feature of the present interpretation is the correspondence of data for $Mo_2O_4(C_2O_4)_2^{2-}$, $Mo_2O_4^{2+}$, and VO^{2+}. The behavior of VO^{2+} is now well established,[17] and the high lability of the trans H_2O has been confirmed using EPR[18,19] as well as NMR line-broadening techniques.[14] Structural similarities of V(IV) and Mo(V) complexes having terminal oxo ligands must again be stressed.[13]

Acknowledgment. G.R.C. is grateful to ICI Ltd. for a postdoctoral fellowship. Helpful discussions with Drs. Garner and Hyde are also acknowledged.

Registry No. $Mo_2O_4(C_2O_4)_2^{2-}$, 60209-19-0; NCS^-, 302-04-5; py, 110-86-1.

Supplementary Material Available: Tables I and II listing reciprocal relaxation times (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 396 (1975).
(2) F. A. Cotton and S. H. Morehouse, *Inorg. Chem.*, **4**, 1380 (1965).
(3) This formulation (with the two inner-sphere aquo ligands omitted) is we feel adequate since it makes clear essential structural differences as compared to the aquo ion $Mo_2O_4^{2+}$.
(4) P. C. H. Mitchell, *J. Chem. Soc. A*, 146 (1969).
(5) Acetate is known to coordinate to di-μ-oxomolybdenum(V): e.g., T. Glowiak, M. Sabat, H. Sabat, and M. F. Rudolf, *J. Chem. Soc., Chem. Commun.*, 712 (1975).
(6) A. Sabatini, A. Vacca, and P. Gans, *Talanta*, **21**, 53 (1974).
(7) J. E. Crooks, M. S. Zetter, and P. A. Tregloan, *J. Phys. E*, **3**, 73 (1970).
(8) R. H. Moore and R. K. Zeigler, Los Alamos Report LA 2367 (1959) and Addenda.
(9) K. Kahmann, H. Sigel, and H. Erlenmeyer, *Helv. Chim. Acta*, **47**, 1754 (1964).
(10) G. Atkinson and J. E. Bauman, *Inorg. Chem.*, **2**, 64 (1963).
(11) Supplementary material.
(12) See, e.g., K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 135 (1970), and references therein.
(13) The difference in cis and trans Mo–NCS bond distances in the complex $Mo_2O_4(NCS)_6^{2-}$ is 0.15 Å: S. R. Fletcher, unpublished work; see also data of B. Spivak and Z. Dori, *Coord. Chem. Rev.*, **17**, 99 (1975). The trans elongation produced in $VOSO_4$ (comparison of V–OH_2 bonds) is 0.18 Å: C. J. Ballhausen, D. F. Djurinskij, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 3305 (1968).
(14) K. Wuthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967).
(15) A. Schlund and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **72**, 653 (1968).
(16) C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *J. Chem. Soc., Dalton Trans.*, 1175 (1975), and personal communication from Dr. C. D. Garner.
(17) E.g., R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, p 363.
(18) F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **48**, 3983 (1968).
(19) R. B. Jordan and N. S. Angerman, *J. Chem. Phys.*, **48**, 3983 (1968).
(20) **Note Added in Proof.** Dr. Y. Sasaki of the Tohoku University, Sendai, Japan, has recently observed that the ^{13}C NMR spectrum of $K_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ in water, pH ~4, gives only one sharp peak at 168.0 ppm at 34 °C. This suggests that there may be some rapid process in solution by which the C atoms assume equivalence.

Contribution from the Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, England

Mechanistic Implications of Kinetic Data for the Formation and Aquation of Acidopentaamminechromium(III) Complexes, $Cr(NH_3)_5X^{2+}$, $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, Br^-, and I^-. Evidence for a Dissociative Mechanism

T. RAMASAMI and A. GEOFFREY SYKES*

Received March 22, 1976 AIC60210U

Rate constants (k_{aq}) for the aquation of six different acidopentaamminechromium(III) complexes, $Cr(NH_3)_5X^{2+}$, with $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, Br^-, and I^-, have been determined at 50 °C, I = 1.00 M ($LiClO_4$). Rate constants (k_f) for the corresponding anation reactions of $Cr(NH_3)_5H_2O^{3+}$ have been obtained for all except $X^- = I^-$. Information regarding equilibrium constants, $K_{OS}K_{IS}$, for the formation of $Cr(NH_3)_5X^{2+}$ from $Cr(NH_3)_5H_2O^{3+}$, using procedures involving ion-exchange separation and determination of products, is reported. The values obtained are in satisfactory agreement with kinetically determined values (k_f/k_{aq}) at 50 °C, I = 1.00 M ($LiClO_4$). A graph of log k_{aq} against $-\log K_{OS}K_{IS}$ gives a slope of 0.91 ± 0.05. A narrow range of formation rate constants, k_f, is observed and when allowance is made for the outer-sphere association constants in cases where K_{OS} has been evaluated (the NCS^- study only in this work) values of k_f/K_{OS} are comparable with the water exchange rate constant for $Cr(NH_3)_5H_2O^{3+}$ at 50 °C. The results suggest that $Cr(NH_3)_5H_2O^{3+}$ exhibits more dissociative character than $Cr(H_2O)_6^{3+}$ in the substitution of H_2O.

The aquation rate constants for the acidopentaamminechromium(III) complexes, $Cr(NH_3)_5X^{2+}$, $X^- = NCS^-$,[1] $CCl_3CO_2^-$,[2] $CF_3CO_2^-$,[3] Cl^-,[4] Br^-, and I^-,[5] have been determined previously. Different ionic strengths and media were used, however, and a meaningful comparison of data is therefore difficult. Duffy and Earley[4] have determined the rate constants for water exchange of $Cr(NH_3)_5H_2O^{3+}$ as well as the anation of this complex with Cl^- and NCS^- and have proposed a dissociative interchange (I_d) mechanism. For a part of their study (the NCS^- anation reaction), NaBr was used to adjust the ionic strength and the inner- and outer-sphere associations of Br^- appear to have been neglected. It has been observed in earlier work that after allowing for outer-sphere association (K_{OS} obtained from kinetics) the rate constants for $C_2O_4^{2-}$, $HC_2O_4^-$,[6] and $^+NH_3CH_2CO_2^-$ [7] are about the same as for water exchange. Hence a dissociative I_d mechanism has been suggested. Swaddle and Stranks,[8] on the other hand favor an associative interchange, I_a, for the water exchange reaction on the basis that a negative volume of activation (−5.8 $cm^3\ mol^{-1}$) has been obtained. It is not clear therefore from these various studies whether the interchange mechanism involved is associative or dissociative.

The aim of this investigation is to extend previous studies to include all relevant kinetic and thermodynamic measurements, thus enabling a firm mechanistic assignment to be made.

