is insufficient to distinguish among the three postulated mechanisms. Nevertheless, on the basis of what are believed to be appropriate rate comparisons, we are inclined to favor mechanism C. The pertinent arguments are as follows.

(31) L. Orgel, "Report of the Tenth Solvay Conference," Brussels, 1956, p 289.

(32) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

(33) J. B. Hunt and J. E. Earley, *J. Am. Chem. Soc.*, **82**, 5312 (1960).

(34) A. Haim, *ibid.*, **88**, 2324 (1966).

(35) H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

(36) J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, **6**, 906 (1967).

(37) M. Ardon, *ibid.*, **4**, 372 (1965).

(38) P. Moore, F. Basolo, and R. G. Pearson, *ibid.*, **5**, 223 (1966).

(39) H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954).

TABLE VII  
COMPARISON OF RATE CONSTANTS FOR SOME HALIDE-CATALYZED REDUCTIONS  
OF COBALT(III) AND CHROMIUM(III) COMPLEXES<sup>a</sup>

Reaction	$\mu^b$	Mechanism <sup>c</sup>	$k_0$	$k_F$	$k_{Cl}$	$k_{Br}$	$k_{Cl}/k_0$	Ref
$Co(NH_3)_6^{3+} + Cr^{2+}$	2.60	OS	$7.2 \times 10^{-3}$	...	0.60	0.31	83	d
$Co(NH_3)_6^{3+} + V^{2+}$	0.4	OS	$4.4 \times 10^{-3}$	$0.2 \times 10^2$	$3.5 \times 10^{-2}$	...	7.9	e
$Co(NH_3)_5OCOCH_3^{3+} + Cr^{2+}$	1.65	IS	0.34	...	0.20	$6.4 \times 10^{-2}$	0.59	d
$Co(NH_3)_5OCO(CH_2)_2COOH^{3+} + Cr^{2+}$	3.4	IS	1.00	...	0.69	0.30	0.69	d
$Co(NH_3)_5OH_2^{3+} + Cr^{2+}$	1.0	IS	0.50	...	<0.5	...	<1	f
$Cr(NH_3)_6Cl^{2+} + Cr^{2+}$	1.15	IS	$5.83 \times 10^{-2}$	<30	< $10^{-2}$	< $10^{-2}$	<0.6	g
$Co(NH_3)_5OH_2^{3+} + V^{2+}$	1.0	Unknown	0.53	$4.5 \times 10^3$	2.5	...	4.7	e
$Co(NH_3)_5F^{2+} + Fe^{2+}$	1.7	Unknown	$7.6 \times 10^{-3}$	13	$2.1 \times 10^{-2}$	$3.5 \times 10^{-3}$	$\approx 3$	h
$Co(NH_3)_5Br^{2+} + Fe^{2+}$	1.7	Unknown	$9.2 \times 10^{-4}$	4	$\leq 1 \times 10^{-3}$	...	<1	h
$CrCl^{2+} + Cr^{2+}$	1.0	OS(?)	< $10^{-5}$	...	0.50	...	$>5 \times 10^4$	j
		IS(?)	$9^i$	...	$1.0^n$	...	0.11	j
$CrI^{2+} + Cr^{2+}$	2.0	OS(?)	< $10^{-4}$	$5.3 \times 10^4 k, l$	$2.74 \times 10^2 l$	$63^l$	$>3 \times 10^6$	This work
		IS(?)	$\approx 10^3(?)^m$	...	< $3 \times 10^2 m$	...	<3	This work

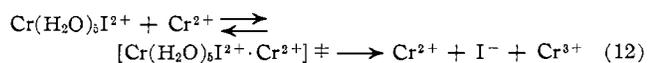
<sup>a</sup> Values at 25°, except where noted. Rate coefficients defined by eq 11. Units of  $k_0$ :  $M^{-1} sec^{-1}$ ; units of  $k_F$ ,  $k_{Cl}$ ,  $k_{Br}$ :  $M^{-2} sec^{-1}$ .  
<sup>b</sup> Ionic strength. <sup>c</sup> OS = outer sphere; IS = inner sphere. <sup>d</sup> Reference 42. <sup>e</sup> Reference 28. <sup>f</sup> Reference 41. <sup>g</sup> Reference 40.  
<sup>h</sup> Reference 43. <sup>i</sup> At 0°. <sup>j</sup> Reference 39. <sup>k</sup> Calculated from the values  $k_{HF} = 41 M^{-1} sec^{-1}$  and  $K_{HF} = 7.7 \times 10^{-4} M$ . <sup>l</sup> Values for  $[HClO_4] = 1.0 M$ . <sup>m</sup> Estimated, see text. <sup>n</sup> The measured<sup>39</sup> value is  $0.5 M^{-2} sec^{-1}$ . However, for purposes of comparison this value must be multiplied by 2.<sup>44</sup>

Recent kinetic work on the reduction of cobalt(III) and chromium(III) complexes by chromium(II), vanadium(II), and iron(II) shows that these reactions are catalyzed by added halide ions according to the rate law<sup>25, 28, 40-43</sup>

