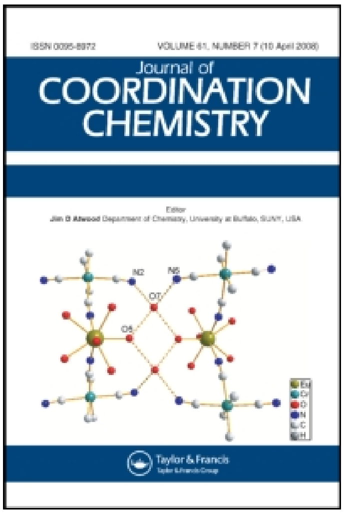

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

KINETICS AND MECHANISM OF THE CHROMIUM(II)-CATALYZED SUBSTITUTION OF BROMIDE ION IN THE BROMOPENTAAQUOCHROMIUM(III) ION BY CHLORIDE AND FLUORIDE IONS

David E. Pennington[a]
[a] Department of Chemistry, Baylor University, Waco, Texas

To cite this Article Pennington, David E.(1980) 'KINETICS AND MECHANISM OF THE CHROMIUM(II)-CATALYZED SUBSTITUTION OF BROMIDE ION IN THE BROMOPENTAAQUOCHROMIUM(III) ION BY CHLORIDE AND FLUORIDE IONS', Journal of Coordination Chemistry, 10: 3, 135 — 141

To link to this Article: DOI: 10.1080/00958978008081007

URL: http://dx.doi.org/10.1080/00958978008081007

J. Coord. Chem., 1980, Vol. 10, pp. 135–141
0095-8972/80/1003-0135 $04.50/0

KINETICS AND MECHANISM OF THE CHROMIUM(II)-CATALYZED SUBSTITUTION OF BROMIDE ION IN THE BROMOPENTAAQUOCHROMIUM(III) ION BY CHLORIDE AND FLUORIDE IONS

DAVID E. PENNINGTON

Department of Chemistry, Baylor University, Waco, Texas 76703

(Received July 23, 1979)

KEY WORDS: Bromopentaaquochromium(III); Substitution, kinetics of chromium(II)-catalyzed; Tetraaquochromium(III), mixed disubstituted.

The substitution of bromide ion in the bromopentaaquochromium(III) ion by chloride and fluoride ions is catalyzed by chromium(II). The rate law for the chloride ion substitution is $-d(\ln[CrBr^{2+}])/dt = k_{Cl}[Cr^{2+}][Cl^-]$ whereas that for fluoride ion substitution is of the form

$$-d(\ln[CrBr^{2+}])/dt = (r[HF]/[H^+])[Cr^{2+}]/(1 + s[HF]/[H^+]).$$

At 25°C and $\Sigma[\text{Anions}] = 1.00$ M the values for $k_{Cl} = 16.1 \pm 0.7$ $M^{-2}s^{-1}$ ($\Delta H^\ddagger = 10.8 \pm 0.9$ Kcal/mol; $\Delta S^\ddagger = -17 \pm 3$ cal/deg mol), $r = 3.06 \pm 0.18$ $M^{-1}s^{-1}$ and $s = 2.3 \pm 0.5$. The results are interpreted on the basis of a mechanism which features the formation of reactive intermediates of the type $CrXBr^+$ (X = Cl, F), but differing in the extent to which they are formed. Indirect evidence for the mechanism is adduced by the isolation of $CrClBr^+$ and $CrFBr^+$ from independent reactions.

INTRODUCTION

Since the earliest days of formal interest in the mechanisms of electron transfer reactions, it has been noted[1-3] that anions can influence both the rates and the stoichiometries of such processes in their role(s) as non-bridging ligands.[4] Some years ago the effects of bromide, chloride, and fluoride ions on the $Cr(H_2O)_5I^{2+}$/Cr(II) system were investigated with the remarkable observation that the iodide ion was quantitatively substituted by the added halide ion.[5] A mechanism analogous to that reported[1] for the chromium(II)-catalized exchange of chloride ion between $CrCl^{2+}$ [6] and free chloride ion was proposed, featuring intermediates of the type $CrXI^+$ (X = Br, Cl, F). Unfortunately, none of the geometries could be specified for these species, leaving unanswered the question of geometric disposition – cis or trans – of the non-bridging anion with respect to the bridging group. In at least two analogous cases it has been demonstrated that such effects are manifest from both cis and trans positions. Thus the effect of chloride ion on the "classic" $Co(NH_3)_5Cl^{2+}$-Cr^{2+} reaction yields 3% *cis-* and 3% *trans*-$CrCl_2^+$.[7] Moreover the oxidation of chromium(II) by triiodide ion in mixed H_2O/DMSO solvents yields *cis-* and *trans*-$Cr(DMSO)I^{2+}$.[8]

