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Substitution at Chromium(III) Centers in Aprotic Solvents. Ion Pairing, Anation, and Solvent Exchange in *N,N*-Dimethylformamide

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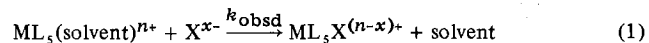
Received January 28, 1976

AIC600731

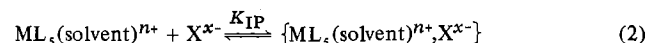
Rate coefficients and enthalpies and entropies of activation have been obtained for anation of $\text{Cr}(\text{DMF})_6^{3+}$ in DMF by Br^- , NCS^- , and N_3^- and for DMF solvent exchange with $\text{Cr}(\text{DMF})_6^{3+}$ in the presence of Br^- , Cl^- , and ClO_4^- , as well as exchange rate data at single temperatures in the presence of NCS^- and N_3^- . Ion-pair formation quotients were also estimated from the kinetics of one or both reactions for Br^- , Cl^- , NCS^- , N_3^- , and ClO_4^- , the last result superseding an earlier inaccurate estimate. Solvent-exchange rates were depressed by ion pairing, but only slightly so, and to roughly the same extent for all of the above anions. These and previously published data confirm the validity of the interchange model of substitution in octahedral cations in solution and indicate an associative interchange mechanism for all of the foregoing reactions. The nucleophilicities of anions X^- toward the Cr(III) complex are simply related to the pK_a of the aqueous acids HX .

Introduction

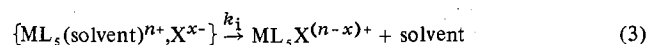
The experimental data presently available on the kinetics of simple anation reactions of cationic octahedral transition metal complexes¹



are generally consistent with, but do not necessarily require, a model known as the interchange mechanism^{1,2} according to which the rapid initial formation of an ion pair (encounter complex)



precedes rate-determining entry of X^- into the first coordination sphere of the complex



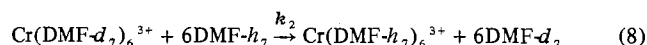
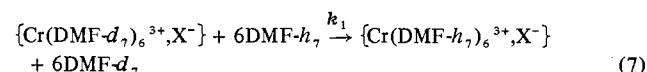
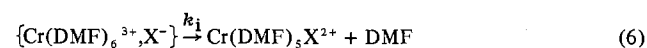
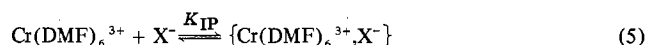
In the case of a dissociative interchange (I_d) mechanism,² the fission of the metal-solvent bond is rate determining, and consequently k_i will in general³ be less than the rate coefficient k_{ex} for the exchange of complexed and uncomplexed solvent



and k_i would be expected to vary only slightly from one ligand X^- to another. These requirements seem to be realized for $\text{M} = \text{Co}(\text{III})$, $\text{L} = \text{NH}_3$, and solvent = H_2O ⁴ and for $\text{M} = \text{Co}(\text{III})$, $\text{L} = \text{en}$ and NO_2^- , and solvent = dimethyl sulfoxide.⁵ Conversely, when $\text{M}-\text{X}^-$ bond making initiates the interchange process, bringing about essentially simultaneous metal-solvent bond breaking, k_i may exceed k_{ex} if X^- is a sufficiently good nucleophile toward ML_5 , and in any event k_i can be expected to vary strongly with the nature of X^- .¹ These phenomena characterize simple substitution reactions of many Cr(III) complexes,¹ $\text{Rh}(\text{NH}_3)_5\text{OH}_2^{3+}$,^{6,7} and $\text{Ir}(\text{NH}_3)_5\text{OH}_2^{3+}$,^{8,9} to which an I_a mechanism may therefore be assigned.

A major weakness of this model lies in the fact that the reactivity of $\text{ML}_5(\text{solvent})^{n+}$ within the ion pair could conceivably be quite different from that of the free complex ion. Watts, in particular, has stressed¹⁰ that the free energy of formation of ion pairs from the constituent ions can be so large

(e.g., -20 kJ mol^{-1} for $\{\text{Cr}(\text{DMF})_6^{3+}, \text{Cl}^-\}$ in DMF at 70°C , as reported below) that a complex ion within an ion pair might justifiably be regarded as a species chemically different from the free complex ion. Thus, for a complex within an ion pair, the value of k_{ex} (hereinafter called k_1) might well be considerably greater or less than that for the free complex (k_2), and accordingly Monacelli,⁶ in his study of the anation of $\text{Rh}(\text{NH}_3)_5\text{OH}_2^{3+}$ by chloride, was careful to establish that k_{ex} was not greatly affected by the presence of chloride ion (cf. Duffy and Earley's work¹¹ with $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$). Unfortunately, ion-pair formation constants K_{IP} for 3:1 electrolytes in water are small, so that k_1 and k_2 are measurable only by extrapolation, and so, because k_1 for chloride anation of $\text{Rh}(\text{NH}_3)_5\text{OH}_2^{3+}$ and $\text{Ir}(\text{NH}_3)_5\text{OH}_2^{3+}$ was found⁶⁻⁹ to be only marginally (2-3 times) greater than the free-ion value of k_{ex} , there is some room for skepticism over the assignment of an I_a mechanism on the sole basis of the above data, while for anation of $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$ in water k_1 is much less than k_{ex} ,¹¹ even though there is other evidence¹ that the mechanism is indeed I_a . We have therefore completed a detailed study of the title reactions, which, in the interchange model, are represented by reactions 5-8 with *N,N*-dimethylformamide



(DMF) as solvent. Here, X^- was Br^- , NCS^- , and N_3^- , and measurements of k_1 for $\text{X}^- = \text{Cl}^-$ were also made to utilize the corresponding k_2 data reported previously.¹² These systems were chosen because the relatively low dielectric constant of DMF leads to high values of K_{IP} , so that k_1 can be measured directly and with satisfactory accuracy. Furthermore, as noted previously,¹³ the use of perdeuterated DMF permits relatively high precision to be attained in k_{ex} measurements. Finally, the use of the aprotic solvent DMF and the hexakis(solvent) substrate $\text{Cr}(\text{DMF})_6^{3+}$ allows the apparently high nucleophilicity toward chromium(III) of Bronsted bases such as

N_3^- ^{12,14} to be studied in the absence of complications due to conjugate base pathways.¹