Experimental Section

Materials. Literature methods were used to prepare the complexes $[Cr(NH_3)_5H_2O](ClO_4)_3$,[9] $[Cr(NH_3)_5(NCS)](ClO_4)_2$,[10] $[Cr(NH_3)_5(O_2CCCl_3)](ClO_4)_2 \cdot H_2O$,[11] $[Cr(NH_3)_5(O_2CCF_3)](ClO_4)_2$,[11] $[Cr(NH_3)_5Cl](ClO_4)_2$,[12] and $[Cr(NH_3)_5I]Cl_2$.[13] The complex $[Cr(NH_3)_5Br]Br_2$ was prepared by heating $[Cr(NH_3)_5H_2O](ClO_4)_3$ (1.0 g) in 50 ml of solution containing 2.5 M NaBr and 0.1 M $HClO_4$ at 50 °C. Crystals of $[Cr(NH_3)_5Br]Br_2$ were obtained within about

45 min. After filtering the filtrate was again heated at 50 °C when more product was obtained. This procedure was repeated three to four times. The bromide salt was converted to perchlorate by grinding in a precooled pestle and mortar with 70% $HClO_4$ till no more fumes of HBr were evolved. The complex was filtered and recrystallized from 1 M $HClO_4$ by the addition of ice-cold 70% $HClO_4$. Anal. Calcd for $[Cr(NH_3)_5Br](ClO_4)_2$: Cr, 12.5; N, 16.82; total halide, 25.6. Found: Cr, 12.4; N, 16.55; total halide, 25.6. Elemental microanalyses for other complexes were consistent with the above formulas. Details of uv–visible spectra, Table I, are in satisfactory agreement with published values (wavelengths ± 1 nm; absorption coefficients within 3–6%).

Perchloric acid (72%, Hopkin and Williams, Analar) was used without further purification. Lithium perchlorate was prepared from Li_2CO_3 and $HClO_4$. Solutions of LiCl, LiBr, and LiNCS (all 3 M) were prepared by metathesis of the potassium salt with $LiClO_4$, followed by the filtering off of insoluble $KClO_4$ at 3–5 °C. Concentrations of Cl^-, Br^-, and NCS^- were determined by direct titration, and total cation concentrations were estimated by exchanging an aliquot onto an Amberlite IR-120(H) ion-exchange column and titrating the H^+ liberated. The agreement between the two estimations was within 2% indicating that the amount of $KClO_4$ was small. The determined cation concentration was used in adjusting ionic strengths. Sodium iodide (BDH, >99.5% purity), trichloroacetic acid (BDH, Analar), and trifluoroacetic acid (BDH, Reagent Grade) were used without further purification.

Preliminary Experiments. Aquation of $Cr(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Br^{2+}$ at 50 °C, $[H^+] = 0.10$ M and $I = 1.00$ M ($LiClO_4$), occurred with retention of isosbestics at 360, 420, and 493 nm (for Cl^-) and 361, 424, and 495 nm (for Br^-). Retention of five isosbestic points was also observed for the aquation of $Cr(NH_3)_5I^{2+}$ at 20 °C, $[H^+] = 0.1$ M and $I = 1.00$ M ($LiClO_4$). Final spectra correspond with that of $Cr(NH_3)_5(H_2O)^{3+}$. The spectrophotometric changes in the cases of $Cr(NH_3)_5(NCS)^{2+}$, $Cr(NH_3)_5(O_2CCCl_3)^{2+}$, and $Cr(NH_3)_5(O_2CCF_3)^{2+}$ occurred slowly at 50 °C, $[H^+] = 0.1$ M for NCS^- and 0.01 M for $CCl_3CO_2^-$ and $CF_3CO_2^-$, $I = 1.00$ M ($LiClO_4$). Spectrophotometric changes in all these cases were more significant in the uv region than in the visible region. Product analyses were carried out using ion-exchange separations on Dowex 50W-X2 resin, in order to assess the reaction paths and interplay of side reactions. The complex, $Cr(NH_3)_5(O_2CCCl_3)^{2+}$, alone gave direct evidence for another minor reaction product along with $Cr(NH_3)_5H_2O^{3+}$ after 18 h at 50 °C, $[H^+] = 0.02$ M, $I = 1.00$ M ($LiClO_4$). Using the micro-Kjeldahl technique and chromate analysis, the minor product was found to have a nitrogen to chromium ratio of 4.1:1.0. Its elution behavior is consistent with a 2+ charge. This product is most probably $Cr(NH_3)_4(H_2O)(O_2CCCl_3)^{2+}$. Therefore ion-exchange and spectrophotometric measurements indicate that the primary reaction is (1), in all cases except $X^- = CCl_3CO_2^-$. With $Cr(NH_3)_5(O_2CCCl_3)^{2+}$,

$$Cr(NH_3)_5X^{2+} + H_2O \xrightarrow{k_{aq}} Cr(NH_3)_5H_2O^{3+} + X^- \quad (1)$$

a modified scheme

$$Cr(NH_3)_5(O_2CCCl_3)^{2+} + H_2O \begin{cases} \xrightarrow{k_{aq}} Cr(NH_3)_5H_2O^{3+} + CCl_3CO_2^- \\ \xrightarrow{k_1} Cr(NH_3)_4(H_2O)(O_2CCCl_3)^{2+} + NH_4^+ \end{cases} \quad (2)$$

has to be considered, where k_1 is the rate constant for aquation of ammonia. The spectrum of $Cr(NH_3)_4(H_2O)(O_2CCCl_3)^{2+}$ is given alongside those of $Cr(NH_3)_5(O_2CCCl_3)^{2+}$ and $Cr(NH_3)_5H_2O^{3+}$ in Figure 1.

The reactions of $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, and Br^- with $Cr(NH_3)_5H_2O^{3+}$ gave rise to the acidopentaammine as the only product and identification of products as well as spectrophotometric changes observed are consistent with equilibration reactions as in (3).

$$Cr(NH_3)_5H_2O^{3+} + X^- \underset{k_{aq}}{\overset{k_f}{\rightleftharpoons}} Cr(NH_3)_5X^{2+} + H_2O \quad (3)$$

The rate constants, k_f, could be determined directly, if (3) proceeds essentially to completion. The rate constants for the equilibration

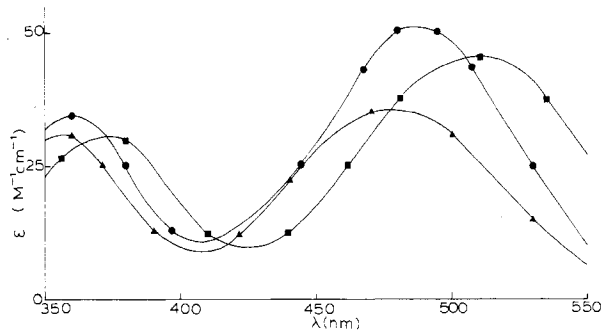

Figure 1. Uv-visible absorption spectra of aquopentaamminechromium(III) (▲), trichloroacetatopentaaminechromium(III) (●), and trichloroacetatoaquotetraamminechromium(III) (■) in aqueous solution. $[HClO_4] = 0.1$ M, $I = 1.0$ M ($NaClO_4$).

processes, k_{eq}, can be expressed as in (4). For further details on the

$$k_{eq} = k_f[X^-] + k_{aq} \quad (4)$$

methods of determination of k_f and k_{eq} see below.