The mixed disubstituted tetraaquochromium(III) species have themselves come into widespread use as reaction intermediates in a variety of additional systems. For example, one of the earliest postulated octahedral trans effects was that of iodide ion in CrI^{2+}, permitting substitution of chloride ion trans to iodide ion prior to aquation of the latter.[9] Similar substitutions have since been observed for chloride ion on $CrBr^{2+}$ and $CrONO_2^{2+}$,[10] for thiocyanate ion on CrX^{n+} (X = CN[11], SH[34], MeOH[12]) and for fluoride ion on $Cr(CF_3)^{2+}$,[13] as well as for aquation of $Cr(CF_3)^{2+}$. Oxyanion catalysis of the aquation of various aquochromium(III) species (with an available water molecule *cis* to the leaving group) has been postulated to proceed *via* Cr(Oxyanion)X^{n+} intermediates.[14] Several additional predominately *cis* isomeric mixtures of $Cr(NCS)X^+$ (X = *S*CN[15] and F[16]) have also been studied. Finally, $Cr(OAc)Cl^+$ has been postulated in the effect of acetate ion on the $Cr(NH_3)_5Cl^{2+}$-Cr^{2+} reaction.[17]

In the present work the effects of chloride and fluoride ions on the $CrBr^{2+}$/Cr(II) system have been studied. A new data treatment for the effect of fluoride ion has been introduced and both intermediates in the proposed mechanisms for these effects have been independently generated.

EXPERIMENTAL

Materials. All chemicals were reagent grade. Triply distilled water was used to prepare all solutions.

Chromium(II) perchlorate solutions were prepared by reduction of acidified chromium(III) perchlorate solutions with lightly 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.[18]

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

Sodium fluoride was prepared by neutralizing sodium carbonate with excess hydrofluoric acid, followed by evaporation of the excess acid. The solution was cooled to 0° to precipitate the salt. The sodium fluoride was then separated by filtration and dried in the oven at 110°.

Perchloric and hydrochloric acid solutions were prepared by dilution of the respective standard acids.

The ion exchange resin, Dowex 50W-X8(50–100 mesh, H^+ form), was treated as follows. A slurry of the resin was boiled in basic hydrogen peroxide for 30 minutes. *Caution!* The slurry should be agitated during this heating period to allow escape of molecular oxygen. The resin was then washed successively with 1 M sodium citrate, 2 M hydrochloric acid, and 2 M perchloric acid; the washings with the different reagents were interspersed by washings with water.

Solutions of bromopentaaquochromium(III) ion were prepared following the method of Taube and Myers[19] (reaction of chromium(II) with a slight excess of aqueous bromine in 0.1 M perchloric acid). Excess bromine was expelled in a current of air, the last traces being removed by reaction with thiosulfate ion. The complex ion was then purified by cation-exchange chromatography. The ion-exchange resin and the solutions used to rinse the column and to elute the bromopentaaquochromium(III) ion were maintained near 0°. The concentrated middle fraction of the eluent containing the $CrBr^{2+}$ ion was stored in a deep-freeze at −20°. The frozen solution was thawed as portions were needed for kinetic or stoichiometric experiments. The total chromium content was measured spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.[20] The visible absorption spectrum of the $CrBr^{2+}$ ion was identical to that reported in the literature[21] [λ_{max}, nm(ϵ, $M^{-1}\,cm^{-1}$) = 622 (19.9) and 432 (22.4)].

