factor" of 1.040 or 1.000 as follows. In the S_N2 scheme, $O^{16}H^-$ is likely to be preferred to $O^{18}H^-$, because of the smaller zero point energy of the "hydrate" of the heavier anion. In an S_N1 CB mechanism a similar though smaller discrimination in favor of H_2O^{16} would be expected. In an S_N2 CB system, a slight preference for H_2O^{16} again seems likely, but now the factor is expected to change according to the nature of the leaving group. In all of the cases, however, the attacking group, whether H_2O or OH^-, is only bonded to the solvent weakly, so that a kinetic isotope effect much bigger than 1.01 is unlikely. The largest value observed by Posey and Taube[7] was 1.012. It therefore seems very improbable that, in deciding the resulting fractionation, the kinetic isotope effect will outweigh the equilibrium factor discussed above. The closeness of the observed values to 1.00 appears to eliminate the possibility of OH^- being the group which makes the bond to Co and thus also rules out an S_N2 mechanism.

In total, the results suggest an S_N1 CB mechanism leading to a common intermediate for $X = Cl^-$, Br^-, or NO_3^-; when $X = F^-$, an S_N2 CB mechanism probable operates. SO_4^{-2} is a special case because about 35% of bond breaking[18] takes place at the S–O position so that the results are not directly comparable for the present purpose to the others we have obtained. Even in this case, however, the S_N2 mechanism is rendered unlikely by the results: suppose the splitting at the Co–O bond occurs by an S_N2 mechanism with a

(18) M. Green and H. Taube, to be published.

fractionation factor of 1.040, then to account for an observed factor between 1.00 and 1.01 with 30% bond fission at S–O, the SO_4^{-2} would have to be depleted in O^{18} relative to water by 5%, and this is very unlikely.

The rate constant for the base hydrolysis of the fluoro complex is 0.7 M^{-1} min.$^{-1}$,[19] compared with 52 and 360 M^{-1} min.$^{-1}$ [20] for the chloro and bromo ions. It is possible that a change from an S_N1 CB to an S_N2 CB reaction scheme occurs as the rate of hydrolysis falls, and that the less labile complexes, such as acetato, follow the latter course.

We were unable to find any other complexes of the pentaammine class in which we could look for an S_N2 CB mechanism of hydrolysis. There were experimental difficulties in the case of the iodo complex. However, its rapid rate of hydrolysis suggests a reaction scheme like that of the chloro and bromo complexes. The rates of hydrolysis of the thiocyanato, acetato, phosphato, azido, and nitro complexes are so small compared with the rate of decomposition of the hydroxo complex that precision measurements of the isotopic fractionation for them seem extremely difficult.

(19) M. Green and H. Taube, unpublished observations.
(20) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

The Exchange of Ammonia between Hexaamminechromium(III) Salts and Anhydrous Solvent Using N-15[1]

By THOMAS W. SWADDLE, LaVERLE F. COLEMAN, and JOHN P. HUNT[2]

Rate data are reported for the homogeneous ammonia exchange between $Cr^{III}(NH_3)_6$ and liquid ammonia in NO_3^- and ClO_4^- media. The exchange rates are slow ($t_{1/2}$ values *ca.* 5 to 700 hr.). Addition of ammonium salts causes a marked reduction in the exchange rate; additions of KNO_3 or $NaClO_4$ cause smaller but appreciable rate reductions. The reaction is from 40 to 5 times faster in the ClO_4^- medium, the factor decreasing as increasing amounts of ammonium salts are added. Small amounts of sodium metal increase the exchange rate. An apparent activation energy of 33 kcal./mole was obtained for solutions containing only $Cr(NH_3)_6(NO_3)_3$. Discussion of possible species present and rate laws is given. The K_{eq} for the reaction $Cr(NH_3)_6^{+3} + N^{15}H_3 \rightleftharpoons Cr(NH_3)_5N^{15}H_3^{+3} + NH_3$ is 6.100 at 20°.