Determination of Overall Equilibrium Constants by Spectrophotometry. This procedure was used for measuring the equilibrium constants for Cl^- and Br^- complexing with $Cr(NH_3)_5H_2O^{3+}$ at 50 °C, $[H^+] = 0.1$ M, and $I = 1.00$ M ($LiClO_4$). Absorption changes, ΔA, were determined at 225 nm for Cl^- and 265 nm for Br^- as a function of halide concentration. At these wavelengths both inner- and outer-sphere complexes absorb. The outer-sphere complexes are known to form,[14] since there is an immediate increase in the absorbance on mixing $Cr(NH_3)_5H_2O^{3+}$ and halides. The absorbance changes ΔA observed are therefore related to the overall equilibrium constant, $K_{OS} + K_{OS}K_{IS}$,[15] where K_{OS} and K_{IS} are as defined in (5) and (6).

$$Cr(NH_3)_5H_2O^{3+} + X^- \overset{K_{OS}}{\rightleftharpoons} Cr(NH_3)_5H_2O^{3+}, X^- \quad (5)$$

$$Cr(NH_3)_5H_2O^{3+}, X^- \overset{K_{IS}}{\rightleftharpoons} Cr(NH_3)_5X^{2+} + H_2O \quad (6)$$

The overall equilibrium constant was obtained from the ratio of intercept to slope of plots of $(\Delta A)^{-1}$ against $[X]^{-1}$. The concentration of X^- was in large excess over that of the complex, $[Cr(NH_3)_5H_2O^{3+}] = 6 \times 10^{-3}$ M for Cl^- and $[Cr(NH_3)_5H_2O^{3+}] = 8 \times 10^{-3}$ M for Br^-. It is assumed that second ion-pair formation and changes in activity coefficients by replacing ClO_4^- with halides are not effective.

Determination of Equilibrium Constants by Ion Exchange. Equilibrium constants, in this case $K_{OS}K_{IS}$, (7), were determined by

$$K_{OS}K_{IS} = \frac{[Cr(NH_3)_5X^{2+}]}{[Cr(NH_3)_5H_2O][X^-]} \quad (7)$$

the separation of equilibrated products by ion-exchange chromatography and analyzing the distribution of chromium(III) in each fraction. Solutions were allowed to equilibrate for at least four to five k_{eq} half-lives at 50 °C. The ranges of anion, hydrogen ion, and initial $Cr(NH_3)_5H_2O^{3+}$ concentrations investigated were as follows: $[NCS^-] = 0.03$–0.08 M, $[Cr(III)] = (2–3) \times 10^{-3}$ M, $[H^+] = 0.1$ M; $[CCl_3CO_2^-] = 0.4$–0.6 M, $[Cr(III)] = (5–8) \times 10^{-3}$ M, $[H^+] = 0.01$ M; $[CF_3CO_2^-] = 0.4$–0.6 M, $[Cr(III)] = (2–3) \times 10^{-3}$ M, $[H^+] = 0.01$ M; $[Cl^-] = 0.1$–0.8 M, $[Cr(III)] = (5–8) \times 10^{-3}$ M, $[H^+] = 0.1$ M; $[Br^-] = 0.2$–0.86 M, $[Cr(III)] = (8–12) \times 10^{-3}$ M, $[H^+] = 0.1$ M. The ionic strength was adjusted to $I = 1.00$ M ($LiClO_4$). All equilibrated solutions (with the exception of $CF_3CO_2^-$) were first diluted with twice the volume of ice-cold water, and the products separated using Dowex 50W-X2 (200–400 mesh) ion-exchange resin columns (1 cm diameter, 8 cm long) thermostated at 0 °C. The equilibrated solutions were diluted with twice the volume of perchloric acid at pH 2.0; in the case of $CF_3CO_2^-$ ion-exchange separations were carried out at room temperature (ca. 20 °C) to avoid crystallization of $Cr(NH_3)_5(OOCCF_3)^{2+}$. No direct evidence for secondary products was seen in the case of $CCl_3CO_2^-$, and $k_{eq} >> k_1$ under these conditions. With I^-, in an attempt to estimate $K_{OS}K_{IS}$, a modified technique was used. Reaction solutions (25 ml) (which had $[I^-] = 0.66$ and 0.78 M, $[Cr(NH_3)_5H_2O^{3+}] = (2–4) \times 10^{-2}$ M, and $[H^+] = 0.1$ M) were thermostated for 90 min under air-free conditions then diluted with an equal volume of ice-cold deaerated

Table VIII. Summary of Equilibrium Constants for Inner- and Outer-Sphere Associations of X^- with $Cr(NH_3)_5H_2O^{3+}$ at 50.0 °C, $I = 1.00$ M ($LiClO_4$)

Ligand X^-	$K_{OS}K_{IS}$,[a] M^{-1}	$K_{OS}K_{IS}$,[b] M^{-1}	K_{OS},[f] M^{-1}	$K_{OS} + K_{OS}K_{IS}$,[e] M^{-1}	Ref
NCS^-	310 ± 15[c]	380 ± 22	0.68 ± 0.04		This work
$CCl_3CO_2^-$	5.3 ± 0.20[d]	3.6 ± 0.2			This work
$CF_3CO_2^-$	2.35 ± 0.20[d]	2.7 ± 0.14			This work
Cl^-	0.48 ± 0.06[c]	0.4 ± 0.02		0.55 ± 0.08	This work
Br^-	0.21 ± 0.03[c]	0.3 ± 0.04		0.26 ± 0.08	This work
$^+NH_3CH_2CO_2^-$			0.55 ± 0.1		7
$HC_2O_4^-$			1.16 ± 0.06		6
$C_2O_4^{2-}$			4.5 ± 0.2		6

[a] Equilibrium constant obtained following ion-exchange separation (and determination) of components in equilibrated solutions. [b] Equilibrium constant from rate constants (k_f/k_{aq}). [c] $[H^+] = 0.10$ M. [d] $[H^+] = 0.01$ M. [e] Obtained spectrophotometrically from absorption changes in the uv range. [f] Obtained from kinetic treatment.

water. The solution was passed down a Dowex 50W-X2 (200–400 mesh) ion-exchange column (10 cm long, 1.2 cm diameter) under N_2 pressure to reduce the residence time of $Cr(NH_3)_5I^{2+}$. The column was further washed with 25 ml of H_2O and with 25 ml of a 0.4 M $NaClO_4$–0.1 M $HClO_4$ mixture. The eluate (total 100 ml) up to this stage was oxidized to Cr(VI) by the alkaline–peroxide method and CrO_4^{2-} was estimated spectrophotometrically. The column was washed with a second batch of 0.4 M $NaClO_4$–0.1 M $HClO_4$ mixture (ca. 250 ml) and tested for Cr. The complex $Cr(NH_3)_5H_2O^{3+}$ was eluted finally using a 0.9 M $NaClO_4$–0.1 M $HClO_4$ mixture under non-air-free conditions. Assuming that the Cr(VI) detected in the first 100 ml of eluate was due to $Cr(NH_3)_5I^{2+}$, four determinations of $K_{OS}K_{IS}$ were made using (7).

Kinetic Methods. Kinetic runs were monitored on a Unicam SP500 spectrophotometer fitted with a thermostated cell housing, except in the case of equilibration with $CF_3CO_2^-$. Due to small absorption changes in the visible region on $CF_3CO_2^-$ equilibration with $Cr(NH_3)_5H_2O^{3+}$, kinetic data were obtained using a thermostated double beam Unicam SP8000 spectrophotometer with scale expansion. The aquation of complexes $Cr(NH_3)_5X^{2+}$, $X^- = Cl^-$, Br^-, and I^-, proceeded to completion and hence measured A_∞ values were used in the evaluation of rate constants. First-order plots of log $(A_\infty - A_t)$ against time were linear to 85–90% completion. Rate constants, k_{aq}, were obtained from the slopes (×2.303) of linear plots. With the complexes $Cr(NH_3)_5X^{2+}$, $X^- = NCS^-$ and $CF_3CO_2^-$, calculated A_∞ values were used on the assumption that the aquation reactions proceeded to completion. First-order plots were linear to 25–35% for NCS^- aquation and 60–70% for $CF_3CO_2^-$ aquation. The aquation rate constants for $Cr(NH_3)_5(O_2CCCl_3)^{2+}$ were measured at an isosbestic point, 505 nm, for the formation of $Cr(NH_3)_4(H_2O)(O_2CCCl_3)^{2+}$ (see Figure 1). Observed A_∞ values were used; first-order plots were linear for two half-lives and gave $(k_{aq} + k_1)$. From the spectrophotometric product analysis (ca. 20% reaction occurs by k_1) k_{aq} was obtained.

