One general conclusion which can be drawn is that, when the electrophilic center enhances the contribution of the polarizability of the reagent in SN2 reactions, then the nucleophilic order and the reactivity are little influenced by the nature of the solvent. In other words, in the reactions at soft centers such as Pt(II), in which the polarizability of the nucleophile exerts an important role, the nature of the solvent becomes relatively less important.

In these reactions, it is therefore possible to distinguish the contribution of solvation from that of the reagent polarizability, owing to the fact that the solvation effect is a relatively small one in comparison to the contribution from the polarizability of the reagents.

In most cases of SN2 reactions at saturated carbon centers, the extent of bond formation realized at the transition state is relatively small.[8] In the case of displacements on Pt(II) complexes, however, one can conclude that bond formation at the transition state is the driving force of the reaction,[25] whereas solvation exerts a secondary effect. This assumption is supported by the fact that stable five-coordinated complexes of d^8 ions have recently been prepared.[26] Furthermore, Pt(II) reactions are accompanied by relatively small activation enthalpies and by rather negative values of activation entropies; this is consistent with a net increase in bonding at the transition state.[27]

Acknowledgments.—This work was supported by the Italian Consiglio Nazionale delle Ricerche (CNR, Rome).

[25] For a discussion on the platinum–nucleophile bond see R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963), and ref 1a and 9a.

[26] For a recent review see L. M. Venanzi, *Angew. Chem., Intern. Ed. Engl.*, **3**, 453 (1964); see also R. O. Cramer, R. V. Lindsey, C. T. Prewitt, and V. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965); C. M. Harris, R. S. Nyholm, and D. J. Philips, *J. Chem. Soc.*, 4379 (1963); C. M. Harris and R. S. Nyholm, *ibid.*, 63 (1957); J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *ibid.*, 1803 (1964); P. C. Westland, *ibid.*, 3060 (1965).

[27] U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

Contribution No. 1821 from the Institute for Atomic Research and Department of Chemistry,
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Kinetics and Mechanism of Electron Exchange between Chromium(II) and Monoamminepentaaquochromium(III)[1]

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Chromium(II) catalyzes replacement of ammonia by water in the complex $Cr(H_2O)_5NH_3^{3+}$; the rate law is $-d[CrNH_3^{3+}]/dt = (k_0 + k_{-1}/[H^+])[Cr^{2+}][CrNH_3^{3+}]$, with $k_0 = 2.5 \times 10^{-5}\ M^{-1}\ sec^{-1}$ and $k_{-1} = 5.9 \times 10^{-5}\ sec^{-1}$ at 25.0° and 2.0 *M* ionic strength. Kinetic measurements have been made from 25 to 70°, and activation parameters have been calculated for each rate constant. The reaction is formulated in terms of a chromium(II)–chromium(III) electron-exchange reaction, and it is inferred indirectly that the reaction proceeds by an inner-sphere mechanism with H_2O and OH^- bridging ligands. Radiotracer experiments on $^*Cr^{2+}$ and the ammine complex establish that chromium exchange, with accompanying NH_3 transfer, does not take place rapidly, compared to the rate at which chromium(II) catalyzes ammonia release.

Introduction

Anderson and Bonner[2] have studied the kinetics of the relatively slow electron exchange between the aquo ions of chromium(II) and -(III) in acidic perchlorate solutions. We report here the results of a study of the electron exchange between aquochromium(II) and the inert monoammine complex of chromium(III).

$$Cr^{2+}(aq) + {}^*Cr(OH_2)_5NH_3^{3+} + H_3O^+ = Cr(OH_2)_6^{3+} + {}^*Cr^{2+}(aq) + NH_4^+ \quad (1)$$

The principal feature distinguishing this reaction from the aquo ion exchange[2] is that net chemical change—replacement of the ammonia molecule by water in the primary coordination sphere of chromium(III)—accompanies electron transfer. It is just this aspect, rather incidental to the main electron-transfer process of interest here, that allows us to follow the rate of reaction 1 by conventional spectrophotometric techniques without recourse to isotopic substitution.