Experimental Section

Materials. Tetraethylammonium chloride and bromide (both reagent grade, Baker Chemical Co.) were recrystallized from hot DMF by the addition of ether and dried under vacuum. Reagent grade potassium thiocyanate (Fisher Scientific Co.) was recrystallized from hot acetone by adding ether and was vacuum dried. *N,N*-Dimethylformamide (reagent grade, Baker Chemical Co.), stored over 4A molecular sieve (Guild Corp.), was fractionally distilled under vacuum as previously described.¹⁵ Anhydrous $LiClO_4$ (City Chemical Co.) was recrystallized from hot water as $LiClO_4 \cdot 3H_2O$ by a slow evaporation of the solution. Water of recrystallization was removed by heating the hydrated salt at 110 °C for 5 days. Tetraethylammonium hexakis(thiocyanato-*N*)chromate(III) was prepared as previously described.¹³

Preparation of Tetraethylammonium Perchlorate. To a solution containing Et_4NCl (15 g) in water (25 cm³) aqueous $NaClO_4$ (20 g in 20 cm³) was added with stirring. The precipitate was collected and washed once with ice-cold H_2O , ethanol, and then ether. This compound was reprecipitated twice from hot water (~50 cm³) by adding aqueous $NaClO_4$ (15 g in 15 cm³) to remove traces of chloride. A final recrystallization from hot acetone by adding ether yielded a pure product (12 g) which gave a negative test for Cl^- with aqueous Ag^+ solution.

Preparation of Tetraphenylarsonium Azide. To a solution containing $(C_6H_5)_4AsCl \cdot HCl$ (1 g) in water (10 cm³) was added with stirring aqueous NaN_3 (10 g in 10 cm³). The mixture was stirred for 5 min and filtered, and the product was washed with 20% acetone-ether and then ether. This compound was reprecipitated from warm acetone (20 cm³) by adding aqueous NaN_3 (10 g in 10 cm³) to remove traces of chloride.

The product was recrystallized twice from hot acetone by the addition of a large excess of ether. The white feathery needles were collected, washed with 10% acetone-ether and then ether, and dried under vacuum (0.7 g). Anal. Calcd for $(C_6H_5)_4AsN_3$: N, 9.9. Found: N, 9.8.

Hexakis(*N,N*-dimethylformamide)chromium(III) perchlorate and partially DMF-*d*₇ labeled $[Cr(DMF)_6](ClO_4)_3$ were batches from previous preparations.¹³ This complex shows two absorption maxima at 591 and 422 nm (molar absorptivity ϵ 57.9 and 45.1 dm³ mol⁻¹ cm⁻¹, respectively) in DMF at 21.8 °C. **Chloropentakis(*N,N*-dimethylformamide)chromium(III) perchlorate** was prepared by a method described elsewhere.¹² This complex in DMF exhibited absorption maxima at 623 and 445 nm (ϵ 71.8 and 49.0 dm³ mol⁻¹ cm⁻¹, respectively) at 21.8 °C.

Preparation of Bromopentakis(*N,N*-dimethylformamide)chromium(III) Tetraphenylborate. A solution containing $[Cr(DMF)_6](ClO_4)_3$ (3 g) and $(t-Bu)_4NBr$ (1.2 g) in DMF (30 cm³) was kept at 110 °C for 6 h. Ether was added to the cooled solution until it became cloudy, thereby precipitating unreacted $Cr(DMF)_6^{3+}$. The mixture was allowed to stand at 0 °C for 10 min and filtered. Excess ether was added to the filtrate precipitating the green $Cr(DMF)_5Br^{2+}$ complex as the $BrClO_4$ salt. This salt is hygroscopic and difficult to recrystallize to purity. Anal. Calcd for $[Cr(DMF)_5Br]BrClO_4$: Cl, 5.24; Br, 23.6. Found: Cl, 4.03; Br, 23.7. It was therefore converted to the tetraphenylborate salt as follows.

The crude $[Cr(DMF)_5Br]BrClO_4$ was dissolved in DMF (25 cm³) acidified with 2 drops of concentrated HCl. To it was added with vigorous stirring aqueous sodium tetraphenylborate (2 g in 50 cm³) followed by more water (100 cm³). The mixture was stirred for 5 min and filtered, and the solid product was washed thoroughly, first with methanol to remove white impurities and then with ether. This crude tetraphenylborate salt was dissolved in DMF (10 cm³) and filtered. Ether was added to the filtrate until it became cloudy, and the mixture was allowed to stand at 0 °C overnight. $[Cr(DMF)_6](BPh_4)_3$ precipitated as blue flakes and was removed by filtration. A large excess of ether was added to the filtrate over a period of 2 days to precipitate green $[Cr(DMF)_5Br](BPh_4)_2$ (1 g). This complex in DMF shows absorption maxima at 639 and 449 nm (ϵ 81.6 and 52.1 dm³ mol⁻¹ cm⁻¹, respectively) at 21.8 °C. The tail of a charge-transfer band was observed in the region 350–300 nm (ϵ 270.8 dm³ mol⁻¹ cm⁻¹ at 310 nm). Anal. Calcd for $[Cr(DMF)_5Br](BPh_4)_2$: C, 66.6; H, 6.7; Br, 7.0. Found: C, 66.6; H, 6.7; Br, 7.2.

Preparation of (Thiocyanato-*N*)pentakis(*N,N*-dimethylformamide)chromium(III) Tetraphenylborate. A solution containing $[Cr(DMF)_6](ClO_4)_3$ (1 g) and KNCS (0.18 g) in DMF (20 cm³) was kept at 100 °C for 2 h and filtered. To the cooled filtrate was added 2 drops of concentrated HCl followed by aqueous $NaBPh_4$ (1.2 g in 20 cm³). The mixture was stirred for 5 min and more water (100 cm³) was added. The precipitate was collected and washed thoroughly with methanol (to remove white impurities) and then ether.

This compound was fractionally recrystallized to purity from 50% acetone-DMF (20 cm³) by adding ether. The first fraction (0.8 g), obtained after adding ether (~50 cm³) and allowing the mixture to stand at 0 °C for 2 h, consisted of equal amounts of $[Cr(DMF)_6](BPh_4)_3$ and $[Cr(DMF)_5NCS](BPh_4)_2$ and was set aside for further purification. The second fraction (0.15 g), obtained after adding excess ether to the filtrate and allowing the mixture to stand at 0 °C for 24 h, consisted mainly of $[Cr(DMF)_5NCS](BPh_4)_2$ as bluish green needles.