Stoichiometry. Duplicate stoichiometric experiments were performed on the $CrBr^{2+}$-Cr^{2+}-Cl^- system in which 0.146 mmole of $CrBr^{2+}$, 2.50 mmoles of chloride ion, and 0.126 mmole of Cr^{2+} were mixed in serum bottles under argon with the Σ[Anions] = 1.0 M. After *ca.* 10 half-lives a solution of aquopentaamminecobalt(III) perchlorate was injected to quench the Cr^{2+}. The resulting solutions were diluted then ion-exchanged; both $CrCl^{2+}$ and Cr^{3+} were eluted. The $CrCl^{2+}$ was identified by its visible absorption spectrum.[22] Total chromium analyses were performed on the respective chromium(III) solutions as described for $CrBr^{2+}$ above.

Kinetics. All kinetics experiments were carried out using a Cary 14 recording spectrophotometer (equipped with a thermostatted cell holder and compartment) by following the changes in absorbance at 280 nm due to the disappearance of $CrBr^{2+}$. Since all reactions studied are catalyzed by chromium(II) and the chloride ion and hydrofluoric acid concentrations were in excess (of $CrBr^{2+}$), pseudo-first-order rate constants were obtained from the slopes of $\log(A_t - A_\infty)$ vs. time plots, where A_t and A_∞ are the absorbances of times t and after 8–10 half-lives, respectively.

RESULTS

Stoichiometry. The results of duplicate experiments performed to establish the stoichiometry of the $CrBr^{2+}$-Cr^{2+}-Cl^- reaction indicate that 105 and 101% $CrCl^{2+}$ were formed and that 94.5 and 100% Cr^{3+}, respectively, were recovered from the quenching of chromium(II) with $Co(NH_3)_5H_2O^{2+}$. Since not more than 5.5% $CrCl^{2+}$ could arise from the quenching process, it is concluded that the production of $CrCl^{2+}$ is quantitative and that the stoichiometry is established as

$$CrBr^{2+} + Cr^{2+} + Cl^- \rightarrow CrCl^{2+} + Cr^{2+} + Br^-. \qquad (1)$$

In the view of the necessity for correcting the stoichiometric results in the CrI^{2+}-Cr^{2+}-HF/F^- system for a quenching blank and the formation of CrF_2^+, the stroichiometry in the $CrBr^{2+}$-Cr^{2+}-HF^- system was *assumed* to proceed analogously.

Kinetics. In Table I are presented the results of kinetic measurements for the chromium(II)-catalyzed substitution of bromide ion in $CrBr^{2+}$ by chloride ion in the temperature range 15–35° and at Σ[Anions] = 1.00 M. Under the conditions of these

TABLE I

Kinetics of the chromium(II)-catalyzed substitution of bromide ion in $CrBr^{2+}$ by chloride ion at Σ[anions] = 1.00 M[a]

Expt.	t, °C	$[H^+]$, M	$10^2(Cl^-)$[b]	$10^2(Cr^{2+})$	$10^3\ k_{obsd}$, sec^{-1}	k, $M^{-2}sec^{-1}$
1	15.2	0.965	2.43	1.16	2.35	8.34
2		0.956	4.89	1.16	4.80	8.47
3		0.959	4.82	1.17	4.76	8.45
4		0.961	7.35	1.16	7.15	8.38
5		0.964	12.1	1.17	12.3	8.66
6		0.964	12.2	1.16	11.9	8.40
						Avg. 8.45 ± 0.08[c]
7	25.4	0.957	1.43	1.08	2.36	15.3
8		0.967	2.40	1.07	4.16	16.0
9		0.967	4.82	1.08	8.49	16.3
10		0.975	7.24	1.08	11.9	15.2
11		0.993	12.1	1.08	21.5	16.6
12		0.944	1.43	1.83	4.38	16.8
13		0.910	1.43	3.66	8.15	15.6
14		0.853	1.43	6.10	15.2	17.4[d]
15		0.966	4.82	1.08	8.04	15.4
						Avg. 16.1 ± 0.7[c]
16	35.2	0.978	1.43	1.17	5.11	30.6
17		0.965	2.40	1.17	9.08	32.3
18		0.964	7.24	1.17	24.7	29.2
19		0.898	2.40	2.35	18.0	31.9[d]
						Avg. 31.0 ± 1.4[c]

[a] $[CrBr^{2+}] = 3.46 - 8.88 \times 10^{-4}$ M; measurements at 280 nm; temp. ± 0.1°C.