The possibility of electron transfer *without* loss of coordinated NH_3 (*i.e.*, NH_3 ligand transfer accompanying electron transfer) has been examined by use of isotopically labeled chromium. This study also provides information on the role of ligands, such as NH_3, which cannot act as efficient electron-transfer bridges.

Experimental Section

Reagents.—Two independent preparations of chloride-free chromium(II) solutions were used: chromium(III) perchlorate solutions were reduced electrolytically at a mercury cathode, and high-purity chromium metal was dissolved in dilute perchloric acid. The preparations, handling, and analyses of these solutions have been described in detail previously.[3] The ion[4] $CrNH_3^{3+}$ was prepared by reaction of chromium(II) and hydrazoic

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[1] Work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission.

[2] M. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

[3] (a) J. H. Espenson, *Inorg. Chem.*, **3**, 968 (1964); (b) *ibid.*, **4**, 1025 (1965).

[4] In general, coordinated solvent molecules will be omitted in formulas for complex ions unless necessary for clarification.

acid in the presence of chloride ion.[5] The solution containing $CrNH_3{}^{3+}$ was passed through a column of Dowex 50W-X8 cation-exchange resin and separated by elution with 3 *F* $HClO_4$. The complex used in most experiments was further purified and concentrated by adsorbing this material, after dilution to lower the electrolyte concentration, onto fine (200–400 mesh) cation resin, followed by slow displacement with 1 *F* barium perchlorate.[6] This technique provides 0.1–0.5 *M* $CrNH_3{}^{3+}$ with relatively low hydrogen ion concentration, free of Ba^{2+}, and substantially free of Cr^{3+}. The visible and ultraviolet absorption spectrum of $CrNH_3{}^{3+}$ agrees with values in the literature.[5,7,8]

Lithium perchlorate, used to maintain ionic strength, was a double recrystallization of the reagent grade salt from water. Reagent grade perchloric acid was used without further purification. Water for all preparations and reaction solutions was a double distillation of laboratory-distilled water from alkaline permanganate in a tin-lined Barnstead still.

Rate Procedures and Measurements.—The extent of reaction was followed spectrophotometrically by recording the decrease in absorbance due to the disappearance of $CrNH_3{}^{3+}$ at wavelengths 5040–5520 A. The relatively slow reactions involved here (reactions with half-times as long as 142 hr were studied) and the extreme sensitivity of chromium(II) to oxygen required special handling procedures. In every instance, reactions were carried out in specially constructed Pyrex reaction cells, completely sealed to prevent atmospheric contamination. These cells were cylindrical horizontal tubes with rounded ends, with a 12-mm diameter access tube sealed vertically into the top of the cell for introduction of solutions. The circular cross section of the tube was *ca.* 25 mm in diameter, and the tubes were 30–70 mm in optical path length.

The absorbance readings were made on solutions in cells with curved optical windows. Our findings here are similar to those of Daugherty and Newton:[9] absorbances of aqueous solutions in such cells can be reproducibly and accurately measured with the cell immersed in water. Beer's law was obeyed by alkaline chromate and by acidic aquochromium(III) solutions in these cells. The details of the thermostated, water-filled cell holder have been described elsewhere.[10]

Each cell, containing all reagents except chromium(II), was purged with purified nitrogen for at least 15 min. The chromium(II) was added by a hypodermic syringe with a long needle, and the cell was sealed with a torch at a constriction in the access tube *ca.* 3 cm above the main cell body.

The cell design was modified to accommodate the higher reaction rates encountered at 70°. A side compartment on the access tube was provided for one chromium reactant. The entire sealed cell, containing the separated reactants under nitrogen, was immersed in a constant temperature bath; after temperature equilibration, the reaction was started by repeated inversion of the cell and mixing of the solutions.

At the lower temperatures (25 and 40°) absorbance measurements were made intermittently; the sealed cells were held in a water bath at the desired temperature from which they were taken occasionally for the brief absorbance measurement. At the higher temperatures (54 and 70°) the reactions were sufficiently rapid (5–72-min half-time) to permit continuous recording of the absorbance of the solution in the sealed and thermostated reaction cell. The continuous readings generally yielded data of somewhat higher precision than did the intermittent readings, where cell-positioning errors caused uncertainties in successive readings of ~0.005 absorbance unit.