The first fraction was taken up in the minimum amount of DMF and filtered. Ether was added to the filtrate until it became cloudy, and the mixture was allowed to stand at 0 °C for 3 days. $[Cr(DMF)_5NCS](BPh_4)_2$ (0.3 g), which precipitated as deep bluish green, feathery needles, was separated by hand from the more massive, light blue needles of $[Cr(DMF)_6](BPh_4)_3$. The combined fractions were recrystallized from DMF (10 cm³) by adding ether (0.4 g). $[Cr(DMF)_5NCS](BPh_4)_2$ in DMF at 21.8 °C shows three absorption maxima, two in the visible region at 591 (ϵ 80.3 dm³ mol⁻¹ cm⁻¹) and 438 nm (ϵ 62.0 dm³ mol⁻¹ cm⁻¹) and a third, a charge-transfer band, at 307.5 nm (ϵ 4425 dm³ mol⁻¹ cm⁻¹). Anal. Calcd for $[Cr(DMF)_5NCS](BPh_4)_2$: C, 69.0; H, 6.7; S, 2.9. Found: C, 68.7; H, 6.9; S, 2.8.

Preparation of the Azidopentakis(*N,N*-dimethylformamide)chromium(III) Cation. This complex could not be isolated as a solid salt and was therefore characterized only in solution, as follows. Solutions containing various amounts of $Cr(DMF)_6^{3+}$ (0.0055–0.0075 mol dm⁻³) and a constant amount of N_3^- (5.0×10^{-3} mol dm⁻³) were equilibrated at 49.9 °C (~30 h) and cooled to room temperature. After the spectra of these equilibrated solutions had been recorded, the concentration of the uncoordinated N_3^- ion was determined spectrophotometrically as $Fe(DMF)_5N_3^{2+}$.¹⁶ In all cases, the formation of $Cr(DMF)_5N_3^{2+}$ was found to be (96 ± 2)% to (98 ± 2)% complete, corresponding to a formation constant of not less than 2×10^4 dm³ mol⁻¹ at 49.9 °C. $Cr(DMF)_5N_3^{2+}$ in DMF shows two absorption maxima at 603 and 445 nm (ϵ 91.0 and 85.9 dm³ mol⁻¹ cm⁻¹, respectively) at 21.8 °C. The tail of a charge-transfer band was observed in the region 350–300 nm with ϵ 2044 dm³ mol⁻¹ cm⁻¹ at 310 nm.

Kinetics of the Solvent-Exchange Reactions. From the appropriate solutions of DMF-*d*₇ labeled $Cr(DMF)_6^{3+}$, in darkened vessels in a thermostat bath (± 0.1 °C), samples were withdrawn at convenient intervals and cooled immediately to 0 °C. The $Cr(DMF)_6^{3+}$ ion was selectively and quantitatively precipitated, leaving any $Cr(DMF)_5X^{2+}$ in solution, by adding an amount of $(Et_4N)_3[Cr(NCS)_6]$ in DMF equimolar with the total Cr(III) already present in the sample (cf. ref 13). The precipitate was collected, washed thoroughly with acetone, and dried. The coordinated solvent molecules were recovered and analyzed isotopically by the method described previously.¹³ In these experiments, the perchlorate salt of $Cr(DMF)_6^{3+}$ was used rather than the tetraphenylborate because BPh_4^- , though even less prone than ClO_4^- to form ion pairs in these systems,¹³ reacts slowly with the various anions X^- in DMF under the conditions of our experiments.

The solvent-exchange reaction of $Cr(DMF)_6^{3+}$ was followed to at least 80% completion in the presence of Br^- or ClO_4^- but only to about 50% when X^- was Cl^- , 15–20% when X^- was NCS^- , and ~4% when X^- was N_3^- , because, in the latter cases, anation outpaced solvent exchange. The first-order coefficients for overall solvent exchange in $Cr(DMF)_6^{3+}$ were reproducible to within 2–4% for $X^- = ClO_4^-$, Cl^- , and Br^- , $\pm 10\%$ for $X^- = NCS^-$, but only $\pm 50\%$ for N_3^- , for which anation is nearly 100-fold faster than solvent exchange.

Kinetics of the Anation Reactions. (a) Gravimetric Method. Again, the appropriate solutions were kept in light-proof vessels in a thermostat (± 0.1 °C), and samples (50.0 ± 0.05 cm³ for $X^- = N_3^-$, 10.0 ± 0.05 cm³ for $X^- = NCS^-$ or Br^-) were withdrawn at selected intervals and cooled immediately to 0 °C. Tetraethylammonium hexathiocyanatochromate(III) (in 10% excess, relative to the Cr content of the sample) in DMF was added, and the mixture was allowed to stand at 0 °C for at least 12 h to ensure complete precipitation of $[Cr(DMF)_6][Cr(NCS)_6]$. The precipitate (0.01–0.05 g) was collected,

washed thoroughly with acetone, dried, and weighed ($\pm 50 \mu\text{g}$) on a Mettler H-20 balance. First-order rate coefficients for the disappearance of $\text{Cr}(\text{DMF})_6^{3+}$ were obtained from log (weight) vs. time plots, which were linear to at least 80% completion of the reaction.

(b) **Spectrophotometric Method.** Alternatively, the progress of the anation reactions was followed spectrophotometrically using a Cary Model 17Hc spectrophotometer fitted with an electrically heated aluminum block, whose temperature was controlled by a Melabs CTC-1A proportional temperature controller and which enclosed the sample cell and protected it from extraneous light. The visible absorption spectra of the complexes were not significantly affected by ion association with X^- , and accordingly pseudo-first-order rate constants were obtained with X^- in excess over Cr(III) at 455 nm for $\text{X}^- = \text{NCS}^-$ and N_3^- (ϵ 21.5, 41.3, and $84.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $\text{Cr}(\text{DMF})_6^{3+}$, $\text{Cr}(\text{DMF})_5\text{NCS}^{2+}$, and $\text{Cr}(\text{DMF})_5\text{N}_3^{2+}$, respectively) and at 690 nm for $\text{X}^- = \text{Br}^-$ (ϵ 9.6 and $65.9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $\text{Cr}(\text{DMF})_6^{3+}$ and $\text{Cr}(\text{DMF})_5\text{Br}^{2+}$; isosbestic points at 597, 514, and 427 nm with ϵ 51.2, 9.8, and $40.8 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively, in DMF at 21.8 °C). The absorbances corresponding to completion of the reactions were calculated on the basis of the known spectra of authentic samples of $\text{Cr}(\text{DMF})_5\text{X}^{2+}$ in DMF.