Introduction

Most studies on the kinetics of complex ion reactions have been carried out in aqueous solution. Detailed studies in nonaqueous solvents are of interest for similar reasons as for aqueous systems and in addition may provide comparisons which can aid in evaluating the precise role played by the solvent. A basic process in

any solvent involves the exchange of solvent molecules acting as ligands in a complex species with the same molecules in the solvent itself.[3a] Several such studies have beeen reported.[3–6] The specific foundations for

(1) This work supported in part by the U. S. Atomic Energy Commission, Contract AT(45-1)-1031.
(2) To whom inquiries should be addressed.

(3) (a) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951); (b) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5690 (1954).
(4) J. H. Swinehart, T. E. Rogers, and H. Taube, *J. Chem. Phys.*, **38**, 398 (1963).
(5) H. U. D. Wiesendanger, W. H. Jones, and C. S. Garner, *J. Chem. Phys.*, **27**, 668 (1957).
(6) J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963).

the present study were laid by Wiesendanger, Jones, and Garner.[5] These authors reported one reliable result for the exchange reaction studied in more detail by us.

Experimental

The procedures used in this research were essentially those of Garner, *et al.*[5] Anhydrous, sodium-free ammonia was prepared by standard techniques, as was $Cr(NH_3)_6(NO_3)_3$. The preparation of $Cr(NH_3)_6(ClO_4)_3$ was effected by simply adding a concentrated $NaClO_4$ solution to a fresh aqueous $Cr(NH_3)_6(NO_3)_3$ solution. The yellow precipitate was quickly filtered off, washed with water, 95% alcohol, and ether, and dried in a vacuum desiccator over $CaSO_4$. The solid was not dried by heating as a safety precaution. Small amounts of NH_4NO_3 or NH_4ClO_4 were handled as solutions in methanol. The methano was removed by heating to 100° followed by pumping on a vacuum line. The exchanges were carried out in darkness in sealed, heavy-walled Pyrex ampoules. Known amounts of the required salts were placed in the ampoule, which was attached to a vacuum system. After pumping on the salts to remove air and moisture, ammonia was condensed from the gaseous state onto the salts. The ampoules were sealed and placed in a thermostated bath. The reaction was quenched by cooling to $< -40°$, the ampoule was opened, and the solvent ammonia evaporated. The residual salts were treated using a Kjeldahl process to yield ammonium ion solutions. The ammonium ions were converted to N_2 using alkaline hypobromite oxidation of air-free solutions. Corrections, required by the presence of ammonium salt along with the chromium salt after evaporation of ammonia, were made in the isotope ratios. Mass-spectrometric analyses of N_2 gas were made with a precise isotope-ratio instrument constructed by Nuclide Analysis Associates and purchased with U.S.A.E.C. funds. The total experimental procedure is involved and very time consuming. Because of the large number of error sources the precision of the data cannot be better than *ca.* ±5%.

Results and Treatment of Data

Up to fivefold increase in the surface–volume ratio using Pyrex helices caused no change in rate. Addition of sodium metal to *ca.* 0.001 M, however, produced a marked increase in the exchange rate. Special care was therefore taken to be certain that sodium was absent from the exchange mixtures. No large photochemical effects have been noted.

It was not found possible to measure the coordination number or "holdback" for the Cr(III) species using the isotope dilution technique[7] because of the low solubilities of the Cr(III) salts in ammonia. It was assumed in this study that six equivalent ammonia ligands are attached to the Cr(III) atom.

The kinetic exchange data were treated in the usual way.[3,8] Good McKay plots were obtained with the lines passing through the origin. Conditions and results are shown in Tables I, II, and III. The value for R refers to the total rate of exchange of ammonia molecules between complex and solvent. The concentrations of species listed are based on the stoichiometric quantities of the salts added. The precision in the R values is thought to be ±5 to 10%. There appear to be several factors which influence the exchange rates. In the absence of other added salts, the exchange rate is

(7) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **18**, 757 (1950).
(8) H. A. C. McKay, *Nature*, **142**, 997 (1938).