The extreme sensitivity of chromium(II) to oxygen required that we analyze each reaction solution for its chromium(II) content. This analysis provided a check not only on the chromium(II) concentration, which must be known accurately, but also on the reaction stoichiometry, shown in eq 1, which indicates no net consumption of chromium(II).[11] The cells containing spent reaction solutions were broken open under nitrogen, and aliquots for chromium(II) analysis were removed by syringe. The very rapid reaction of chromium(II) with $Co(NH_3)_5Cl^{2+}$ in dilute perchloric acid was used for analysis; the cobalt(II) produced was analyzed spectrophotometrically as the thiocyanate complex in 50 vol % acetone solution at 6230 A where the molar absorbancy index is 1843 M^{-1} cm^{-1}, a maximum.[12]

Some duplicate reactions run in darkened vessels gave identical kinetic behavior. There is apparently no significant photochemical effect on the reaction rates measured at 25 and 40°, where the sealed cell was immersed in the water bath exposed to ordinary room illumination.

Radiotracer Experiments.—Labeled chromium(II) was prepared by adding chromium-51 activity (in the form of a chromium(III) solution in hydrochloric acid). Exchange is expected to be rapid,[13] and chromium(II) is expected to reach isotopic equilibrium. This was demonstrated by experiment; the specific activity of separated chromium(II) was the same as the specific activity of the bulk of the chromium(II) stock solution. In the tracer experiments, and in the controls, the chromium(II) was removed by anion exchange after air oxidation in the presence of oxalate ion.[2] The cationic species Cr^{3+} and $CrNH_3{}^{3+}$ were separated on a 200–400 mesh cation-exchange resin contained in a transparent Tygon column. Slices of the column were taken, and the complex was displaced from the resin by addition of 4 *F* perchloric acid. The solution was counted for Cr^{51} activity in a well-type scintillation counter and was analyzed for its chromium content spectrophotometrically as chromate ion.

Results

Spontaneous Aquation of $CrNH_3{}^{3+}$.—The rate at which aquation (eq 2) proceeds is relevant to the present study, since the electron-exchange rate is being equated

$$Cr(H_2O)_5NH_3{}^{3+} + H_3O^+ = Cr(H_2O)_6{}^{3+} + NH_4{}^+ \qquad (2)$$

to the rate of disappearance of $CrNH_3{}^{3+}$. Jørgensen and Bjerrum[14] have reported a kinetic study of the rate of reaction 2 in which the complex was prepared from decomposition of higher ammine complexes. Their specific rates lead to $t_{1/2}$ = 70 hr at 40° in >0.1 *F* HNO_3. We have made a few similar measurements and find $t_{1/2}$ = 220 hr at 40° in 0.096 *F* HNO_3 (I = 0.17 *M*) and $t_{1/2}$ = 180 hr at 40° in 0.15 *F* HNO_3 (I = 0.22 *M*). These rates are substantially lower than those reported previously but are not necessarily inconsistent with the earlier work, in view of the uncertainty in comparing the two reaction media. In solutions containing perchlorate ion as the only anion, however, aquation proceeds much more slowly. For example, at 0.005 *F* $HClO_4$, 45°, $t_{1/2}$ is ~4 × 10^3 hr; at 0.1 *F* $HClO_4$

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[5] M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

[6] J. E. Finholt, K. G. Caveton, and W. J. Libbey, *Inorg. Chem.*, **3**, 1801 (1964).

[7] M. R. Edelson and R. A. Plane, *ibid.*, **3**, 231 (1964).

[8] Our spectral results, wavelength maximum, A (molar absorbancy index, M^{-1} cm^{-1}) are: 5470 (20.5), 3970 (19.0), and 2490 (5.6). Literature values are 5450 (22.1), 3970 (21.8) (ref. 5); and 5520 (18.0), 4000 (17.3) (ref 7). Any contamination with $Cr(OH_2)_6{}^{3+}$ will shift the spectrum to longer wavelengths and give lower apparent absorbancy indices.

[9] N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **67**, 1090 (1963).