Results

Anation Reactions. The isolation of authentic solid salts of $\text{Cr}(\text{DMF})_5\text{Br}^{2+}$ and $\text{Cr}(\text{DMF})_5\text{NCS}^{2+}$ and the characterization of $\text{Cr}(\text{DMF})_5\text{N}_3^{2+}$ in solution, together with their spectroscopic identification in reaction mixtures in which the total $[\text{X}^-]$ did not exceed the total $[\text{Cr}(\text{III})]$, were used to establish that the initial products of the anation reactions were indeed $\text{Cr}(\text{DMF})_5\text{X}^{2+}$ and that the reactions went effectively to completion under our reaction conditions (except when X^- was ClO_4^- , which seemed not to form inner-sphere complexes with Cr(III) in DMF). Thus, the spectra of solutions containing equimolar amounts of X^- and $\text{Cr}(\text{DMF})_6^{3+}$ in DMF corresponded, after equilibration, with those of authentic $\text{Cr}(\text{DMF})_5\text{X}^{2+}$ solutions ($\pm 4\%$ in ϵ).

Attempts were made to follow the progress of these anation reactions, in cases where $[\text{X}^-] < [\text{Cr}(\text{III})]$, by observing the development of the $\text{Cr}(\text{DMF})_5\text{X}^{2+}$ charge-transfer bands in the ultraviolet region, but it was found that, in contrast with the analogous DMSO systems,¹² the light absorption of the $\{\text{Cr}(\text{DMF})_6^{3+}, \text{X}^-\}$ and $\{\text{Cr}(\text{DMF})_5\text{X}^{2+}, \text{X}^-\}$ ion pairs¹⁷ led to insuperable complications. Thus, the absorbance at 310 nm of a solution containing Br^- and excess $\text{Cr}(\text{DMF})_6^{3+}$ in DMF first rose steadily and then fell toward a final absorbance which was nevertheless relatively high; this disconcerting behavior is attributable to the initial formation of $\{\text{Cr}(\text{DMF})_5\text{X}^{2+}, \text{X}^-\}$ ion pairs which must dissociate subsequently as X^- is consumed in the anation reaction.

Accordingly, the anation rates were measured spectrophotometrically by following changes in the visible spectra, which are not influenced by ion association. These changes are, however, relatively small and so require the use of X^- concentrations in excess of $[\text{Cr}(\text{III})]$. This introduced a new complication in that secondary reactions, presumably forming $\text{Cr}(\text{DMF})_4\text{X}_2^+$ (etc.), became significant beyond about 60% reaction when X^- was NCS^- or N_3^- and as little as 8% when X^- was Br^- (which may cause marked "trans labilization"¹¹), although repeated attempts to isolate solid salts of $\text{Cr}(\text{DMF})_4\text{Br}_2^+$ failed. Nevertheless, when artificial "infinite-time" absorbances were calculated from the known spectra of $\text{Cr}(\text{DMF})_5\text{X}^{2+}$, pseudo-first-order rate coefficients could be calculated which agreed well ($\pm 6\%$) with those obtained by the gravimetric method. This latter method, though tedious, provided an unambiguous measure of the rate of disappearance of the starting material and hence of the first anation step alone and was therefore used almost exclusively in the study of anation by bromide ion.

Initial pseudo-first-order rate coefficients k_{obsd} obtained for the anation of $\text{Cr}(\text{DMF})_6^{3+}$ by excess X^- ($\text{X} = \text{NCS}^-, \text{N}_3^-, \text{Br}^-$) to form $\text{Cr}(\text{DMF})_5\text{X}^{2+}$ are collected in Table I. According

Table I. Pseudo-First-Order Rate Coefficients k_{obsd} for the Reaction $\text{Cr}(\text{DMF})_6^{3+} + \text{X}^- \rightarrow \text{Cr}(\text{DMF})_5\text{X}^{2+} + \text{DMF}$, in DMF

X^-	Temp, °C	$10^3 \cdot [\text{Cr}(\text{DMF})_6^{3+}]_{\text{initial}}^a$ mol dm ⁻³	$10^2 \cdot [\text{X}^-]_{\text{initial}}$ mol dm ⁻³	$10^5 k_{\text{obsd}}^b$ s ⁻¹
NCS^-^c	71.3	5.05	0.842	6.09 ± 0.12
			1.62	8.75 ± 0.20
			2.50	11.0 ± 0.2
			2.50	10.6 ± 0.2^d
			4.55	13.1 ± 0.3
			6.44	15.1 ± 0.3
			10.3	15.6 ± 0.3
			15.7	16.7 ± 0.3
			15.7	15.8 ± 0.3^d
			20.0	18.1 ± 0.4
			20.0	17.3 ± 0.4^d
			50.1	17.3 ± 0.4
			20.0	5.43 ± 0.15
			50.3	1.54 ± 0.03
			41.1	0.475 ± 0.015
			49.9	7.25 ± 0.20
			$\text{N}_3^-^e$	49.9
0.197	13.3 ± 0.3			
0.331	16.7 ± 0.3			
0.502	21.5 ± 0.4			
0.770	25.9 ± 0.6			
1.03	28.5 ± 0.6			
1.93	32.0 ± 0.7			
2.95	35.0 ± 0.7			
3.27	35.8 ± 0.7^d			
45.0	19.0 ± 0.4			
39.5	9.4 ± 0.2			
30.4	2.67 ± 0.06			
89.9	3.23 ± 0.08^d			
Br^-^f	89.9	5.04	0.765	4.83 ± 0.15^d
			5.03	5.6 ± 0.2^d
			5.03	6.2 ± 0.2^d
			5.09	6.9 ± 0.2^d
			5.05	7.4 ± 0.2^d
			5.08	7.3 ± 0.2^d
			5.06	7.3 ± 0.2^d
			5.08	7.3 ± 0.2^d
			80.1	2.27 ± 0.04^d
			71.3	2.2 ± 0.1
61.2	0.65 ± 0.02^d			
	0.171 ± 0.004^d			

^a As the perchlorate salt. ^b Uncertainty limits based upon the maximum errors anticipated in the absorbance measurements or (in the gravimetric method) the weighings. ^c As KNCS . ^d By the gravimetric method; all other k_{obsd} values by the spectrophotometric method. ^e As the tetraphenylarsonium salt. ^f As the tetraethylammonium salt.