TABLE I
$N^{15}H_3$–$Cr^{III}(NH_3)_6$ EXCHANGE AT 20.54° USING NO_3^- AS ANION

Cr(III), $M \times 10^3$	NH₄NO₃ (added), $M \times 10^3$	KNO₃ (added), $M \times 10^2$	$t_{1/2}$, hr.	R, M^{-1} sec.$^{-1} \times 10^7$
2.55	0	0	5.2	5.7
2.55	1.08	4.6	195	0.15
5.11	0	0	13.1	4.5
5.11	1.08	3.1	172	0.34
10.2	0	0	32	3.7
10.2[a]	0	0	32	3.7
10.2	.54	0	64	1.84
10.2	1.08	0	88	1.34[b]
10.2	2.17	0	204	0.58
10.2	3.26	0	310	.38
10.2	5.42	0	470	.25
10.2	1.08	3.44	158	.75
10.2	1.08	6.87	179	.66
13.4	0.12	0	51	3.0
19.9	0	0	62.5	3.7
26.6	0	0	85	3.6
26.7	.12	0	99	3.1

[a] Repeat of previous run, in presence of Pyrex helices to increase surface–volume ratio by a factor of five. [b] Average of three runs with maximum spread of *ca.* 3%.

TABLE II
$N^{15}H_3$–$Cr^{III}(NH_3)_6$ EXCHANGE AT 20.54° USING ClO_4^- AS ANION

| [Cr(III)], $M \times 10^2$	[NH₄ClO₄ (added)], $M \times 10^3$	[NaClO₄ (added)], $M \times 10^2$	$t_{1/2}$, hr.	R, M^{-1} sec.$^{-1} \times 10^5$
1.00	0	0	1.05	1.10
1.00	1.92	0	18.9	0.061
1.00	3.85	0	40.3	.029
2.00	0	0	1.7	1.36
2.00	0	7.37	2.7	0.86
3.00	0	0	2.3	1.51

TABLE III
TEMPERATURE COEFFICIENT OF R AT [Cr(III)] = 0.02 M (NO ADDED SALTS, NO_3^- ANION)

$t°$	$t_{1/2}$, hr.	R, M^{-1} sec.$^{-1} \times 10^7$
33.18	5.9	39
20.54	62.5	3.7
8.70	704	0.33

changed only a small amount with variation of the chromium salt concentration. If, however, added ammonium salt and total nitrate concentrations are kept nearly constant the rate is about first order in chromium(III). Addition of KNO_3 at constant Cr(III) and NH_4NO_3 produces a decrease in rate, which effect may level off at high KNO_3. Addition of relatively small amounts of NH_4NO_3 at constant Cr(III) and roughly constant total NO_3^- shows an approximately inverse relation between the exchange rate and the amount of added NH_4NO_3. This relationship can be seen in Fig. 1. The deviation from the straight line for the observed rates at low added NH_4NO_3 suggests that some ammonolysis of Cr(III) is occurring. On the assumption that all the points should lie on a straight line through the origin, one can estimate that the effective NH_4NO_3 concentration in an experiment with no added NH_4NO_3 is *ca.* 3.4×10^{-4} M, corresponding to *ca.* 3% ammonolysis or a formal pK of *ca.* 5, which seems not unreasonable. We have attempted to correct approximately the stoichiometric ammonium salt concentration
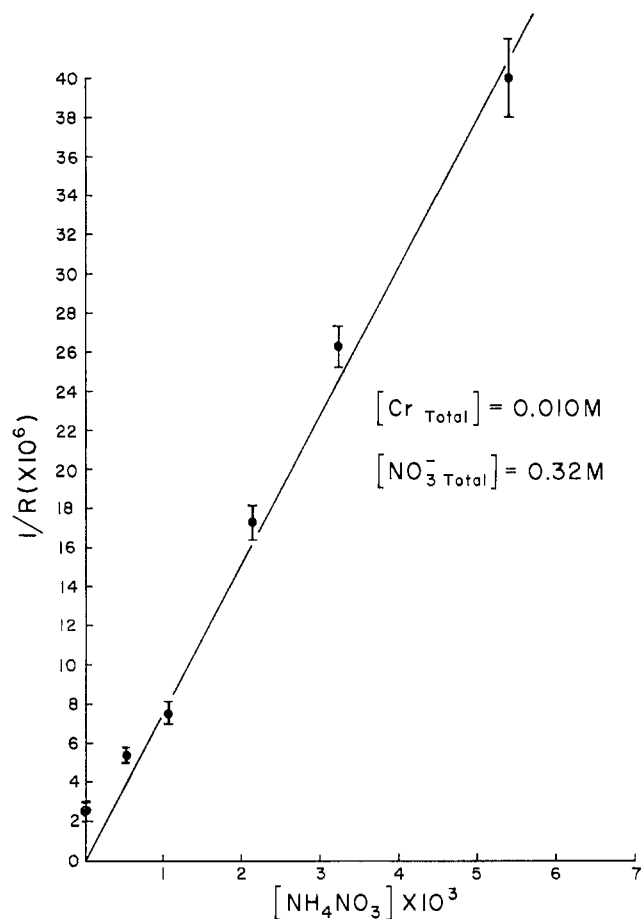
Fig. 1—Effect of added NH_4NO_3 on the exchange rate.