[10] J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[11] Several experiments were performed to test how quantitatively chromium(II) can be transferred and stored in these cells under similar conditions. We found 0–2% decrease in chromium(II) at 0.02–0.1 *M*. In kinetics runs where chromium(II) was added as accurately as possible, the recovery at the end of the run was generally 90–97%. In every instance the loss was assumed to have occurred at the start of the reaction, and the analyzed chromium(II) concentration used in the computation.

[12] (a) B. A. Zabin and H. Taube, *Inorg. Chem.*, **3**, 963 (1964); (b) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Press, New York, N. Y., 1959, p 202.

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

[14] E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958).

($I = 0.17$ *M*), 40–45°, $t_{1/2}$ is $\sim 2.5 \times 10^3$ hr; at 0.5 *F* $HClO_4$, 1.5 *F* $LiClO_4$, 45°, $t_{1/2}$ is $>3 \times 10^3$ hr; and at 1.5 *F* $HClO_4$, 0.5 *F* $LiClO_4$, 45°, $t_{1/2}$ is $>6 \times 10^3$ hr. The values in perchlorate solution were obtained in experiments followed to less than 20% completion and represent only rough estimates.

This result indicates that the spontaneous aquation of $CrNH_3^{3+}$ (1) does not compete with the electron-exchange reaction during the times involved for the latter (up to 7 hr half-life at 40°), and (2) itself deserves further investigation with regard to the enormous effect of replacing perchlorate ion with nitrate ion.[15]

Form of the Rate Law.—In any given experiment the reaction followed pseudo-first-order kinetics, with only $CrNH_3^{3+}$ changing concentration; $[Cr^{2+}]$ remained constant (eq 1), as demonstrated also by analysis, and $[H^+]$, generally rather high relative to $[CrNH_3^{3+}]$, decreased only slightly. In all experiments ionic strength 2.0 *M* was maintained with lithium perchlorate. The first-order dependence of rate upon $[CrNH_3^{3+}]$ was verified by the absorbance–time data in each run, generally taken for 3–5 half-times, and by variation of its initial concentration (total variation in $[CrNH_3^{3+}]_0$, sixfold, 0.006–0.038 *M*). The chromium(II) concentration lay in the range 0.024–0.23 *M*.[16] The data are consistent with a mixed second-order rate law (eq 3), over this range of $[Cr^{2+}]$, at a particular $[H^+]$, temperature, and ionic strength

$$-d[CrNH_3^{3+}]/dt = k_{obsd}[CrNH_3^{3+}][Cr^{2+}] \quad (3)$$

Hydrogen ion exhibits an inverse rate effect, similar to that in the aquo ion reaction.[2] A plot of k_{obsd} *vs.* $[H^+]^{-1}$ at each temperature is linear for $[H^+] = 0.09$–1.8 *M*, at ionic strength 2.0 *M;* intercepts of such plots are small, but apparently not zero. Figure 1 shows this graphical treatment of all the data. The complete rate law is

$$-d[CrNH_3^{3+}]/dt = (k_0 + k_{-1}[H^+]^{-1})[CrNH_3^{3+}][Cr^{2+}] \quad (4)$$

Evaluation of the Rate Constants and Their Temperature Dependences.—The assumption has been made in correlating the effect of temperature on the rate that both k_0 and k_{-1} follow the absolute rate theory equation, $k_i = (k_BT/h)e^{\Delta S_i^*/R}e^{-\Delta H_i^*/RT}$. A least-squares computer program was used to calculate the best values of ΔS^* and ΔH^* for k_0 and k_{-1} using the rate constants at each $[H^+]$ and temperature simultaneously.[17]