Anation reactions of $Cr(NH_3)_5H_2O^{3+}$ with $X^- = Cl^-$, Br^-, and $CF_3CO_2^-$ proceeded to 5–35% completion for $X^- = Cl^-$ and Br^- and 20–50% completion for $X^- = CF_3CO_2^-$ (depending on $[X^-]$). The anation with NCS^- reached completion for all $[NCS^-]$ used. Using the measured A_∞ values, pseudo-first-order plots were linear to 65–95% completion in all these cases. The anation with $CCl_3CO_2^-$ was monitored at 505 nm and calculated A_∞ values were used assuming complete reaction. The pseudo-first-order plots were linear to 35–40%. Ranges of $[H^+]$ covered were 0.1–0.5 M for $X^- = NCS^-$, Cl^-, and Br^- and 0.005–0.02 M for $X^- = CCl_3CO_2^-$ and $CF_3CO_2^-$. Aquation and equilibration reactions (except in the case of $CCl_3CO_2^-$) were monitored at more than one wavelength. The ionic strength was maintained at 1.00 M ($LiClO_4$). Data for all systems were computed using a nonlinear least-squares program[16] with a weighting factor $1/y^2$.

Results

Equilibrium constants which have been determined for inner- and outer-sphere associations of X^- with $Cr(NH_3)_5H_2O^{3+}$ at 50 °C are listed collectively in Table VIII (see Discussion). Graphs used to evaluate $K_{OS} + K_{OS}K_{IS}$ for Cl^- and Br^- are illustrated in Figure 2. The ion-exchange method for determination of $K_{OS}K_{IS}$ was considered satisfactory for all X^- (except iodide); consistent results were obtained and equilibrium constant estimations were reproducible to within at least ±15%. Although using the modified

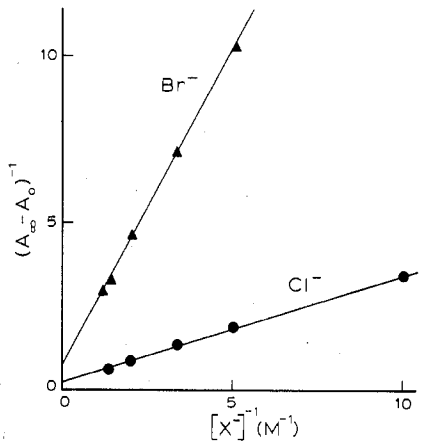

Figure 2. Determination of overall equilibrium constant, $K_{OS} + K_{OS}K_{IS}$, for the complexing of chloride and bromide with aquopentaamminechromium(III) from uv spectrophotometric measurements at 50 °C, $I = 1.0$ M ($LiClO_4$). For Cl^- (●), $[H^+] = 0.1$ M, $[Cr(III)] = 6.0 \times 10^{-3}$ M, λ 225 nm; Br^- (▲), $[H^+] = 0.1$ M, $[Cr(III)] = 8.0 \times 10^{-3}$ M, λ 265 nm.

procedure described consistent values of 0.016, 0.023, 0.023, and 0.025 M^{-1} were obtained for the I^- equilibration, there is no proof that $Cr(NH_3)_5I^{2+}$ is the 2+ (or only 2+) species present. The equilibrium constant and hence the concentration of $Cr(NH_3)_5I^{2+}$ is so small that no colored band was observed on the column. Prolonged ion-exchange procedures involving large volumes of equilibrated solution were not attempted because of the relatively high rate of aquation of $Cr(NH_3)_5I^{2+}$. The solutions collected after the ion-exchange procedure used could not be identified either by spectrophotometry or from the rate of aquation and chromium was detectable only by using the sensitive chromate method of analysis. These values were not considered further in the assignment of mechanism although they are consistent with other $K_{OS}K_{IS}$ values and the correlation with k_{aq} data (see Discussion).

Rate constants k_{aq} for the aquation of all six $Cr(NH_3)_5X^{2+}$ complexes, for the anation with NCS^- and $CCl_3CO_2^-$, and k_{eq}, for the equilibrations of Cl^-, Br^-, and $CF_3CO_2^-$, are listed in Tables II–VII,[17] respectively. No systematic $[H^+]$ dependence was observed for any of the aquation or anation processes, $[H^+] = 0.1$–0.5 M for Cl^-, Br^-, I^-, and NCS^- and $[H^+] = 0.005$–0.02 M for $CCl_3CO_2^-$ and $CF_3CO_2^-$. A lower range of $[H^+]$ was selected for the reactions with $CCl_3CO_2^-$ and $CF_3CO_2^-$ to avoid protonation effects (CCl_3CO_2H, $pK_a = 0.66$;[18] and CF_3CO_2H, $pK_a = 0.23$[19]).

The dependence of k_f on $[X^-]$ for NCS^- and $CCl_3CO_2^-$ anations is illustrated in Figures 3 (NCS^-) and 4 ($CCl_3CO_2^-$). The dependence of k_{eq} on $[X^-]$ for the equilibration of $CF_3CO_2^-$, Cl^-, and Br^- is shown in Figures 5, 6, and 7, respectively. A marked curvature of k_{obsd} with $[X^-]$ was observed only in the case of NCS^-. Similar curvature in the forward step for Br^- equilibration could also be considered (see

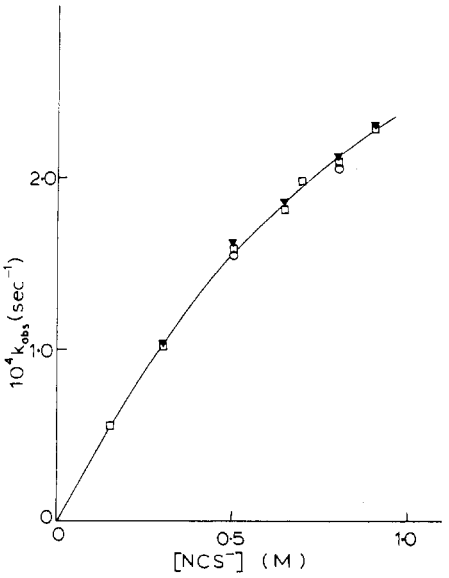

Figure 3. The [NCS$^-$] dependence of the pseudo-first-order rate constants, k_{obsd}, for the reaction of aquopentaamminechromium(III) with thiocyanate at $I = 1.0$ M ($LiClO_4$), 50 °C, [H$^+$] = 0.01 M (▼), 0.10 M (□), 0.20 M (○).

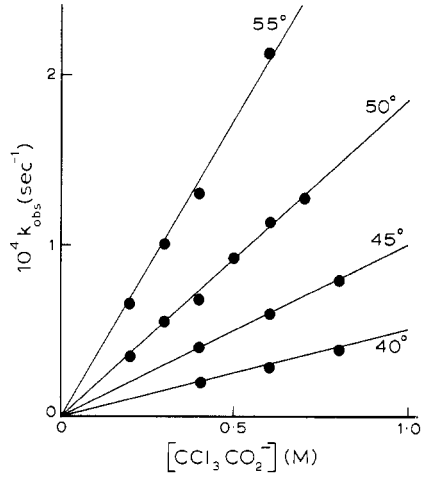

Figure 4. The [$CCl_3CO_2^-$] dependence of pseudo-first-order rate constants, k_{obsd}, for the reaction of aquopentaamminechromium(III) with trichloroacetate at [H$^+$], $I = 1.0$ M ($LiClO_4$).