[b] Corrected to yield $[Cl^-]_{avg}$ over two half-lives.

[c] Std. Dev.

[d] Measurements at 300 nm with a CrO_4^{2-} filter in ref. compartment.

experiments the contributions of the spontaneous and chromium(II)-catalyzed aquations to the disappearance of $CrBr^{2+}$ are less than five percent even at the lowest chloride ion concentration. Hence the observed rate constants are uncorrected for these minor effects. The data in Table I were treated on the basis of the rate equation.

$$-d(\ln[CrBr^{2+}])/dt = k_{Cl}[Cr^{2+}]\,[Cl^-] \qquad (2)$$

The values of k_{obsd} are given in column 6. The values of k_{Cl} listed in column 7 were calculated by dividing the observed rate constants by the respective concentrations of chromium(II) and chloride ion. It is seen that these values are reproducible to within about one percent at 15° and within about five percent at 25 and 35°. The acidities in these runs were maintained between 0.85 and 0.99 M to suppress the chromium(II)-catalyzed aquation, and no attempt was made to assess the relative importance of medium effects in the system. The activation parameters associated with k_{Cl} were derived from the slopes of log k vs. 1/T plots and the equations $E_a = \Delta H^{\ddagger} + RT$ and $k = (RT/N_0h)\exp(\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R)$, yielding $\Delta H^{\ddagger} = 10.8 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -17 \pm 3$ cal/deg·mol.

In Table II are presented the kinetic results of the chromium(II)-catalyzed substitution of bromide ion in $CrBr^{2+}$ by fluoride ion. The fluoride ion concentration, $[HF]/[H^+]$, is varied sixfold in expts. 1–5 while [HF] (column 3) is held constant. The values of k_{obsd}^{corr} (k_{obsd} corrected for chromium(II)-catalyzed aquation of $CrBr^{2+}$) in column 6 are seen to increase with increasing $[HF]/[H^+]$, though less than first order. From a comparison of expts. 1, 6–7, where the hydrofluoric acid concentration is varied sixfold and $[HF]/[H^+]$, i.e., $[F^-]$, is held constant, it is seen that k_{obsd}^{corr} is virtually constant. Although there is a modest trend toward increased k_{obsd}^{corr} with increasing [HF], it may reflect a medium effect and/or an overcorrection for the

TABLE II
Kinetics of the chromium(II)-catalyzed substitution of bromide ion in $CrBr^{2+}$ by fluoride ion[a]

Expt.	$10^2[Cr^{2+}]$, M	$10^2[HF]$, M	$[H^+]$, M	$10^3 k_{obsd}$, s^{-1}	$10^3 k_{obsd}^{corr}$, s^{-1} [b]
1	1.21	6.00	0.900	2.35	2.33
2	1.21	6.00	0.600	2.90	2.86
3	1.21	6.00	0.300	4.74	4.67
4	1.21	6.00	0.300	5.63	5.56
5	1.21	6.00	0.150	0.755	7.43
6	1.21	3.00	0.450	2.16	2.11
7	1.21	1.00	0.150	2.12	1.98
8	2.41	6.00	0.607	6.20	6.13
9	1.16	6.00	0.140	7.57	7.40
10	0.35	6.00	0.600	0.965	0.950

[a] At 25.0 ± 0.2°C, Σ[Anions] = 1.00 M; measurements at 280 nm; $[CrBr^{2+}] = 3.36 - 4.20 \times 10^{-4}$ M.
[b] Corrected for the chromium(II)-catalyzed aquation of $CrBr^{2+}$.

chromium(II)-catalyzed aquation of $CrBr^{2+}$ since the latter results were obtained at $\mu = 2.0$ M (Li^+) instead of 1.0 M (Na^+) as essentially employed here. Various attemps to include an [HF] term in the rate law were not successful except for expressing $[F^-]$. Expts. 2, 8 and 10 serve to confirm the first-order dependence of k_{obsd}^{corr} on $[Cr^{2+}]$. The data have been fit to a rate law of the form

$$-d[CrBr^{2+}]/dt = k_{obsd}^{corr}[CrBr^{2+}],$$

$$\text{where } k_{obsd}^{corr} = \frac{(r[HF]/[H^+])[Cr^{2+}]}{1 + s[HF]/[H^+]} \qquad (3)$$