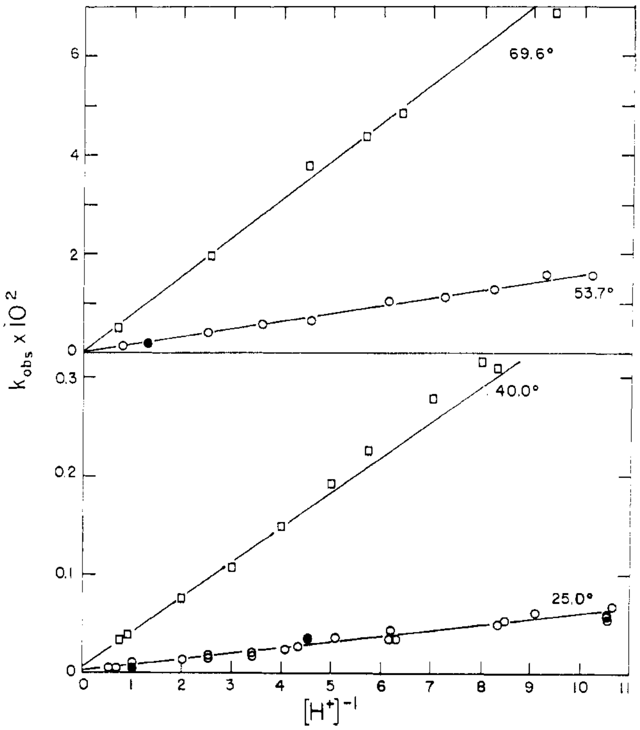

Figure 1.—Plot illustrating dependence of observed second-order rate constant upon $[H^+]$. Points shown are observed values (some data at 25° have been omitted for the sake of clarity). Lines shown are those calculated from activation parameters derived from all data, Table I. Solid points indicate cases where the deviation of observed and calculated points exceeded 15%.

In every calculation, each individual rate constant was weighted as the reciprocal of its square (the standard weighting for quantities whose per cent error remains roughly constant) and also as the reciprocal variance of the fit this rate constant generated between observed and calculated absorbance values in a run. The computation was carried out with several variations. First of all, the calculation was performed using all 63 data points with the two-term rate law, eq 4. Five of the runs had deviations exceeding 15%. These runs did not represent concentration extremes, and, where duplicates were performed, the rate constants agreed better with the calculated fit. The computation of ΔH^* and ΔS^* was repeated with these five points omitted. Finally, the data were required to fit only a single-term rate equation, inverse in hydrogen ion concentration, with the k_0 term arbitrarily set to zero. These computations are summarized in Table I.[18]

The inclusion of the k_0 term in the rate law is justified by the substantially poorer fit when it is omitted.

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(15) We suggest, without further evidence, that the rate enhancement of nitrate ion might be due to its reaction in an oxidation–reduction equilibrium producing chromium(IV). If such an equilibrium existed, it would lie far toward the reactants and would result in inappreciable loss of chromium(III) and nitrate ion. The lability of chromium(IV) would, however, account for loss of coordinated ammonia. This path is analogous to that suggested [A. Ogard and H. Taube, *J. Phys Chem.*, **62**, 357 (1958)] for loss of chloride ion by $Cr(H_2O)_5Cl^{2+}$ catalyzed by oxidizing agents, *e.g.*, manganese(III) and cerium(IV). These suggestions should be capable of experimental verification. Since this reaction is incidental to the theme of this paper, it will not be discussed further here. In all of our solutions used for the electron-exchange experiments, perchlorate ion was the only anion present.

(16) A series of experiments was performed at substantially lower chromium(II) concentration, *ca.* 0.004 *M*. Since the reactions were quite slow under these conditions, the accuracy of rate measurements and Cr^{2+} analyses were not high. Although the rates had values not inconsistent with the values at higher Cr^{2+} and with eq 4, the scatter in these runs was so large that they have not been reported here. These experiments do help substantiate the stoichiometry of chromium(II) catalysis since a solution, 0.01 *M* $CrNH_3^{3+}$ and *ca.* 0.004 *M* Cr^{3+}, for example, forms Cr^{3-} completely and analyzes for a reasonable chromium(II) concentration at completion.

(17) This program is based on a report from Los Alamos Scientific Laboratory, LA2367 plus Addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for these programs.