Fig. 2.—Correlation of rate data with stoichiometric concentrations.

for this effect although in many cases the correction is not very significant. It should be noted that NH_4NO_3 has a considerably greater effect on the rate than does KNO_3. The bulk of the NO_3^- data can be roughly correlated using the total stoichiometric Cr concentration, the total stoichiometric NO_3^- concentration, and the corrected NH_4NO_3 concentration. A plot is given in Fig. 2 of $R[NH_4NO_3]/[Cr_{total}]$ *vs.* $1/[NO_3^-_{total}]$. The data can be approximately represented by a straight line having the form $10^9 R[NH_4NO_3]/[Cr_{total}] = 5.2 + 0.25/[NO_3^-_{total}]$. We cannot, however, be certain that the line is straight over the entire range. Unfortunately, the nitrate concentration cannot be significantly increased without excessively reducing the chromium salt solubility. The ionic strength is likely not constant for the runs shown and perhaps the correlation is as good as can be expected.

The limited temperature coefficient data lead to an apparent activation energy of *ca.* 33 kcal./mole. This is a reasonable number but may well be a composite figure as is mentioned later.

The effect of changing from a NO_3^- to a ClO_4^- medium is quite striking. The exchange rate is greater for the ClO_4^- system, ranging from a factor of *ca.* 40 to *ca.* 5 times depending on the ammonium salt concentration. The ClO_4^- data indicate a smaller amount of ammonolysis for the ClO_4^- salt compared to the NO_3^- salt (pK for ClO_4^- ~6) which can partly account for the factor of *ca.* 40. The factor of *ca.* 5 persists
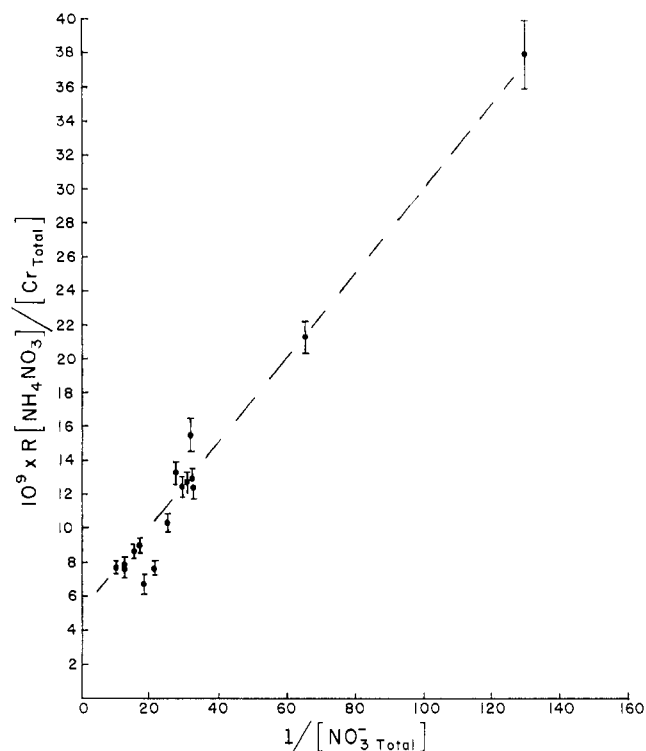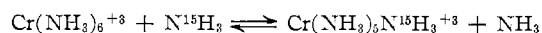
even at high added ammonium salt concentrations suggesting that another factor is also involved, perhaps a "salt effect."