to the interchange mechanism of eq 5 and 6, the dependence of k_{obsd} on $[\text{X}^-]_f$, the concentration of free anions X^- , is given by

$$k_{\text{obsd}} = k_i K_{\text{IP}} [\text{X}^-]_f / (1 + K_{\text{IP}} [\text{X}^-]_f) \quad (9)$$

if the ionic strength is constant. This latter condition could not be met, in the present studies, but in all cases limiting values of k_{obsd} were reached at high $[\text{X}^-]$, so that k_i (which, being the rate coefficient for an internal process occurring within an ion pair, should be essentially independent of electrolyte effects) was directly measurable. Estimates of the ion-pair formation quotients K_{IP} may be obtained from the expression

$$K_{\text{IP}} = 1 / ([\text{X}^-]_{1/2} - 0.50 [\text{Cr}(\text{III})]) \quad (10)$$

where $[\text{X}^-]_{1/2}$ is the formal initial concentration of X^- for which $k_{\text{obsd}} = 1/2 k_i$, where 50% of the $\text{Cr}(\text{DMF})_6^{3+}$ must be present initially as $\{\text{Cr}(\text{DMF})_6^{3+}, \text{X}^-\}$. Graphical estimates of $[\text{X}^-]_{1/2}$ led to the K_{IP} values at the ionic strength of $(4[\text{Cr}(\text{III})] + [\text{X}^-]_{1/2})$, and these are listed in Table II along with the entropies ΔS_i^\ddagger and enthalpies ΔH_i^\ddagger of activation, from which

Table II. Ion-Pair Formation Constants Governing Reaction 5 and Kinetic Parameters Associated with Reaction 6, at 71.3 °C

X ⁻	10 ⁵ k ₁ , s ⁻¹	K _{IP} , dm ³ mol ⁻¹	I, ^a mol dm ⁻³	ΔH ₁ [*] , ^b KJ mol ⁻¹	ΔS ₁ [*] , ^b J K ⁻¹ mol ⁻¹
Cl ⁻ ^c	7.53	1.0 × 10 ³	0.015	130.6 ± 1.7	53.9 ± 4.9
Br ⁻	0.65	140 ^d	0.030	130.3 ± 2.1	32.3 ± 6.1
NCS ⁻	17.3	73	0.036	105.5 ± 1.6	-11.6 ± 4.7
N ₃ ⁻	424 ^e	330 ^f	0.008	105.0 ± 1.2	13.3 ± 3.5

^a Ionic strength relevant to K_{IP} value (I = 4[Cr(III)] + [X⁻]_{1/2}; see eq 10 and text). ^b Uncertainties are standard deviations.

^c Calculated from data of ref 12. ^d Value at 89.9 °C. ^e Extrapolated value. ^f Value at 49.9 °C.

the k₁ values may be regenerated within the experimental uncertainty.

Solvent-Exchange Reactions. Pseudo-first-order rate coefficients k_{ex} for the exchange of coordinated solvent molecules in Cr(DMF)₆³⁺ with DMF solvent in the presence of X⁻ = Cl⁻, Br⁻, ClO₄⁻, NCS⁻, or N₃⁻, as functions of temperature and of [X⁻], are listed in Table III. In general, increasing the amount of added X⁻ decreased k_{ex} slightly until a limiting value was reached. If we attribute this effect to the formation of {Cr(DMF)₆³⁺, X⁻} ion pairs as in eq 7, then this limiting value of k_{ex} may be identified with k₁, and we can write

$$k_{\text{ex}} = (k_1 K_{\text{IP}} [X^-]_f + k_2) / (1 + K_{\text{IP}} [X^-]_f) \quad (11)$$

where k₂ is the value of k_{ex} for unpaired Cr(DMF)₆³⁺ (eq 8), previously determined.¹³ If this interpretation is correct, then K_{IP} values derived from eq 11 should agree with those of Table II (for the same ionic strengths); the data of Table IV show that this is true within a factor of 2, which is acceptable in view of the smallness of the effect of ion pairing on k_{ex} and the consequent uncertainty in K_{IP} values calculated by eq 11. K_{IP} values were found to increase with increasing ionic strength, throughout the range of electrolyte concentrations used here, but k₁ showed no evidence of ionic strength dependence.

The accuracy of the rate data of Tables III and IV was limited by the fact that solvent exchange within the ion pair (reaction 7) must compete with anation (reaction 6). This became a serious limitation when X⁻ was N₃⁻, in which case solvent exchange was about 100-fold slower than anation. The estimated values of k_{ex} for X⁻ = N₃⁻ are therefore subject to a possible ± 50% error but are very close to the corresponding data for X⁻ = Cl⁻, Br⁻, and ClO₄⁻ at the same temperature and are decidedly smaller than the interpolated value of k_{ex} for the free Cr(DMF)₆³⁺ ion¹³ (0.72 × 10⁻⁵ s⁻¹ at 49.9 °C).

Recognition that some of the tetraethylammonium perchlorate, used (in large excess) in our previous study¹³ of reaction 7 when X⁻ = ClO₄⁻, may have contained small amounts of chloride ion necessitated a reexamination of this solvent-exchange reaction in the presence of carefully purified LiClO₄ and Et₄NClO₄. In the present study, the concentration of ClO₄⁻ was taken 5 times higher than before, and a limiting exchange rate coefficient k₁ was unambiguously observed which was nevertheless higher than that reported previously¹³ as a nonlimiting k_{ex} value at high [ClO₄⁻]. The new k₁ value for {Cr(DMF)₆³⁺, ClO₄⁻} is 77% of that for free Cr(DMF)₆³⁺, rather than ~40% as previously claimed,¹³ and K_{IP} is correspondingly some 5 times higher (Table IV). The tendency of the anions used in this study to engage in ion-pair formation may be seen to be BPh₄⁻ << ClO₄⁻ < NCS⁻ < Br⁻ < N₃⁻ < Cl⁻, ion pairing by BPh₄⁻ being undetectable.¹³

Spectra. The first major absorption bands of the complexes Cr(DMF)₆³⁺ and Cr(DMF)₅X²⁺ in the visible region near 600 nm may be assigned to the ⁴T_{2g} ← ⁴A_{2g} transition and are consistent with the ligand field strength order DMF ~

Table III. Pseudo-First-Order Rate Coefficients k_{ex} for the Exchange of All Six Ligands in Cr(DMF)₆³⁺ with DMF Solvent, in the Presence of Anions X⁻