(18) A tabulation of the individual experiments, giving concentrations and observed and calculated rate constants, has been deposited as Document No. 8704 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

VALUES OF ΔH^*, ΔS^*, AND k

	All data	Omitting 5 runs	k_{-1} term only
ΔH_0^*, kcal mole^{-1}[a]	13.9 ± 1.6	14.5 ± 1.2	. . .
ΔS_0^*, cal mole^{-1} deg^{-1}	−33 ± 5	−31 ± 4	. . .
10^5k_0 (25.0°), M^{-1} sec^{-1}	2.39 ± 0.14	2.46 ± 0.11	0
ΔH_{-1}^*, kcal mole^{-1} deg^{-1}	21.6 ± 0.2	21.6 ± 0.1	20.5 ± 0.3
ΔS_{-1}^*, cal mole^{-1} deg^{-1}	−5.6 ± 0.5	−5.6 ± 0.4	−8.8 ± 0.9
10^5k_{-1} (25.0°), sec^{-1}	5.92 ± 0.10	5.91 ± 0.09	7.2 ± 0.2
% dev[b]	7.0	5.4	13.2

[a] Uncertainties represent standard deviations of calculated values and those observed values used in deriving the parameters. [b] Comparison of observed and calculated rate constants; the average per cent deviation, 100(c − o)/o, of all points used in the particular computation.

In that case, the average deviation was 13.2%, and the number of runs with large deviations increased greatly; 26 of the 63 runs had calculated values differing from the observed by more than 15%. In addition, when the k_0 term was omitted, the calculated rate constants showed large deviations at the extremes of the hydrogen ion concentration range. Since these errors appear to lie considerably outside the experimental error, we conclude that the two-term rate equation is required. In any instance, the relatively small contribution of the k_0 term is reflected in the large uncertainties for the activation parameters ΔH_0^* and ΔS_0^*.[19]

Tracer Results.—The experiments using labeled chromium(II) demonstrated that transfer of NH_3 is far from complete during periods of time such that reaction 1 went *ca.* halfway to completion. In every instance, however, the remaining $CrNH_3^{3+}$ contained appreciable activity (say 10–40% of the calculated, were NH_3 exchange rapid and complete). The majority of this activity can be accounted for by the separation procedure and has its origin in the separation of $CrNH_3^{3+}$ both from Cr^{2+} and from Cr^{3+}. In control experiments where untagged $CrNH_3^{3+}$ is added to $^*Cr^{2+}$, already oxidized by air plus oxalate, the separated $CrNH_3^{3+}$ has a specific activity 5–7% of the value it would have were all chromium species at isotopic equilibrium. Additional control experiments were done with added Cr^{3+}, both normal and tagged (the latter situation resembles that in the actual runs, for the Cr^{3+} produced in reaction 1 arises from $^*Cr^{2+}$). We observed that, although $CrNH_3^{3+}$ appears to separate nicely from Cr^{3+}, the $CrNH_3^{3+}$ specific activity was higher when the added Cr^{3+} was tagged than when it was not and that it increased as the concentration ratio of tagged Cr^{3+} to $CrNH_3^{3+}$ increased.

In tracer experiments searching for NH_3 exchange, the measured specific activity of the $CrNH_3^{3+}$ was always somewhat higher in the sample than in the controls, even when the controls contained the estimated $^*Cr^{3+}$. If NH_3 exchange has taken place (between $CrNH_3^{3+}$ and either Cr^{2+} or Cr^{3+}), the extent of such exchange is the difference of two close numbers. Our data lack sufficient precision and reproducibility to learn the extent of any such exchange. We conclude, then, that, although these results prove that NH_3 exchange is not a rapid process compared to reaction 1, they leave unsettled the question of whether such exchange takes place at all.

Discussion

The rate law, eq 4, implies that the reaction proceeds along two parallel and independent pathways; the activated complexes along each pathway differ by one proton. The mechanism may be described in terms of two parallel net activation processes

$$Cr^{2+}(aq) + Cr(H_2O)_5NH_3^{3+} = [(H_2O)_nCr(H_2O)Cr(H_2O)_4NH_3^{5+}]^* \quad (5)$$

$$Cr^{2+}(aq) + Cr(H_2O)_5NH_3^{3+} = [(H_2O)_nCr(OH)Cr(H_2O)_4NH_3^{4+}]^* + H^+ \quad (6)$$

where an undetermined number of solvent molecules is involved in each. Subsequent decomposition of these activated complexes results in release of ammonia from the coordination sphere of the labile chromium(II).