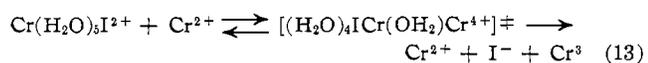
$$\frac{-d[M(III)]}{dt} = [M(III)][M(II)](k_0 + k_X[X^-]) \quad (11)$$

The results of these studies are summarized in Table VII. One feature emerges from an examination of the values of  $k_{Cl}/k_0$  listed in column 8. For reactions known to proceed by an outer-sphere mechanism, appreciable acceleration ( $k_{Cl}/k_0 \geq 8$ ) by chloride ion obtains. For reactions known to proceed by an inner-sphere mechanism, the chloride ion effect is quite small ( $k_{Cl}/k_0 \leq 0.7$ ). These comparisons provide support for the suggestion<sup>41</sup> that inner-sphere reactions may be less susceptible to halide ion catalysis than outer-sphere reactions. It is also seen that, regardless of mechanism, the chloride ion catalysis is relatively modest, and values of  $k_{Cl}/k_0$  are  $\leq 10$ , except for the  $Co(NH_3)_6^{3+} - Cr^{2+}$  reaction.

In the  $CrI^{2+} - Cr^{2+} - X^-$  reactions, we found a term in the rate law of the form  $k_X[CrI^{2+}][Cr^{2+}][X^-]$ , which is entirely analogous to the  $k_X$  term of eq 11. Now, in order to assess the acceleration caused by chloride ion in the  $CrI^{2+} - Cr^{2+}$  system, we need to compare the value of  $k_X$  with that of  $k_0$  in a term of the form  $k_0[Cr^{2+}][CrI^{2+}]$ . Depending on the mechanism (A, B, or C) different values of  $k_0$  must be used. If mechanism A or B is operative, then the value of  $k_0$  to be used corresponds to either the outer-sphere reaction

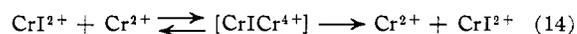


or the water-bridged reaction



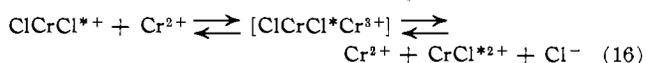
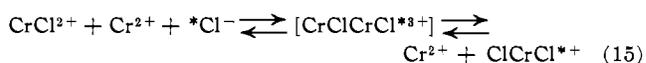
Values of the rate constants for reactions 12 or 13 are not known. However, in the chromium(II)-catalyzed aqution of  $CrI^{2+}$  we found no evidence for a reaction path independent of  $[H^+]$ , and on this basis it is possible to set an upper limit for the rate constant  $k_0$  governing a term  $k_0[CrI^{2+}][Cr^{2+}]$ . (Notice that this term necessarily involves either an outer-sphere or a water-bridged transition state.) The least-squares treatment yielded the limit  $k_0 \leq \approx 10^{-4} M^{-1} sec^{-1}$ . Therefore  $k_{Cl}/k_0 \geq 3 \times 10^6$ . Such rate enhancement appears unreasonable whether a water-bridged or an outer-sphere mechanism is invoked.

If mechanism C is adopted, then the  $k_0$  value to be used in the comparison corresponds to the inner-sphere, iodide-bridged transition state



Unfortunately reaction 14 has not been studied. However, from the measurements in the analogous chloride and bromide systems,<sup>21</sup> we estimate that  $k_0 \sim 10^3 M^{-1} sec^{-1}$ . According to mechanism C,  $k_{Cl} = k_9/(1 + k_{-9}/k_{10})$ . Since the postulated intermediate  $CrIX^+$  can return to reactants in this mechanism, the appropriate comparison involves the rate coefficient  $k_9$ . It is unlikely that  $k_{-9}/k_{10}$  will be larger than 10. Therefore,  $k_9/k_0 < 3$ , a result quite reasonable for the effect of chloride ion in an inner-sphere reaction (eq 9).

An entirely analogous argument can be developed for the chromium(II)-catalyzed exchange of free chloride ion with  $CrCl^{2+}$ .<sup>39</sup> For an outer-sphere or water-bridged mechanism  $k_{Cl}/k_0 > 5 \times 10^4$ . For the mechanism originally proposed by Taube and King<sup>39</sup>



$2k_{Cl}/k_0^{44} = 0.11 (0^\circ)$ . Again this comparison suggests that the mechanism represented by eq 15 and 16 is operative.

(44) The factor of the 2 in the numerator is necessary because only half of the events in the forward reaction lead to chlorine exchange.

(40) A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

(41) H. Taube, "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research," Houston, Texas, Vol. VI, 1962, p 7.

(42) P. V. Manning and R. C. Jarnagin, *J. Phys. Chem.*, **67**, 2884 (1963).

(43) H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).