Values of $r = 3.06 \pm 0.18$ M^{-1} s^{-1} and $s = 2.3 \pm 0.5$ were derived from the slope ($3.27 \pm 0.20 \times 10^{-1}$ Ms) and intercept ($7.3 \pm 2.0 \times 10^{-1}$ Ms), respectively, of a linear least squares fit of the data to the equation

$$[Cr^{2+}]/k_{obsd}^{corr} = (1/r)[H^+]/[HF] + s/r. \qquad (4)$$

A correlation of 0.984 was obtained compared to only 0.963 obtained for $k_{obsd}^{corr}/[Cr^{2+}] = 0.123\ M^{-1}s^{-1} + 1.27\ M^{-1}s^{-1}[HF]/[H^+]$. (See Discussion for a more serious problem with the latter empirical rate law.) The data from the CrI^{2+}-Cr^{2+}-HF/F^- system was reanalyzed on the basis of eq. 4, yielding a slope of $2.12 \pm 0.01 \times 10^{-2}$ Ms and intercept = $2.71 \pm 0.75 \times 10^{-1}$ Ms (correlation = 0.984) from which $r^I = 4.72 \pm 0.03 \times 10^1$ $M^{-1}s^{-1}$ and $s^I = 1.28 \pm 0.36 \times 10^1$ were calculated. Errors in the above data treatments are standard errors as described by Squires.[23] Interestingly, there is a precedent for the form of dependence of k_{obsd}^{corr} on $[HF]/[H^+]$ in the $Cr(NH_3)_5Cl^{2+}$-Cr(II) reaction reported by Cannon and Stillman[17] in an acetic acid/acetate ion buffer. There the observed rate coefficient becomes less than first-order in acetate ion concentration at high values.

DISCUSSION

Although the rate laws differ slightly for the chromium(II)-catalyzed chloride and fluoride ion substitutions of bromide ion in $CrBr^{2+}$, both can be accommodated by a common mechanism differing only in detail. Of the three mechanisms advanced earlier,[5] an outer-sphere process; a water-bridged, inner-sphere process; and a halide ion-bridged, inner-sphere process – the last was most highly favored and is considered first.

$$Cr^{2+} + X^-(HX) \rightleftharpoons CrX^+ + (H^+) \qquad (K_5) \quad (5)$$

$$CrBr^{2+} + CrX^+ \rightleftharpoons [CrBrCrX^{3+}]^\ddagger \rightleftharpoons Cr^{2+} + CrXBr^+ \quad (k_6, k_{-6}) \quad (6)$$

$$CrXBr^+ + Cr^{2+} \rightleftharpoons [BrCrXCr^{3+}]^\ddagger \rightleftharpoons Br^- + Cr^{2+} + CrX^{2+} (k_7) \quad (7)$$

The first step in the earlier report[5] has been broken down into two steps which were implicit there. This mechanism implies the prior formation of $CrXBr^+$, either in an equilibrium step or at steady-state. In reaction 6 the forward step represents a bromide ion-bridged, inner-sphere process with transfer of bromide ion from chromium(III) to chromium(II). Equation 7 and the reverse of equation 6 represent chromium(II)-catalyzed dissociations of disubstituted tetraaquochromium(III) ions entirely analogous to those reported for CrF_2^+,[24] $Cr(N_3)_2^+$,[25] $CrCl_2^+$,[26] $CrXI^+$.[5] Changing one mechanistic detail, namely the extent to which the proposed intermediate $CrXBr^+$ is formed, can accommodate the observed rate laws which are first-order in chloride ion concentration and less than first-order in fluoride ion concentration, respectively. Thus in the case of substitution by fluoride ion, but not chloride ion, a kinetically significant fraction of the $CrBr^{2+}$ reactant is diverted to a $CrXBr^{+}$ species of unspecified geometry. (Statistically, a four : one mixture of *cis* : *trans* isomers is expected.) As noted previously,[5] the inclusion of $[Cr^{2+}]$ in the rate law is not mandated by the data, i.e., here $CrXBr^{+}$ could be formed from $CrBr^{2+}$ and X^{-} (or HX). However, spontaneous substitution of chloride ion for bromide ion in $CrBr^{2+}$ produces $\leqslant 22\%$ $CrCl^{2+}$ even in 1.0 M HCl,[10] whereas the present substitution by chloride ion is essentially quantitative.