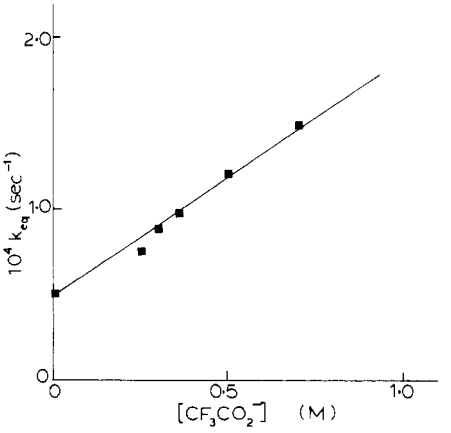

Figure 5. The [$CF_3CO_2^-$] dependence of the pseudo-first-order rate constants, k_{eq}, for the equilibration of aquopentaamminechromium(III) with trifluoroacetate at various [H$^+$], 50 °C, I = 1.0 M ($LiClO_4$).

Figure 7). Such curvature is attributable to outer-sphere association of X$^-$ with $Cr(NH_3)_5H_2O^{3+}$. With X$^-$ =

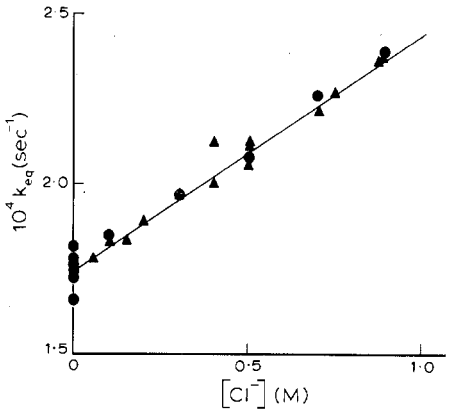

Figure 6. The [Cl$^-$] dependence of pseudo-first-order rate constants, k_{eq}, for the equilibration of chloride with aquopentaamminechromium(III) (▲), and with chloropentaamminechromium(III) (●) at various [H$^+$], 50 °C, $I = 1.0$ M ($LiClO_4$).

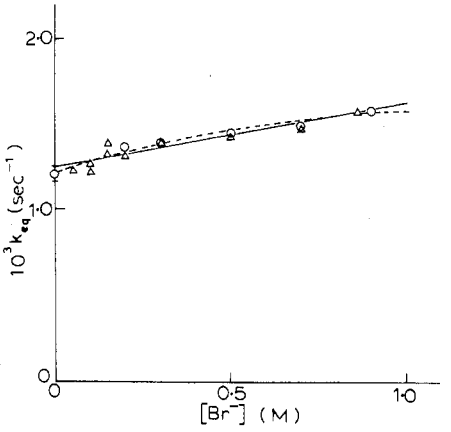

Figure 7. The [Br$^-$] dependence of pseudo-first-order rate constants, k_{eq}, for equilibration of bromide with aquopentaamminechromium(III) (△) and with bromopentaamminechromium(III) (○) at various [H$^+$], 50 °C, $I = 1.0$ M ($LiClO_4$).

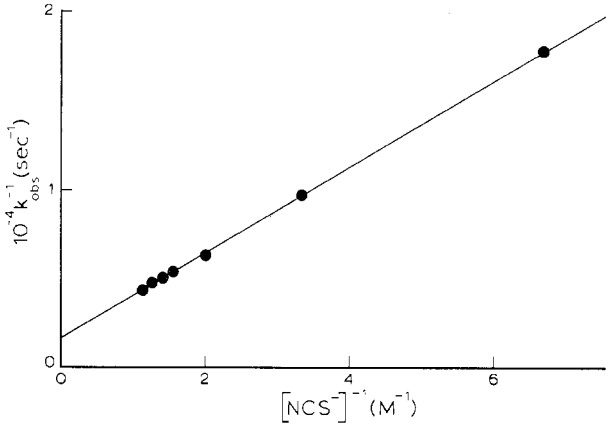

Figure 8. The dependence of k_{obsd}^{-1} on [NCS$^-$]$^{-1}$ for the NCS$^-$ anation of aquopentaamminechromium(III) at 50 °C, $I = 1.00$ M ($LiClO_4$).

$CCl_3CO_2^-$, $CF_3CO_2^-$, and Cl$^-$, there is no compelling evidence for deviations of forward rate constants, k_f, from a first-order dependence on [X$^-$]. However, a general scheme, reaction 8,

$$Cr(NH_3)_5H_2O^{3+} + X^- \overset{K_{OS}}{\rightleftharpoons} Cr(NH_3)_5H_2O^{3+}, X^-$$
$$Cr(NH_3)_5H_2O^{3+}, X^- \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} Cr(NH_3)_5X^{2+} + H_2O \quad (8)$$

could be considered for all the equilibrations. The rate

Table IX. Summary of Rate Constants for the Formation (k_f) and (k_{an}) and Aquation (k_{aq}) of $Cr(NH_3)_5X^{(3-n)+}$ Complexes at 50.0 °C, I = 1.00 M ($LiClO_4$)

Ligand X^-	10^4k_f, M^{-1} s^{-1}	10^4k_{an},[d] s^{-1}	10^4k_{aq}, s^{-1}	Ref
NCS^-	4.16 ± 0.08	6.12 ± 0.55	0.011 ± 0.001	This work
	3.3 ± 0.15[a]			4
$CCl_3CO_2^-$	1.81 ± 0.02		0.51 ± 0.01	This work[f]
$CF_3CO_2^-$	1.37 ± 0.04		0.50 ± 0.02	This work
Cl^-	0.69 ± 0.02		1.75 ± 0.01	This work
	0.53 ± 0.04[b]			4
Br^-	3.71 ± 0.34[c]		12.5 ± 0.2	This work
I^-			102 ± 3	This work
$^+NH_3CH_2CO_2^-$	7.82 ± 0.74[e]	14.2 ± 3.98[e]		7
$HC_2O_4^-$	6.45	5.86		6
$C_2O_4^{2-}$	29.1	6.46		6
H_2O		13.7[e]		8

[a] Temp 45 °C, I = 0.11 M ($NaClO_4$). [b] Temp 45 °C, I = 1.71 M ($NaClO_4$). [c] Computer fit of the kinetic data at 50.0 °C with an allowance for ion-pair saturation gives $k_f = (6.32 \pm 1.3) \times 10^{-4}$ M^{-1} s^{-1}, $K_{OS} = (0.78 \pm 0.44)$ M^{-1}. [d] $k_{an} = k_f/K_{OS}$. [e] Extrapolated data. [f] Data for this study further refined following T. Ramasami and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 378 (1976).

constants for the equilibration, k_{eq}, are therefore given by (9).

$$k_{eq} = k_{aq} + \frac{k_{an}K_{OS}[X^-]}{1 + K_{OS}[X^-]} \quad (9)$$

When X^- = NCS^- and $CCl_3CO_2^-$, the rate of aquation, k_{aq}, makes negligible contribution to the rate constant, k_{eq}. Therefore (9) reduces to (10). However, only in the case of

$$k_{obsd} = k_{an}K_{OS}[X^-]/(1 + K_{OS}[X^-]) \quad (10)$$

X^- = NCS^- is $K_{OS}[X^-]$ significant compared to 1, so that a less than first-order dependence is observed, Figure 3. The intercept and intercept/slope ratio of a plot of $(k_{obsd})^{-1}$ against $[NCS]^{-1}$ give k_{an} and K_{OS}, respectively, Figure 8. When $K_{OS} << 1$, as in other cases of X^-, the forward rate constant, k_f, is given by (11). When X^- = I^-, the rate of aquation, k_{aq},

$$k_f = k_{an}K_{OS}[X^-] \quad (11)$$

predominates over the forward step in (9) and so k_{eq} approximates to k_{aq}. The rate constants, k_{eq}, were found to be independent of the identity of the starting complex, whether this was $Cr(NH_3)_5H_2O^{3+}$ or $Cr(NH_3)_5X^{2+}$, with X^- = Cl^- and Br^-. As the kinetics of the anation with $CCl_3CO_2^-$ were monitored at the isosbestic point, 505 nm, for the process involving the product $Cr(NH_3)_4(H_2O)(O_2CCCl_3)^{2+}$ the term k_1 in (2) does not contribute. Rate constants k_f, k_{an}, and k_{aq} are listed collectively with those for other comparable ligands in Table IX (see below).