X ⁻	Temp., °C	10 ³ [Cr- (DMF) ₆ ³⁺], mol dm ⁻³	10 ² [X ⁻], mol dm ⁻³	10 ⁵ k _{ex} , ^a s ⁻¹
Cl ⁻ ^b	71.1	3.04	0.363	6.0 ± 0.2
		3.00	0.635	5.6 ± 0.2
		3.06	1.06	5.1 ± 0.2
		2.98	1.51	4.60 ± 0.15
		3.02	2.40	4.67 ± 0.09
		3.05	3.20	4.70 ± 0.09
		60.7		1.46 ± 0.04
		50.3		0.452 ± 0.009
		39.9		0.131 ± 0.003
		71.3		6.4 ± 0.2
Br ⁻ ^b	71.3	5.03	0.714	6.4 ± 0.2
		5.06	1.53	5.74 ± 0.2
		5.05	3.06	5.22 ± 0.11
		5.07	4.04	4.91 ± 0.09
		5.04	5.44	4.61 ± 0.09
		5.13	9.99	4.36 ± 0.09
		5.05	7.49	4.48 ± 0.09
		87.5		23.8 ± 0.6
		80.1		11.4 ± 0.3
		60.4		1.35 ± 0.03
ClO ₄ ⁻	71.3	2.66-11.5 ^c	0	7.37 ± 0.05
		3.01	0.903	7.1 ± 0.2
		5.74	1.72	6.8 ± 0.2
		11.7	3.51	6.5 ± 0.2
		23.0	6.90	6.2 ± 0.2
		6.00	5.93 ^d	6.2 ± 0.2
		5.84	11.7 ^d	5.97 ± 0.12
		5.95	21.6 ^d	5.80 ± 0.12
		5.92	30.1 ^d	5.69 ± 0.11
		5.88	54.3 ^e	5.62 ± 0.10
5.88	82.8 ^e	5.67 ± 0.11		
5.80	102.9 ^e	5.70 ± 0.10		
80.6		14.6 ± 0.4		
61.1		1.81 ± 0.04		
48.2		0.440 ± 0.009		
NCS ⁻ ^f	71.3	4.95	0.966	6.08 ± 0.12
		5.26	2.07	5.1 ± 0.2
		4.99	11.6	5.4 ± 0.5
		4.99	16.5	4.7 ± 0.5
		5.05	20.7	5.4 ± 0.6
N ₃ ⁻ ^g	49.9	1.05	2.04	0.4 ± 0.2
		1.04	3.05	0.4 ± 0.2

^a Uncertainty limits based upon maximum anticipated mass spectrometric errors. ^b As the tetraethylammonium salt. ^c As the tetraphenylborate salt; [Cr(DMF)₆](ClO₄)₃ used in all other cases. ^d LiClO₄ added. ^e [(C₂H₅)₄N]ClO₄ added. ^f As KNCS. ^g As the tetraphenylarsonium salt.

Table IV. Kinetic Parameters Governing Reaction 7 and Corresponding Estimates of Ion-Pair Formation Constants from Eq 11, at 71.3 °C

X ⁻	10 ⁵ k ₁ , s ⁻¹	K _{IP} , dm ³ mol ⁻¹	I, ^a mol dm ⁻³	ΔH ₁ [*] , ^b KJ mol ⁻¹	ΔS ₁ [*] , ^b J K ⁻¹ mol ⁻¹
None	7.37 ^{c,d}			97.1 ± 0.9 ^d	-43.5 ± 2.8 ^d
Cl ⁻	4.68 ^e	0.5 × 10 ³ ^f	0.02	100.1 ± 1.2	-38.4 ± 3.5
Br ⁻	4.36	80 ^f	0.03	104.2 ± 1.2	-26.9 ± 3.5
ClO ₄ ⁻	5.70	30	0.08	98.8 ± 1.2	-40.6 ± 3.5
NCS ⁻	~5.5				

^a Ionic strength relevant to quoted K_{IP} value. ^b Uncertainty limits are standard deviations. ^c Represents k₂ of eq 8 and 11. ^d Reference 13. ^e Interpolated value. ^f Rough value only for purposes of comparison with data of Table II.

NCS⁻ > N₃⁻ > Cl⁻ > Br⁻. Two minor features at 693 and ~655 nm in the spectrum of Cr(DMF)₆³⁺, previously reported by Windolph and Leffler and ascribed to the spin-forbidden ²E_g ← ⁴A_{2g} and ²T_{1g} ← ⁴A_{2g} transitions, respectively, were

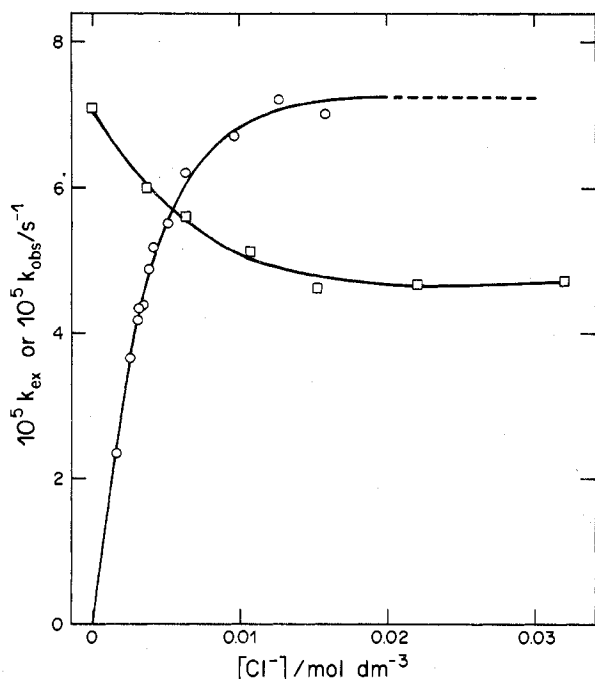


Figure 1. Pseudo-first-order rate coefficients for the formation of $\text{Cr}(\text{DMF})_5\text{Cl}_2^{2+}$ from $\text{Cr}(\text{DMF})_6^{3+}$ (circles; data from ref 12) and the exchange of $\text{DMF}-h_7$ solvent with $\text{Cr}(\text{DMF}-d_7)_6^{3+}$ in the presence of chloride (squares; this work), both at 71.1°C and $[\text{Cr}] \approx 0.003 \text{ mol dm}^{-3}$.

also observed in the spectra of $\text{Cr}(\text{DMF})_5\text{Cl}_2^{2+}$ (at 694 and $\sim 662 \text{ nm}$) and $\text{Cr}(\text{DMF})_5\text{Br}_2^{2+}$ (at 695 and $\sim 666 \text{ nm}$) but not in those of $\text{Cr}(\text{DMF})_5\text{NCS}_2^{2+}$ or $\text{Cr}(\text{DMF})_5\text{N}_3^{2+}$.