On the basis of the above mechanism the empirical rate coefficient $k_{Cl} = K_5 k_6/(1 + k_{-6}/k_7)$. In order to assess the magnitude of the halide ion effect the appropriate comparison of rate parameters is $K_5 k_6/k_0$, where k_0 is the rate coefficient for the exchange reaction

$$CrBr^{2+} + {}^{*}Cr^{2+} \rightleftharpoons [CrBr^{*}Cr^{4+}]^{\ddagger} \rightleftharpoons {}^{*}CrBr^{2+} + Cr^{2+}.$$

Ball and King[27] reported a lower limit of 60 $M^{-1}s^{-1}$ for the exchange process. If it is assumed[28] that $k_{-6}/k_7 \sim 10$, then $K_5 k_6/k_0 \leqslant 2.7\ M^{-1}$, a value quite comparable to that ($\sim 3\ M^{-1}$) obtained in the CrI^{2+}–Cr^{2+}–Cl^{-} system.[5] If one were to accept a provisional value of 1.5 M^{-1} for K_5,[30] then $k_6 \sim 110\ M^{-1}s^{-1}$.

Indirect support for the mechanism comes from the preparation (in low yields) of $CrClBr^{+}$ from the reaction of chromium(II) with aqueous bromine in 0.5 M hydrochloric acid. The reaction solution was diluted to 0.2 M, passed through a Dowex 50W-X8 resin (to remove $CrBr^{2+}$), and collected – all at 0–5°C. The complex exhibited spectral maxima at ~ 655 nm and ~ 452 nm and an aquation rate constant for loss of bromide ion ($CrCl^{2+}$ was the exclusive product) equal to $4.3 \times 10^{-4} s^{-1}$ in a single experiment at 0.2 M HCl.

On the basis of the above mechanism (eqs. 5–7), the empirically derived parameter *r* and *s* in the $CrBr^{2+}$-Cr^{2+}-HF/F^{-} system are interpreted as follows. Since the rate is expressed in terms of $-d[CrBr^{2+}]_{stoic}/dt$ and since $[CrBr^{2+}]_{stoic} = [CrBr^{2+}] + [CrFBr^{+}]$, the expression $-d[CrBr^{2+}]/dt = (K_5 K_6 k_7 [HF]/[H^{+}])[Cr^{2+}]/(1 + K_5 K_6 [HF]/[H^{+}])$ can be readily derived whereupon $r = K_5 K_6 k_7$ and $s = K_5 K_6$. Thus $K_5 K_6 = 2.3 \pm 0.5$ and $k_7 = 1.4 \pm 0.4\ M^{-1}s^{-1}$. Similarly, the reevaluated data in the CrI^{2+}-Cr^{2+}-HF/F^{-} system yielded $K_5^{I} K_6^{I} = 1.28 \pm 0.36 \times 10^{1}$ and $k_7^{I} = 3.7 \pm 0.8\ M^{-1}s^{-1}$. In the HF/$F^{-}$ systems $K_5 = K_{HF}K_1$, where K_1 is the formation constant for CrF^{+} from Cr^{2+} and F^{-}. Taking $K_{HF} = 1.1 \times 10^{-3}$ M[29] and a provisional value of 7.4 M^{-1} for K_1,[30] one may calculate $K_5 = 8.1 \times 10^{-3}$ and values of $K_6 = 2.8 \times 10^{2}$ for the bromo-complex and $K_6^{I} = 1.6 \times 10^{3}$ for the iodo complex.