Activation parameters for the forward rate constants, ΔH_f^* and ΔS_f^*, for the Cl^- and NCS^- anation of $Cr(NH_3)_5H_2O^{3+}$ have been reported by Duffy and Earley[4] (in the absence of Br^-) and have now been obtained for the anation with X^- = Br^- and $CCl_3CO_2^-$ (see Table X). Activation parameters for the aquation reactions, ΔH_{aq}^* and ΔS_{aq}^*, for all six $Cr(NH_3)_5X^{2+}$ complexes are available in the literature. For X^- = Br^- and I^-, ΔH_{aq}^* and ΔS_{aq}^* have been redetermined.

Discussion

The equilibrium constants for inner- and outer-sphere associations are summarized in Table VIII. The need to estimate K_{OS} independently with high accuracy limits the usefulness of $K_{OS} + K_{OS}K_{IS}$. Kinetic measurements also have been found to be useful only in cases where equilibrium constants are large. The method involving ion-exchange separation of equilibrated solutions appears to be the most realistic for slow equilibrations such as those involved in this study. Even this technique, due to lengthy procedures, nonstoichiometric recovery of total Cr(III) (±3%), and the possibility of resin catalyzed processes, requires careful assessment. This same technique has been used to obtain even smaller equilibrium constants, $K_{OS}K_{IS}$, than those encountered in the $Cr(NH_3)_5X^{2+}$ series, for example, a value of 10^{-5} M^{-1} for X^- = I^- in the case of the $Cr(H_2O)_5X^{2+}$ series.[20] Difficulties experienced in determining small equilibrium constants have been discussed previously.[21-24] Equilibrium constants, $K_{OS}K_{IS}$ obtained by ion-exchange and kinetic methods in this study, are, however, in good agreement (Table VIII). The rate constants k_f and k_{aq} and the equilibrium constant (k_f/k_{aq} = $K_{IS}K_{OS}$) could be obtained with sufficient accuracy (see Table VIII) by kinetic methods, though in the case of Br^- uncertainties are involved in k_f due to outer-sphere complexing. Since the ion-exchange procedures used in the separation of $Cr(NH_3)_5X^{2+}$ involved only 4–5 h, the aquation of $Cr(NH_3)_5Br^{2+}$ at 0 °C (k_{aq} at 0 °C = 4.5×10^{-6} s^{-1}) is alone relevant. The inaccuracies even in this case are minimal. This is supported by the observation that in a blank experiment performed on $Cr(NH_3)_5Br^{2+}$, 98% of Cr(III) could be recovered as $Cr(NH_3)_5Br^{2+}$ under the conditions employed in equilibrium constant estimations. The reproducibility of equilibrium constants estimated by the ion-exchange method confirms the validity of data, and errors are well within the accuracy of the technique.

Table X. Summary of Activation Parameters for the Forward Rate Constants (k_f) for the Reactions of X^- with $Cr(NH_3)_5H_2O^{3+}$

Ligand X^-	ΔH_f^*, kcal mol^{-1}	ΔS_f^*, cal K^{-1} mol^{-1}	Ref
NCS^-	24.4	3	4
$CCl_3CO_2^-$	25.2 ± 0.32	2.2 ± 1.0	This work
Cl^-	25.6	2	4
$HC_2O_4^-$	26.7	9.4	6
$C_2O_4^{2-}$	24.9	7.8	6
$^+NH_3CH_2CO_2^-$	25.3 ± 0.93	5.6 ± 2.9	This work
H_2O[a]	23.2	0	8
Br^-[b]	21.9 ± 1.2	−4.0 ± 3.9	This work

[a] Activation parameters for water exchange. [b] From a least-squares treatment (with unit weighting) of $k_{an}K_{OS}$ values at each temperature.

The results obtained with X^- = NCS^- give direct kinetic evidence for outer-sphere association in $Cr(NH_3)_5H_2O^{3+}$ anation studies. It is assumed that a mechanism involving outer-sphere association also holds for X^- = $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, and Br^- and spectrophotometric and kinetic data are consistent with this. The outer-sphere association constants, K_{OS}, obtained by kinetic procedures for NCS^- at 50 °C, I = 1.00 M ($LiClO_4$), Table VIII, compare well with the previously reported K_{OS} values such as 1.1 M^{-1} at 50 °C for $Cr(NH_3)_5H_2O^{3+}$,$HC_2O_4^-$ [6] and 1.0 M^{-1} at 25 °C for $Cr(H_2O)_6^{3+}$,NCS^- [25] at I = 1.0 M ($NaClO_4$). The outer-sphere association constants, K_{OS}, reported by Duffy and Earley[4] for $Cr(NH_3)_5H_2O^{3+}$ from spectrophotometric measurements are around (3 ± 2) M^{-1} for Cl^- and (10 ± 4) M^{-1} for NCS^- at I = 0.16 M ($NaClO_4$), 23.3 °C. As King et al.[26] have pointed out, it is not always possible to obtain K_{OS} by spectrophotometry for weak outer-sphere complexes. This is especially true when $[X^-]$ is large and spectrophotometric contributions from second ion-pairing and activity changes may also contribute. An examination of spectrophotometric changes in the uv range for outer-sphere association of X^- = $CCl_3CO_2^-$, Cl^-, and Br^- with $Cr(NH_3)_5H_2O^{3+}$ indicated that when $[X^-]$ = 0.1–0.9 M, K_{OS} values cannot be determined accurately since spectrophotometric changes due to the second outer-sphere association process may also be contributing. Outer-sphere association constants of about 1.0

M^{-1} are to be expected for 3+,1− ions from theoretical calculations at $I = 0.5$ M.[6,27] The value of K_{OS} for $X^- = NCS^-$ obtained in the present kinetic studies is consistent with such theoretical values. Failure to observe any form of ion-pair saturation in the kinetic studies with $X^- = CF_3CO_2^-$, Cl^-, and $CCl_3CO_2^-$ requires further comment. With the first two, the experimentally measured rate constants, k_{eq}, contain a substantial contribution from k_{aq}, Figures 5 and 6. Hence minor deviations in the forward rate constant, k_f, may well escape experimental detection. With $X^- = CCl_3CO_2^-$, however, the forward rate constant, k_f, was measured independent of k_{aq} and a K_{OS} value comparable to that obtained for NCS^- would certainly have been detected. A significantly smaller value of K_{OS} seems likely therefore for $CCl_3CO_2^-$ at least. Other instances are known where from kinetic behavior smaller than expected K_{OS} values are apparent.[28]

A summary of second-order rate constants ($k_{an}K_{OS}$) is given in Table IX along with the previous data for Cl^- and NCS^- from ref 4. Very low limits of k_{an} have been set up by Duffy and Earley,[4] $\geq 3.3 \times 10^{-6}$ s^{-1} for Cl^- and $\geq 4.4 \times 10^{-6}$ s^{-1} for NCS^- at 30 °C, possibly due to an overcorrection for ion pairing. A plot of k_{aq} at 45 °C against $[X^-]$ for the data reported[4] does not indicate any curvature due to ion-pair saturation either for Cl^- or for NCS^-. A statistical treatment of the reported data does not yield any kinetically significant outer-sphere association constant. Considering the temperature and ionic strength differences, the second-order rate constant, $k_{an}K_{OS}$, is in satisfactory agreement with those obtained in the present study, see Table IX.