Isotopic equilibrium constants referring to the exchange

$$Cr(NH_3)_6^{+3} + N^{15}H_3 \rightleftharpoons Cr(NH_3)_5 N^{15}H_3^{+3} + NH_3$$

were measured and the results are shown in Table IV.

TABLE IV
EQUILIBRIUM ISOTOPE EFFECTS

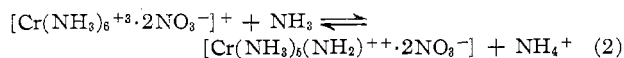| [Cr(III)], M	Anion	Temp., °C.	K_{eq}
0.0199	NO_3^-	33.18	6.094 ± 0.002
.0102	NO_3^-	20.54	6.100
.0266	NO_3^-	20.54	6.100 ± 0.006
.00769	ClO_4^-	20.54	6.100 ± 0.006
.0200	ClO_4^-	20.54	6.100

Discussion

The general features of the exchange reactions seem to be reasonable for Cr(III) and qualitatively understandable. A major obstacle to quantitat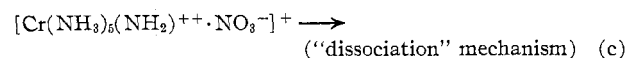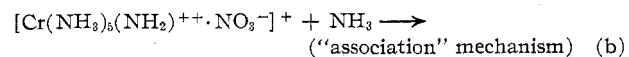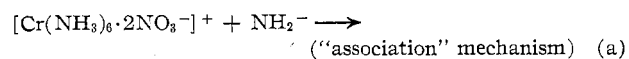ive or detailed explanation of the results is the lack of knowledge concerning the species actually present in the solutions. The dielectric constant of liquid ammonia at 20° is *ca.* 15, a relatively low value. One can expect, therefore, considerable ion association and specific ion effects. Dissociation constants (K) for NH_4NO_3,[9] NH_4ClO_4,[9] and KNO_3[10] in liquid ammonia have been reported to be (at $-40°$) 4.3×10^{-3}, 5.4×10^{-3}, and 1.47×10^{-3}, respectively. Using the approach of Fuoss and Kraus[10] we estimate that the K values would be smaller at 20°

(9) E. N. Gur'yanova and V. A. Pleskov, *Zh. Fiz. Khim.*, **8**, 345 (1936).
(10) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

by a factor of about three. There is thus extensive ion-pairing of the above mentioned salts in our solutions. The NH_4NO_3 and NH_4ClO_4 values are similar and the differences in rates observed for NO_3^- and ClO_4^- systems require other explanation. Further qualitative considerations suggest that ions with a charge of two or greater would be essentially completely associated. It seems reasonable that the Cr(III) species and equilibria involved might be

$$[Cr(NH_3)_6^{+3}\cdot 3NO_3^-] \rightleftharpoons [Cr(NH_3)_6^{+3}\cdot 2NO_3^-]^+ + NO_3^- \tag{1}$$

$$[Cr(NH_3)_6^{+3}\cdot 2NO_3^-]^+ + NH_3 \rightleftharpoons$$
$$[Cr(NH_3)_5(NH_2)^{++}\cdot 2NO_3^-] + NH_4^+ \tag{2}$$

$$[Cr(NH_3)_5(NH_2)^{++}\cdot 2NO_3^-] \rightleftharpoons$$
$$[Cr(NH_3)_5(NH_2)^{++}\cdot NO_3^-]^+ + NO_3^- \tag{3}$$