Discussion

The consistency of the K_{IP} values obtained in the anation studies with those from the solvent-exchange reactions demonstrates that the ion aggregates of the postulated reactions 5–7 are indeed the same (isotopic labeling apart) and hence shows that the interchange mechanism (reactions 5–8) is a valid model of substitution processes occurring in the title systems at least. This point can be made without reference to specific K_{IP} values by examination of Figure 1, in which chloride anation rate coefficients¹² are seen to tend toward a limiting value in step with the corresponding solvent-exchange rate coefficients as $[\text{Cl}^-]$ is increased.

The data of Table IV show clearly that *ion pairing does not significantly affect the intrinsic reactivity of the complex cation*. The effect of ion pairing is to reduce the solvent-exchange rate slightly, the extent to which this and the associated enthalpies and entropies of activation are affected being very similar for $\text{X}^- = \text{ClO}_4^-$, Cl^- , Br^- , NCS^- , and (as far as could be ascertained) N_3^- , despite a 30-fold range in K_{IP} and a 10^3 -fold range (or more, if the apparently non-complexing anion ClO_4^- is included) in k_i . These observations provide support for our hypothesis¹³ that the chief effect of ion pairing upon solvent-exchange rates is simply to displace some of the solvent molecules available for exchange from the second coordination sphere (solvation sheath) of the complex cation.

This latter finding makes it extremely difficult to defend the assignment of an I_d mechanism, involving a common five-coordinate intermediate, to both solvent exchange and anation, since the fact that the rate of the latter reaction can exceed that of the former by factors of 1.6 (Cl^- , 71.3°C), 3.1 (NCS^- , 71.3°C), or 90 (N_3^- , 49.9°C) can no longer be ascribed to activation of the $\text{Cr}(\text{DMF})_6^{3+}$ complex by ion pairing. The former two ratios might, in isolation, be reconciled with an I_d mechanism by a rather extreme argument,³

but that for N_3^- could scarcely be accommodated. A common I_d mechanism becomes quite untenable in the face of ΔH_i^\ddagger values for $\text{X}^- = \text{Br}^-$ and Cl^- which are 25–30 kJ mol^{-1} higher than for solvent exchange or anation by NCS^- or N_3^- (Tables II and IV) and which, incidentally, result in k_i being greater than k_1 even for $\text{X}^- = \text{Br}^-$ above 154°C , the corresponding temperature for Cl^- being 58°C .

Evidence that the mechanism is in fact an *associative* interchange (I_a) is provided by the rate coefficients k_i for internal anation (Table II), which depend strongly on the nature of X^- , rising in the ratios 1:12:27:650 for $\text{Br}^-:\text{Cl}^-:\text{NCS}^-:\text{N}_3^-$ at 71.3°C . This spread in reactivities cannot be ascribed to some consequence of ion pairing, for reasons given above and also because the ratios are quite unrelated to the corresponding relative K_{IP} values. These relative reactivities may therefore be taken as a measure of the nucleophilicities of the various X^- toward $\text{Cr}(\text{DMF})_6^{3+}$. The nucleophilicity sequence $\text{X}^- = \text{ClO}_4^- \ll \text{Br}^- < \text{Cl}^- < \text{NCS}^- < \text{N}_3^-$ for reaction 6 is that of the increasing $\text{p}K_a$ values for the acids HX . Using Edwards'¹⁹ $\text{p}K_a$ values for aqueous HX , the observed k_i data can be roughly represented by

$$\log k_i = 0.21\text{p}K_a - 3.4 \quad (12)$$

which suggests $k_i = 2 \times 10^{-6}$, 2×10^{-3} , 4×10^{-2} , and 1 s^{-1} for the respective anions I^- , F^- , CN^- , and OH^- , for which direct measurements could not be made on account of solubility problems or side reactions with DMF. Monacelli²⁰ reported a similar correlation for the *reverse* process (aquation) with $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ in water, inevitably with a negative coefficient of $\text{p}K_a$; there, however, $\text{Cr}(\text{H}_2\text{O})_5\text{N}_3^{2+}$ deviated sharply from the correlation, apparently because in this system, in contrast with the DMF analogue, the azide ligand can leave as HN_3 .²¹ These correlations are consistent with the classification of $\text{Cr}(\text{III})$ centers as typical "hard" acids.²²

Finally, we note that an I_a mechanism was previously assigned to the solvent-exchange reaction (eq 8) on the entirely independent criterion of pressure effects on the reaction rate.¹³ The intuitive expectation that the intimate mechanisms of solvent exchange and simple anation should be the same is therefore justified. It is therefore legitimate to regard anation as a special case of solvent exchange in which an anion from the second coordination sphere becomes the entering ligand rather than a solvent molecule from the same region.¹ This reaffirms the importance of investigations of solvent-exchange reactions in the study of the mechanisms of substitution of transition metal complexes in solution.

Acknowledgment. We thank the National Research Council of Canada for financial assistance.

Registry No. $[\text{Cr}(\text{DMF})_5\text{Br}](\text{BPh}_4)_2$, 59448-66-7; $[\text{Cr}(\text{DMF})_5\text{NCS}](\text{BPh}_4)_2$, 59448-68-9; $\text{Cr}(\text{DMF})_5\text{N}_3^{2+}$, 59448-69-0; $\text{Cr}(\text{DMF})_6^{3+}$, 45303-44-4; $[\text{Cr}(\text{DMF})_6](\text{ClO}_4)_3$, 33594-59-1; $[\text{Cr}(\text{DMF})_5\text{Br}]\text{BrClO}_4$, 59448-70-3; Et_4NClO_4 , 2567-83-1; $(\text{C}_6\text{H}_5)_4\text{AsN}_3$, 54663-87-5; NCS^- , 302-04-5; N_3^- , 14343-69-2; Br^- , 24959-67-9; Cl^- , 16887-00-6; ClO_4^- , 12133-63-0; DMF, 68-12-2.