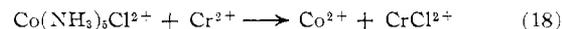
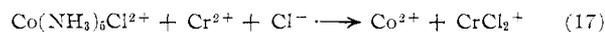
To be sure, conclusive evidence for mechanism C would be provided by the direct detection of the postulated intermediates  $\text{CrXI}^+$ . Various attempts were made to detect  $\text{CrCII}^+$  in the flow apparatus. By using 2.0 *M* chloride ion concentration we hoped to build up the steady-state concentration of  $\text{CrCII}^+$  to the point where it could be observed spectrophotometrically. However, all that could be seen in the 700–230- $\mu$  region was the disappearance of  $\text{CrI}^{2+}$ , and we must conclude that, if mechanism C obtains, the steady-state concentration of  $\text{CrICI}^+$  is too small and/or its spectral properties are too similar to those of  $\text{CrI}^{2+}$  and  $\text{CrCl}^{2+}$ .

Some indirect evidence in favor of mechanism C comes from studies<sup>45</sup> of the effect of added chloride ion on the well-known  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}-\text{Cr}^{2+}$  reaction.<sup>35</sup> In the presence of 0.50 *M* chloride ion, the reaction products consist of 97%  $\text{CrCl}^{2+}$  and 3%  $\text{CrCl}_2^+$ . This result demonstrates that even for a reaction as rapid as the  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}-\text{Cr}^{2+}$  reaction ( $k \approx 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>46</sup> the addition of chloride ion leads to its incorporation into the coordination sphere of the chromium(III) product. Additional examples of incorporation of an anion from the solution into the coordination sphere of the chromium(III) product formed by an inner-sphere reaction are:  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{P}_2\text{O}_7^{4-}$ <sup>35</sup> and  $\text{Co}(\text{NH}_3)_5\text{OCOCH}_2\text{COOH}^{2+} + \text{Cl}^-$ .<sup>42</sup> In all of these cases, the most plausible formulation of the transition state is  $[(\text{NH}_3)_5\text{CoL}(\text{CrL}'^n)]$ , where L is the bridging ligand (chloride, fumarate) and L' the nonbridging ligand (chloride, pyrophosphate). This transition state is entirely analogous to the one postulated in eq 9 of mechanism C.

(45) D. E. Pennington and A. Haim, to be published.

It is interesting to note that the order of efficiency of the halide ions in promoting electron transfer ( $\text{F}^- \gg \text{Cl}^- > \text{Br}^-$ ) is remarkably similar for all of the reactions of Table VII, in spite of the fact that both outer-sphere and inner-sphere (with variable bridging ligands) mechanisms are featured in these reactions. Possibly, there is some relation between the stability of the product formed ( $\text{F}^- \gg \text{Cl}^- > \text{Br}^-$ ) and the catalytic efficiency of the halide ion.

Finally, it is useful to point out why the halide ion effects are readily observed in the  $\text{CrI}^{2+}-\text{Cr}^{2+}$  reaction at low halide ion concentrations, whereas very high concentrations are necessary to bring out the halide ion dependent path in the case of the inner-sphere reactions of Table VII. Taking as an example the  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}-\text{Cr}^{2+}-\text{Cl}^-$  system, it is clear that the halide ion effect will be observed only if reaction 17 is competitive with reaction 18. As indicated above, the



halide ion nonbridging ligand effects are quite modest, and high concentrations of chloride ion are necessary to observe reaction 17. For the  $\text{CrI}^{2+}-\text{Cr}^{2+}-\text{Cl}^-$  system, the reactions to be compared are (2) and (14). Reaction 14 does not lead to any chemical change and can only be detected by using radioactive chromium, whereas reaction 2 produces a net chemical change and can, therefore, be readily observed at low chloride ion concentrations, *e.g.*, under conditions where reaction 2 is not competitive with reaction 14.

(46) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

## Proton Nuclear Magnetic Resonance Studies of Several Molybdenum(V) Chelates

BY LOUIS V. HAYNES AND DONALD T. SAWYER

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Proton nmr measurements have been employed to study the formation, stability, and dynamics of the ethylenediaminetetraacetate (EDTA), *dl*-1,2-propylenediaminetetraacetate (PDTA), *trans*-(1,2-cyclohexylenedinitrilo)tetraacetate (CyDTA), *N*-methyliminodiacetate (MIDA), and nitrilotriacetate (NTA) complexes of molybdenum(V). The EDTA, PDTA, and NTA chelates have been synthesized, isolated, and analyzed for the elements. Nmr spectral evidence indicates the formation of a  $\text{Mo}(\text{V})$ -MIDA complex in solution; no evidence has been observed for the formation of the CyDTA complex. The nmr spectra establish that these chelates are diamagnetic which implies the existence of dimeric molybdenum units in the chelate structures. Structures have been proposed on the basis of the nmr spectra for the EDTA and PDTA complexes.

Molybdenum(V) ( $d^1$  electronic configuration) forms a variety of complexes, many of which contain bridging oxygen atoms (bonded to two molybdenum atoms) and terminal oxygen atoms (multibonded to one molybdenum atom).<sup>1,2</sup> Magnetic moment measure-

(1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 776-800.

ments indicate some of these complexes are diamagnetic while others are paramagnetic.<sup>3,4</sup> The paramagnetic

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(3) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 4570 (1962).

(4) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 444.