$$NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^- \tag{4}$$

$$KNO_3 \rightleftharpoons K^+ + NO_3^- \tag{5}$$
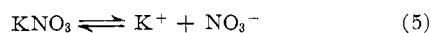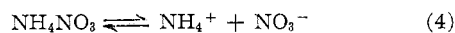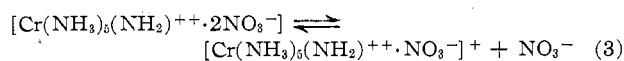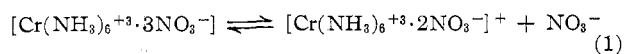
Calculations of the amounts of the various species present and the ionic strength cannot be made without a knowledge of the relevant equilibrium constants. Such knowledge appears to be lacking at the present time. Although a detailed treatment of the data cannot be made, it may still be useful to make some qualitative observations. The NO_3^- data taken as a whole suggest first-order dependence of the rate of exchange on Cr(III) concentration and inverse first-order dependence on both the NH_4NO_3 concentration and some quantity related to the total anion concentration. If one assumes extensive but not complete ion association of the various species, the results are qualitatively accounted for by rate-determining steps such as the following (assuming a one-term rate law for simplicity)

$$[Cr(NH_3)_6\cdot 2NO_3^-]^+ + NH_2^- \longrightarrow$$
("association" mechanism) (a)

$$[Cr(NH_3)_5(NH_2)^{++}\cdot NO_3^-]^+ + NH_3 \longrightarrow$$
("association" mechanism) (b)

$$[Cr(NH_3)_5(NH_2)^{++}\cdot NO_3^-]^+ \longrightarrow$$
("dissociation" mechanism) (c)

In the above steps one would have to assume that further association of the Cr(III) species with NO_3^- reduces the rate. Possibility (a) can be ruled out on the grounds that the NH_2^- concentration is so low as to require an impossibly high rate from this step ($[NH_4^+]$-$[NH_2^-] \simeq 2 \times 10^{-28}$).[11] In principle (b) and (c) might be distinguished if the ammonia concentration

could be varied by adding another "inert" substance. In any case, however, nothing really unusual has to be postulated to explain our results. The measured activation energy probably contains some contributions from various equilibria and thus cannot be simply interpreted. The value of 33 kcal./mole is similar to the value of 27 kcal./mole obtained for the analogous water exchange reaction.[3b]

More extensive work is currently in progress on the ClO_4^- system. As suggested earlier the relative rates for the ClO_4^- system compared to the NO_3^- depend on the amount of ammonium salt present, the ratio R ClO_4^-/R NO_3^- decreasing as the solution becomes more "acid." It seems likely that the effect is due partly to the difference in the amount of ammonolysis for the Cr(III)–ClO_4^- system compared to the Cr(III)–NO_3^- system (differences in ion association may also be involved in ammonolysis) and partly to an inherent difference in reactivity of similar species. The ClO_4^- system has a number of practical experimental advantages involving shorter half-times and greater solubilities in liquid ammonia so that it may be possible to obtain more data than for the NO_3^- system.

The values for the equilibrium isotope effects are similar to those found for the hexaaquochromium(III) system[3a] where the analogous K was found to be 6.2 ± 0.13 at 25°.

We feel that a start has been made toward exchange studies of complexes in liquid ammonia. It is clear that there will be added difficulties in this medium, involving, *e.g.*, specific ion effects even with NO_3^- and ClO_4^- ions at concentrations which are low by usual aqueous standards. More information is needed on ammonolysis and ion association processes. The increase in exchange rate caused by sodium metal might be due to formation of Cr(II). We plan to investigate this point further for possible electron-transfer reactions. It is to be hoped that several metal ions can be studied for comparison purposes. A search for more soluble salts to permit holdback studies is being made.

(11) L. V. Coulter, J. R. Sinclair, A. G. Cole, and G. C. Roper, *J. Am. Chem. Soc.*, **81**, 2986 (1959).