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 (16) $\text{Fe}(\text{DMF})_5\text{N}_3^{2+}$ shows an absorption maximum at 478 nm (ϵ 4089 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) in DMF at 21.8 °C. Inner-sphere complexing of N_3^- by $\text{Fe}(\text{DMF})_6^{3+}$ (ϵ 23.2 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ at 478 nm at 21.8 °C) in DMF is complete, provided that the iron(III) concentration (0.01 mol dm^{-3}) is much greater than that of the azide ion to be complexed ($(1-5) \times 10^{-4}$ mol dm^{-3}). The $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ used in these measurements was made by the method of J. Hodgkinson and R. B. Jordan, *J. Am. Chem. Soc.*, **95**, 763 (1973).
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Chlorine Atom Abstraction Reaction of Dichloromethylchromium(III) Ions with Chromium(II). Kinetics and Radiotracer Determinations¹

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Received March 22, 1976

AIC602238

Reaction with Cr^{2+} in aqueous HClO_4 converts the complex CrCHCl_2^{2+} to $\text{CrCH}_2\text{Cl}^{2+}$, with accompanying formation of Cr^{3+} and CrCl^{2+} in equivalent amounts. Kinetic data indicate that the first and rate-limiting step ($k = 0.016 \text{ dm}^3 \text{mol}^{-1} \text{ s}^{-1}$, 25.1 °C) is a bimolecular halogen atom abstraction reaction of CrCHCl_2^{2+} and Cr^{2+} , forming CrCl^{2+} and CrCHCl^{2+} . The latter intermediate, according to chromium-51 tracer results, rapidly exchanges with Cr^{2+} via an intermediate $\text{Cr}_2\text{CHCl}^{4+}$, the latter subsequently being converted to Cr^{3+} and $\text{CrCH}_2\text{Cl}^{2+}$ in a protonolysis step. The chemistry of these reactions is discussed, and reference is made to the observation of an intensely absorbing transient formed at lower $[\text{H}^+]$ (0.01–0.05 M), which is believed to be a nonproductive intermediate lying off the main reaction pathway. A mechanism to account for these observations is proposed.

Introduction

One of the first known complexes of chromium(III) containing a metal-carbon σ bond was the dichloromethyl complex $(\text{H}_2\text{O})_5\text{Cr}-\text{CHCl}_2^{2+}$ prepared by Anet² in the heterogeneous reaction of aqueous Cr^{2+} and chloroform (eq 1). Dodd and

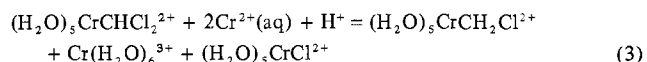
$$2\text{Cr}^{2+}(\text{aq}) + \text{CHCl}_3 = (\text{H}_2\text{O})_5\text{CrCl}^{2+} + (\text{H}_2\text{O})_5\text{CrCHCl}_2^{2+} \quad (1)$$

Johnson³ found it convenient to utilize this same reaction under homogeneous conditions (acetone cosolvent), and also prepared the monochloromethyl complex by the analogous reaction of Cr^{2+} with methylene chloride (eq 2). They suc-

$$2\text{Cr}^{2+}(\text{aq}) + \text{CH}_2\text{Cl}_2 = (\text{H}_2\text{O})_5\text{CrCl}^{2+} + (\text{H}_2\text{O})_5\text{CrCH}_2\text{Cl}^{2+} \quad (2)$$

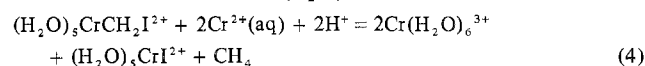
cessfully separated the highly water-soluble organochromium complexes from the other components of the reaction mixture using cation-exchange chromatography.^{3,4}

Dodd and Johnson also noted that when reaction 1 was carried out with large molar excesses of Cr^{2+} , a lower yield of the dichloromethyl complex resulted, with monochloromethylchromium(III) formed instead. They attributed this to the conversion of the one complex to the other by reaction with excess Cr^{2+} , which was confirmed by direct observation of this reaction (eq 3).



In relation to this, Castro and Kray⁵ observed the stepwise reduction of haloforms and methylene halides by CrSO_4 ; in $\text{DMF}-\text{H}_2\text{O}$ these reactions proceed eventually to methane and undoubtedly proceed through a series of organochromium intermediates— CrCHX_2^{2+} , $\text{CrCH}_2\text{X}^{2+}$, and CrCH_3^{2+} —each in turn formed from the preceding halide by a reaction with Cr^{2+} analogous to eq 1–3. In contrast to the results in $\text{DMF}-\text{H}_2\text{O}$ and in the presence of sulfate ions, the only reaction we found to occur in perchlorate solution is that given by eq 3.

In the present work we report the results of a mechanistic study of this reaction including a determination of the reaction kinetics and isotopic studies to investigate further steps in the mechanism. The study of a related reaction of the iodo-methylchromium complex with Cr^{2+} was reported recently.⁶ In this case the products include liberated methane, presumably arising from acidolysis of an unstable methylchromium⁷ intermediate (eq 4).



Experimental Section

Materials. The organochromium complexes were prepared and isolated as described in the literature,^{1,2} with certain variations to ensure the recovery of a pure compound. The procedure used for $(\text{H}_2\text{O})_5\text{CrCHCl}_2^{2+}$ was as follows. A 50-cm³ sample of an aqueous solution of 0.1 M Cr^{2+} and 0.1 M H^+ was mixed with ca. 10 cm³ of chloroform under nitrogen. After ca. 30 min of vigorous stirring the excess chloroform was removed and the solution made ca. 0.1 M in Hg^{2+} by addition of a concentrated solution of mercuric perchlorate.⁸ After 15 min, HCl was added to provide a solution ca. 0.2 M, and the solution was filtered. The filtrate was placed on a column (30 × 1.5 cm) of Dowex 50W-X8 cation-exchange resin. The column was eluted with 0.1 M HCl until the eluate gave a negative test for $\text{Hg}(\text{II})$ with Na_2S and then with water until a negative test for Cl^- was obtained. Finally, the column was eluted with 1.0 M HClO_4 to collect CrCHCl_2^{2+} leaving Cr^{3+} on the resin. In some instances separation of the desired complex was achieved without addition of Hg^{2+} , eluting first the green CrCl^{2+} from the resin column with 0.5 M perchloric acid and then the orange CrCHCl_2^{2+} with 1.0 M perchloric acid or lithium perchlorate. For some experiments the eluted solutions of CrCHCl_2^{2+} in LiClO_4 were concentrated by lyophilization, first freezing them in dry ice-acetone and then evacuating to ca. 0.01 Pa for 8–12 h. The deuterio complex CrCDCl_2^{2+} was prepared in an analogous fashion using CDCl_3 , and the ⁵¹Cr-labeled complex was prepared starting with ⁵¹Cr²⁺.

The preparation of $\text{CrCH}_2\text{Cl}^{2+}$ was performed similarly except that CH_2ClBr was used as the reactant (eq 5), and the reaction time