Rate constants reported for the acetate, $CH_3CO_2^-$, anation of $Cr(NH_3)_5H_2O^{3+}$ may or may not correspond to the formation of $Cr(NH_3)_5(O_2CCH_3)^{2+}$. The spectrum reported (and used) by the authors[29] as that of $Cr(NH_3)_5(O_2CCH_3)^{2+}$ (λ_{max}, 410 and 560 nm) differs significantly from that of an authenticated spectrum of $Cr(NH_3)_5(O_2CCH_3)^{2+}$ (λ_{max} 367 and 494 nm)[2]. Therefore $CH_3CO_2^-$ data have not been included in the summary of anation rate constants for various X^{n-} with $Cr(NH_3)_5H_2O^{3+}$.

The data summarized in Table IX show that the second-order rate constants k_f ($=k_{an}K_{OS}$) vary by only one order of magnitude for eight ions of 1− charge. The value for $C_2O_4^{2-}$ is understandably bigger and outside this range because K_{OS} is bigger for 2− charged species. Comparable $k_{an}K_{OS}$ values for the anation of $Cr(H_2O)_6^{3+}$ give a spread of at least three orders of magnitude.[30] The choice of anions is limited in the case of the pentaammine series due to interference from subsequent reactions involving loss of ammonia. Thus in the anation studies with SO_4^{2-}, NO_3^-, F^-, and others secondary processes are involved, which make the determination of k_f difficult. It has been suggested previously that the ratio of anation (k_f) rate constants for the reactions of NCS^- and Cl^- is diagnositic of the mechanism. The value for $Cr(H_2O)_6^{3+}$ is 60 and is believed to support an associative mechanism whereas values <10 are believed to be more in keeping with a dissociative process.[31] The value for $Cr(NH_3)_5H_2O^{3+}$ is 6.

Anation reactions of $Cr(NH_3)_5H_2O^{3+}$ are significantly faster than those involving $Cr(H_2O)_6^{3+}$. The water exchange rate constants are also two orders of magnitude different for the two cations, $Cr(NH_3)_5H_2O^{3+}$ (5.2×10^{-5} s^{-1} at 25 °C) and $Cr(H_2O)_6^{3+}$ (4.3×10^{-7} s^{-1} at 25 °C for one ligand).[32] These water exchange rate constants along with the differences in acid dissociation constants, $Cr(NH_3)_5H_2O^{3+}$ ($pK_a = 5.2$)[33] and $Cr(H_2O)_6^{3+}$ ($pK_a = 3.6$),[34] are consistent with H_2O in the ammonia ligand evironment being a better leaving group. Similar reasoning might be invoked to explain why H_2O and not NH_3 is the leaving group in $Cr(NH_3)_5H_2O^{3+}$.

It is possible to obtain the values of k_{an} in those cases in which K_{OS} has been determined, $X^- = NCS^-$, $^+NH_3CH_2CO_2^-$, $HC_2O_4^-$, $C_2O_4^{2-}$. Values of k_{an} obtained in these four cases lie in a narrow range ($5–14$) $\times 10^{-4}$ s^{-1} at 50 °C and are comparable to the rate constant for H_2O exchange on $Cr(NH_3)_5H_2O^{3+}$ ($k_{ex} = 13.7 \times 10^{-4}$ s^{-1} at 50 °C). This observation that rate constants k_{an} for 1−, 2−, and zero charged reactants as well as the zwitterion are comparable is indicative of $Cr–OH_2$ bond breaking being the dominant factor.

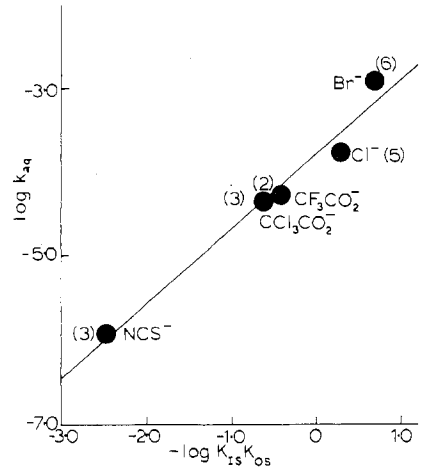

Figure 9. Linear free-energy plot for the relationship between log k_{aq} and $-\log K_{IS}K_{OS}$ for acidopentaamminechromium(III) complexes at $I = 1.0$ M ($LiClO_4$), 50 °C. Numbers in parentheses indicate the number of equilibrium constant determinations by the ion-exchange method.

Dissociative processes have been suggested previously by Parris and Wallace[35] following their studies on the aquation of $Cr(NH_3)_5X^{2+}$, $X^- = Cl^-$, Br^-, and I^-. Jones and Phillips[36] have observed that in the aquation of halogenopentaamminechromium(III) complexes, the rate constants increased in the order $I^- > Br^- > Cl^-$ indicating that the bond strength of Cr–X is important. However, greater dependence of aquation rate constants on the nature of the leaving group as compared to $Co(NH_3)_5X^{2+}$ complexes has also been suggested by other workers.[37,38] The linear relationship reported by Monacelli[39] between the rate constants of aquation of the $Cr(NH_3)_5X^{2+}$ complexes, $X^- = Cl^-$, Br^-, and I^-, and pK_a of the strong acids HCl, HBr, and HI has been criticized for its choice of pK_a values.[40,41]

From the data reported herein, Tables VIII and IX, a linear relation of log k_{aq} against $-\log K_{OS}K_{IS}$ is observed for complexes $Cr(NH_3)_5X^{2+}$, $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, and Br^-, Figure 9. The slope, 0.91 ± 0.05, of the line obtained for the $Cr(NH_3)_5X^{2+}$ series is much larger than the slope, 0.56, observed for the corresponding plot for the $Cr(H_2O)_5X^{2+}$ series, where the slope of these lines is believed to be a measure of the degree of bond breaking in the transition state.

Activation parameters, ΔH_f^* and ΔS_f^*, for the anation rate constants, k_f, for $Cr(NH_3)_5H_2O^{3+}$ have been tabulated in Table X. It is evident that a spread of activation enthalpies, ΔH_f^*, for $Cr(H_2O)_6^{3+}$ (5.5 kcal mol^{-1}) and a narrower range for $Cr(NH_3)_5H_2O^{3+}$ (3.5 kcal mol^{-1}) are observed. This again suggests a much smaller dependency on the nature of the entering group. Activation parameters, ΔH_{aq}^* and ΔS_{aq}^*, for aquation reactions of $Cr(NH_3)_5X^{2+}$ complexes are given in Table XI. A bigger spread of ΔH_{aq}^* values is apparent for $Cr(NH_3)_5X^{2+}$ complexes again in keeping with a dissociative process.