In Table III are summarized the rate constants for various fluoride ion-bridged electron transfer reactions of chromium(III)-chromium(II), as well as a few related systems. By comparison, the rate constants for fluoride ion-bridged electron transfer between $CrFBr^{+}$ and the $CrIF^{+}$ and Cr^{2+} are among the highest reported to date. These results would therefore imply significant nonbridging ligand effects for bromide and iodide ions; however, the geometries are not specified for the $CrXF^{+}$ species

TABLE III
A comparison of rate constants for various fluoride ion-bridged and related electron transfer reactions of chromium(III)-chromium(II) at 25°C

Oxidant	trans	k, $M^{-1}s^{-1}$	cis	Ref.
CrF_2^{+} [a]	7.5×10^{-4}		5.0×10^{-3}	24
$Cr(NCS)F^{+}$ [b]		5.4×10^{-2}		16
$CrIF^{+}$ [b,c]		3.7		5
$CrBrF^{+}$ [b]		1.4		e
CrF^{2+} [d]		2.6×10^{-2}		27
$Cr(NH_3)_5F^{2+}$ [d]		1.8×10^{-2}		31
$CrCl_2^{+}$ [a]	2.0×10^{2}		1.4×10^{2}	26
$Cr(N_3)_2^{+}$ [a]	–		3.8	25

[a] Corrected for statistical factor.
[b] Geometry unspecified (but probably predominately cis).
[c] Recalculated from the data in Ref. 5.
[d] At 27°C.
[e] This work.

such that definitive arguments could be made for the effects. It is noteworthy, and perplexing, that the CrF_2^+ isomers differ in reactivity by nearly an order of magnitude and that both isomers react more slowly than does CrF^{2+}.

Again, indirect support for the proposed mechanism comes from the preparation of ~30% $CrFBr^+$ in the chromium(II) reduction of excess $Co(NH_3)_5Br^{2+}$ in the presence of hydrofluoric acid at 0°C. The reaction is directly analogous to that in the present study.

While it was noted in the Results that an empirical rate law of the form $k = (k_0 + k_F[HF]/[H^+])[CrBr^{2+}][Cr^{2+}]$ gave a reasonable fit of the data, the k_0 term is devoid of physical meaning. The observed rate coefficient was corrected for chromium(II)-catalyzed aquation of $CrBr^{2+}$, albeit only for the inverse acid term. However, the derived value of $k_0 = 1.23 \times 10^{-1}$ $M^{-1}s^{-1}$ greatly exceeds even the most generous estimate ($\leqslant 5 \times 10^{-4}$ $M^{-1}s^{-1}$) which could be made from the data of Adin and Sykes[32] for an acid independent, chromium(II)-catalyzed aquation. On the basis of this argument and the poorer data fit the above form of rate law is discarded.

Finally, the two alternative mechanisms, an outer-sphere process and a water-bridged inner-sphere process, are rendered less likely than that discussed for the following reasons. First, there is no confirmed evidence for the operation of a water-bridged, inner-sphere process since Toppen and Linck[33] demonstrated that the acid independent term in the rate law of the $Co(NH_3)_5OH_2^{3+}–Cr^{2+}$ reaction was best considered the result of a medium effect rather than the rate constant for a truly water-bridged, inner-sphere process. Second, the outer-sphere mechanism would have led to $k_{Cl}/k_0 \geqslant 3 \times 10^4$, a value totally out of character for a chloride ion effect on an outer-sphere reaction.[5] The outer-sphere k_0 value was taken equal to the previously mentioned estimate of $\leqslant 5 \times 10^{-4}$ $M^{-1}s^{-1}$ for the acid independent term in the chromium(II)-catalyzed aquation of $CrBr^{2+}$.[32]

NOTE ADDED IN PROOF

Asher and Deutsch (*Inorg. Chem.*, **15**, 1531 (1976)) have reported an extensive study on the substitutions of bromide and chloride ions, as well as hydrofluoric and acetic acids, on thiolatopentaaquochromium(III) species (SR = 4-thioanalinium or 2-thioethylaminium). Rate saturation was observed for chloride ion but not for bromide ion, hydrofluoric acid, or acetic acid – a result in marked contrast to results reported herein. Strikingly, however, the efficiency of these spontaneous substitutions rivals that of the chromium(II)-catalyzed processes for CrI^{2+} and $CrBr^{2+}$.