The acid dissociation quotient for $CrNH_3^{3+}$ is not known, but its value is undoubtedly not greatly different from that of Cr^{3+} ($Q_a \sim 2 \times 10^{-4}$ M). The predominant form of the ammine complex throughout the H^+ range 0.1–2 M is $Cr(H_2O)_5NH_3^{3+}$. The k_{-1} path for electron exchange as formulated in eq 6 may represent a bimolecular reaction of $Cr(NH_3)(H_2O)_4(OH)^2 + Cr^{2+}$(aq) with second-order rate constant given by $k_{OH^-} = k_{-1}/Q_a$. Lack of an exact value for Q_a prevents computing the value of k_{OH^-}.

The question arises as to whether the reaction proceeds by an outer-sphere mechanism, *e.g.*, electron

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(19) Disagreement sometimes exists on the number of rate law terms demanded by the data to express the hydrogen ion dependence of an observed rate constant. A recent communication [A. G. Sykes, *Chem. Commun.* (London), 442 (1965)] commented upon the mechanism we had proposed for the reaction of vanadium(III) and chromium(II) (ref 3b). Sykes' point appears to be that the original two-parameter equation does not describe adequately the hydrogen ion dependence of the rate, and he provided a three-parameter relation which does. His proposed mechanism resembled that which we had formulated originally except that an additional reaction path leading to the same $V(OH)Cr^{4+}$ intermediate has been added. The rate laws are $a/(c + [H^+])$ and $(a + b[H^+]^{-1})/(c + [H^+])$. Is the three-parameter equation in better accord with experiment than the original two-parameter one? The agreement is undoubtedly better, the fit of calculated and observed rate constants with values Sykes derived from our published data being 1.4% average deviation (4.9% maximum deviation), compared to 3.7% (7.0% maximum) originally derived. The average deviation from the mean of individual runs at each particular $[H^+]$ at 25.0° was 3.0%, however, as cited in the published paper. The original two-parameter equation represents the *minimum* description of the system and is all the precision that the kinetic data warrants. *Sykes' formulation certainly is consistent with the data, as are a multitude of mechanisms more complicated than the original proposal.* The question of the form of the rate law could be settled by data of higher precision, say rate constants accurate to 1% or better, or by studies carried to much lower hydrogen ion concentrations (a number of factors indicate that, for this reaction system, extending $[H^+]$ much below 0.03 M, the lowest concentration studied previously, would not be fruitful). Definitive evidence for the additional reaction pathway suggested by Sykes will be difficult to obtain. There is no requirement for it in the available data, at any rate.

tunneling or hydrogen-atom exchange, or by an inner-sphere mechanism in which the activated complexes for electron exchange contain a bridging ligand, H_2O or OH^-, occupying simultaneously the first coordination sphere of each of the two metal ions. Although Anderson and Bonner[2] postulated for the aquo ion exchange an outer-sphere reaction process in which transfer of a hydrogen atom accomplishes electron exchange, the results are also consistent, as noted by Sutin,[20] with an inner-sphere mechanism for both the aquo and the ammine reactions. The analogous $Cr(H_2O)_5X^{2+} + Cr^{2+}$ electron-exchange reactions,[13] where the product criterion applies (X^- transfer accompanies electron exchange), proceed *via* inner-sphere mechanisms in which ligand X constitutes the electron-transfer bridge. Oxygen-18 tracer experiments[21] have also verified ligand (OH^-) transfer for the reaction of $Co(NH_3)_5OH^{2+}$ and Cr^{2+}. The demonstration[22] that Cr^{2+} catalyzes the $Cr(H_2O)_6{}^{3+}$–H_2O exchange is not sufficient, however, to establish the Cr^{2+}–Cr^{3+} exchange mechanism.[23]

If one assumes the same inner-sphere mechanism in the $Cr(H_2O)_5X^{2+} + Cr^{2+}$ reactions for $X = OH^-$ as demonstrated for other anionic ligands, then the relative rate for OH^- occurs at the same place as in the known inner-sphere $Co(NH_3)_5X^{2+} + Cr^{2+}$ reactions; namely, OH^- falls between Cl^- and F^- (this comparison utilizes the acid dissociation quotients of $Cr(H_2O)_6{}^{3+}$ and $Co(NH_3)_5H_2O^{3+}$). Although this comparison may infer a similarity of mechanism and lend some validity to the inner-sphere role of OH^-, it must not be viewed as constituting a proof of similar mechanisms. Reactions involving OH^- complexes are generally much slower than those with other ligands, not for the reason that OH^- is a poor electron-transfer group, but rather that its concentration in complexes in acidic solution is quite low.