The results obtained in this study therefore favor a considerable degree of dissociative character for substitution reactions involving the formation and aquation of $Cr(NH_3)_5X^{2+}$ complexes. It is difficult to reconcile the kinetic

Table XI. Summary of Activation Parameters for the Aquation Reactions of $Cr(NH_3)_5X^{2+}$ Complexes

Ligand X^-	ΔH_{aq}^*, kcal mol^{-1}	ΔS_{aq}^*, cal K^{-1} mol^{-1}	Ref
NCS^-	24.3	−8	1
$CCl_3CO_2^-$	21.5	−11.3	2
$CF_3CO_2^-$	20.2	−13.9[a]	3
Cl^-	20.7	−11	4
Br^-	20.9 ± 0.26	−7.2 ± 0.8	This work
I^-	18.3 ± 0.19	−10.8 ± 0.63	This work

[a] Recalculated value from the data presented in ref 3.

data obtained with the I_a mechanism previously proposed on the basis of ΔV^* for the water exchange of $Cr(NH_3)_5H_2O^{3+}$ [8] and other aquation reactions of $Cr(NH_3)_5X^{2+}$ complexes, $X^- = Cl^-$, Br^-, I^-, and NCS^-.[42]

The assignment of a dissociative process such as I_d for $Cr(NH_3)_5H_2O^{3+}$ reactions whereas an associative process is favored for $Cr(H_2O)_6^{3+}$ lends support to the hypothesis that a metal may not be associated with a single type of mechanism in all ligand environments. With Co(III), it is now established that $Co(NH_3)_5H_2O^{3+}$ and $Co(CN)_5H_2O^{2-}$ undergo I_d and D substitutions respectively.[43-45] The comparisons with $Co(H_2O)_6^{3+}$ may not be strictly valid, because the spin state of Co(III) in $Co(H_2O)_6^{3+}$ is not very certain. Rate constants for the anation of $Co(H_2O)_6^{3+}$ with NCS^- (86.5 M^{-1} s^{-1})[46] and Cl^- (≤2.0 M^{-1} s^{-1})[47] differ by a factor ≥43 suggesting some associative character[31] in keeping with other tripositive hexaaquo metal ions, e.g., Ti(III), V(III), and Mo(III).[31,48,49] Although a dissociative mechanism might at one time have been envisaged for all Co(III) substitutions, it is now clear that the ligand environment plays an important role.

The general features of the present study indicate that $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_5H_2O^{3+}$ differ in substitution properties. Considering the bonds Cr–NH_3 and Cr–OH_2, it might be expected that since oxygen is more electronegative than nitrogen the donation of electron density to the metal will be more favorable in the Cr(III)–NH_3 bond as compared to the Cr(III)–OH_2 bond. As no π back-bonding is possible in the two cases, the net electron density on Cr(III) might be expected to be higher in the case of pentaammine environments than in the case of pentaaquo environments. This is likely to reduce the susceptibility to an associative attack and will tend to favor dissociative processes. Langford and Sastri[50] from the correlations drawn by Hunt and co-workers[51] on water exchange of Ni(II)–ammine complexes, have estimated that five NH_3 groups would be expected to labilize one water ligand by a factor of 10^3 as compared to an environment of five H_2O ligands. It is not surprising therefore that for such drastic labilizing effects a change of mechanism is sometimes observed.

Acknowledgment. T.R. is grateful to the Indian Government for the award of a National Merit Scholarship.

Registry No. $Cr(NH_3)_5H_2O^{3+}$, 28101-85-1; $Cr(NH_3)_5NCS^{2+}$, 16884-60-9; $Cr(NH_3)_5CCl_3CO_2^{2+}$, 38551-80-3; $Cr(NH_3)_5CF_3CO_2^{2+}$, 38551-83-6; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; $Cr(NH_3)_5I^{2+}$, 17979-08-7; $Cr(NH_3)_4H_2O(Cl_3CCO_2)^{2+}$, 60306-01-6; $^+NH_3CH_2CO_2^-$, 56-40-6.

Supplementary Material Available: Tables I–VII listing kinetic data (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954).
(2) E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, **11**, 1746 (1972).
(3) R. Davies, G. B. Evans, and R. B. Jordan, *Inorg. Chem.*, **8**, 2025 (1969).
(4) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 272 (1967).
(5) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).
(6) O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1232 (1973).
(7) T. Ramasami, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **15**, 2318 (1976).
(8) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972).
(9) T. Ramsami, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, **14**, 359 (1975).
(10) M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allg. Chem.*, **278**, 287 (1955).
(11) E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Inorg. Nucl. Chem.*, **31**, 449 (1969).
(12) J. H. Espenson and S. R. Hubbard, *Inorg. Chem.*, **5**, 686 (1966).
(13) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **266**, 49 (1957).
(14) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).
(15) T. Ramasami, Ph.D. Thesis, University of Leeds, 1976, pp 93–95.
(16) Los Alamos report LA 2367 (1959) and Addenda by R. M. Moore and R. K. Zeigler. See also ref 15, pp 99–102.
(17) Supplementary material.
(18) H. V. Halban and J. Brill, *Helv. Chim. Acta*, **27**, 1719 (1944).
(19) A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, **73**, 2323 (1951).
(20) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).
(21) J. Bjerrum, *Proc. Symp. Coord. Chem., 3rd*, (1970).
(22) S. Ahrland, *Coord. Chem. Rev.*, **8**, 21 (1972).
(23) G. H. Nancollas, *Coord. Chem. Rev.*, **5**, 379 (1970).
(24) J. Bjerrum, *Pure Appl. Chem.*, **34**, 71 (1972).
(25) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).
(26) E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).
(27) M. R. Hyde and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1340 (1972).
(28) W. J. Reynolds, I. Murati, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 719 (1974).
(29) D. Banerjea and S. Sarker, *Z. Anorg. Allg. Chem.*, 373, 73 (1970).
(30) D. Thusius, *Inorg. Chem.*, **10**, 1106 (1970).
(31) Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1048 (1975).
(32) D. R. Stranks and T. W. Swaddle, *J. Am. Chem. Soc.*, **93**, 2783 (1971).
(33) W. K. Wilmarth, H. Graff, and S. T. Gustin, *J. Am. Chem. Soc.*, **78**, 2683 (1956).
(34) L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 25** (1971).
(35) M. Parris and W. J. Wallace, *Inorg. Chem.*, **3**, 133 (1964).
(36) T. P. Jones and J. K. Phillips, *J. Chem. Soc. A*, 674 (1968).
(37) S. C. Chan, *J. Chem. Soc. A*, 2375 (1964).
(38) N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 129 (1966).
(39) F. Monacelli, *Ric. Sci.*, **37**, 777 (1967).
(40) L. E. Asher and E. Deutsch, *Inorg. Chem.*, **12**, 1774 (1973).
(41) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
(42) G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **51**, 821 (1973).
(43) A. Haim, *Inorg. Chem.*, **9**, 426 (1970).
(44) C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, N.Y., 1961, p 55.
(45) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).
(46) G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).
(47) A. McAuley, M. W. Malik, and J. Hill, *J. Chem. Soc. A*, 2461 (1970).
(48) R. C. Patel and H. Diebler, *Ber. Bunsenges. Phys. Chem.*, **76**, 1035 (1972).
(49) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).
(50) C. H. Langford and V. S. Sastri, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. 1*, **9**, 203 (1972).
(51) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **92**, 978 (1970).