ACKNOWLEDGMENT

The author is grateful to the Faculty Development Committee at Baylor University for a sabbatical leave and to The Robert A. Welch Foundation for financial support of this work.

REFERENCES

1. H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (195
2. H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).
3. H. Taube, *Adv. Inorg. Chem. Radiochem.*, **1**, 1 (1959).
4. For reviews of nonbridging ligand effects consult:
   a. J. E. Earley, *Prog. Inorg. Chem.*, **13**, 243 (1970).
   b. D. E. Pennington, in A. E. Martell, Ed., "Coordination Chemistry" Vol. 2, ACS Monograph No. 174, American Chemical Society, Washington, D.C., 1978, Ch. 3, pp. 536–548.
5. D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).
6. Here and subsequently coordinated waters on aquochromium species will be omitted for brevity of notation.
7. D. E. Pennington and A. Haim, *Inorg. Chem.*, **7**, 1659 (1968).
8. D. B. Vanderheiden and E. L. King, *J. Am. Chem. Soc.*, **95**, 3860 (1973).
9. P. Moore, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **5**, 223 (1966).
10. L. R. Carey, W. E. Jones, and T. W. Swaddle, *Inorg. Chem.*, **10**, 1566 (1971).
11. A. A. Schilt and W. B. Schaap, *Inorg. Chem.*, **12**, 1424 (1973).
12. R. J. Baltisberger, C. L. Knudson, and M. F. Anderson, *Inorg. Chem.*, **13**, 2354 (1974).
13. S. K. Malik, W. Schmidt, and L. O. Spreer, *Inorg. Chem.*, **13**, 2986 (1974).
14. S. N. Choi and D. W. Carlyle, *Inorg. Chem.*, **13**, 1818 (1974) and references therein.
15. L. D. Brown and D. E. Pennington, *Inorg. Chem.*, **10**, 2117 (1971).
16. F. N. Welch and D. E. Pennington, *Inorg. Chem.*, **15**, 1515 (1976).
17. R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, **14**, 2202 (1975).
18. I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, NY, 1952, p. 579.
19. H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).
20. G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).
21. F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).
22. T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

23. G. L. Squires, "Practical Physics," McGraw-Hill, New York, NY, 1968, Chapter 4.
24. Y. T. Chia and E. L. King, *Discussions Faraday Soc.*, 29, 109 (1960).
25. A. Haim, *J. Am. Chem. Soc.*, 88, 2324 (1966).
26. J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, 6, 906 (1967).
27. D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, 80, 1091 (1958).
28. The assumption is entirely reasonable if it is noted that at 0°C the rate constants for the CrX^{2+}-Cr^{2+} exchanges differ by a factor $\geqslant 5.5$ for X = Br and Cl[27] and that any discrimination in rates between Br and Cl in $CrClBr^+$ is expected to be diminished for the faster $CrClBr^+$-Cr^{2+} reaction. The statistically corrected rate constant for the *t*-$CrCl_2^+$-Cr^{2+} reaction is 200 $M^{-1} s^{-1}$.[26] Thus k_{-6} is probably ~ 1200 $M^{-1} s^{-1}$.
29. A. E. Martell and L. G. Sillén, "Stability Constants" Supplement No. 1, Special Publication of the Chemical Society, No. 25, 1971.
30. C. F. Wells and M. A. Salam, *Chem. Ind.* (*London*), 2079 (1967). Note: Part of the kinetic data in this paper has been questioned (W. Schmidt, J. H. Swinehart and H. Taube, *Inorg. Chem.*, 7, 1984 (1968)), but the value is not altogether unreasonable in view of the value of K_1 = 12 for thiocyanate ion reported by K. B. Yatsimirsku and T. I. Federova, *Izvest. Vysshikh Ucheb. Zavedenii, Khim, i. Khim. Tekhnol.*, No. 3, 40 (1958): CA: 53, 1977c (1959).
31. A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, 80, 1084 (1958)
32. A. Adin and A. G. Sykes, *J. Chem. Soc.*, Sect. A, 1504 1967.
33. D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 10, 2635 (1971).
34. T. Ramasami and A. G. Sykes, *Inorg. Chem.*, 15, 1010 (1976).