The spectrophotometric kinetic measurements cannot settle the question of whether amide ion can act as a bridging ligand since the activated complex

$$(H_2O)_5Cr^{III}\text{–}NH_2\cdots Cr^{II}(aq)$$

accomplishes no net change. The tracer experiments using labeled Cr^{2+} were designed to learn whether such a path plays an important role. Unfortunately, the separation procedure we employed allowed us to place only an upper limit on the rate of NH_3 exchange. Since coordinated NH_3 is a much weaker acid than is H_2O,[24] for the NH_2^--bridged mechanism to compete effectively, its specific rate would necessarily have to be much larger than that of OH^-. Although this appears unlikely, our data do not allow us to rule it out completely.

Comparison of our kinetic results with the aquo ion reaction reveals some similarities. The rate equations have identical forms, and values of the two rate constants and their activation parameters are nearly the same (for Cr^{3+}–Cr^{2+}, $k_0 \leq 1.9 \times 10^{-5}$ compared to $k_0 = 2.4 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$ for $CrNH_3{}^{3+}$–Cr^{2+} at 25.0°, and $k_{-1} = 10 \times 10^{-5}\ \text{sec}^{-1}$, $\Delta H_{-1}{}^{*} = 21$ kcal compared to $6 \times 10^{-5}\ \text{sec}^{-1}$ and 21 kcal). This comparison ignores medium effects (the ionic strength was $\sim 1.1\ M$ for Cr^{3+}–Cr^{2+} and $2.0\ M$ in the present study) and ignores also any difference in the acid dissociation quotients of the two chromium(III) complexes. Assuming that only statistical effects operate, the $CrNH_3{}^{3+}$–Cr^{2+} reaction would proceed at a rate $^5/_6$ that of Cr^{3+}–Cr^{2+}.

A point of interest here is that replacement of one water molecule by ammonia causes no dramatic effect on the rate of reaction with Cr^{2+}, in contrast to the diminution in rate toward Cr^{2+} of $\sim 10^3$ on going from $Cr(OH_2)_5Cl^{2+}$[13] to $Cr(NH_3)_5Cl^{2+}$.[25] The suggestion has been made that the group *trans* to the bridging ligand is responsible, in part, for the reaction rate, such that a *trans* group with a higher ligand field splitting strength (*e.g.*, NH_3 compared to H_2O) causes lower rates.[25] Since $Cr(OH_2)_5NH_3{}^{3+}$ has available bridging ligands *trans* to H_2O, these may be the preferred reaction sites, with no appreciable diminution beyond statistical in rate for $Cr(OH_2)_5NH_3{}^{3+}$ compared to $Cr(OH_2)_6{}^{3+}$. A test of these ideas may lie in an examination of the relative rates toward Cr^{2+} of *cis* and *trans* $Cr^{III}(NH_3)_3X_3$ or $Cr^{III}(NH_3)_4X_2$ ($X = H_2O$, Cl^-), for in these complexes the bridging group has different *trans* substituents, and extraneous effects such as different chemical composition are eliminated for isomeric pairs.

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[23] As pointed out by H. Taube [*Advan. Inorg. Chem. Radiochem.*, **1**, 36 (1960)], depending on whether electron exchange proceeds by an inner- or outer-sphere mechanism, one finds the $Cr(H_2O)_6{}^{3+}$–H_2O exchange occurring at a rate equal to $^5/_6$ or 1.0 times that of electron exchange. The existing data (ref 21, 22) apply to different reaction media and lack sufficient accuracy to permit a definitive answer to this question.

[24] For example, pK_a for $Co(NH_3)_6{}^{3+}$ is >14, compared to 5.7 for $Co(NH_3)_5H_2O^{3+}$: R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

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