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The Mechanism of Base Hydrolysis of Substituted Pentaamminecobalt(III) Complexes

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The values of isotopic fractionation factors, d ln $[O^{16}]$/d ln $[O^{18}]$, in the hydrolysis of some complex ions of the type $[Co^{III}(NH_3)_5X]$ have been investigated. The comparison of the values and the actual magnitudes provide a basis for distinguishing between different mechanisms of the reactions. We conclude that when X = Cl^-, Br^-, and NO_3^-, an SN1 CB mechanism occurs, but when X = F^-, there is probably an SN2 CB reaction.

The mechanism of the base hydrolysis of substituted pentaamminecobalt(III) complexes, $[Co(NH_3)_5{}^{III}X]$, is controversial. Brown, Ingold, and Nyholm[2a] suggest that an SN2 mechanism operates, with OH^- replacing X as shown in eq. 1.

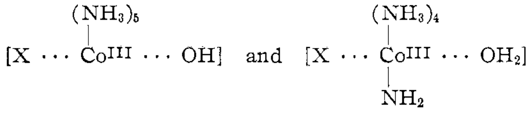
$$OH^- + [Co(NH_3)_5{}^{III}X] \rightarrow [Co(NH_3)_5OH]^{++} + X \quad (1)$$

However, Garrick[3] has suggested that a conjugate base mechanism of the type ascribed by Brönsted[4] to the hydrolysis of $[Co(NH_3)_4NO_3H_2O]^{++}$ may occur here also. By this mechanism, the reactant complex HMX is put into the form MX^- by reaction with OH^- in a rapid, equilibrium step

$$HMX + OH^- = H_2O + MX^-$$

and the intermediate MX^- then undergoes a rate-determining loss of X^-. The concept of the conjugate base (CB) mechanism has been developed further by Basolo and Pearson,[5] who have distinguished between two kinds of CB processes depending on the fate of the intermediate MX^-. The different reaction schemes can lead to identical kinetic equations. Although Pearson, Schmidtke, and Basolo[6] have good evidence for a conjugate base mechanism in dimethyl sulfoxide, the situation in water is still unresolved.

In this paper we are reporting experiments similar to those of Posey and Taube[7,8] that we have performed to try to resolve this problem. If an SN1 CB mechanism operates, a common intermediate, $[Co(NH_3)_4NH_2]^{++}$, will be produced whatever the nature of X, the outgoing ligand, may be, at least if the lifetime of the intermediate is sufficiently long. The ratio of O^{16} to O^{18} in the final hydroxo product would therefore be independent of the nature of X. If, however, an SN2 or SN2 CB mechanism occurs the composition of the respective intermediates



$$[X \cdots \overset{(NH_3)_5}{Co^{III}} \cdots OH] \quad \text{and} \quad [X \cdots \underset{NH_2}{\overset{(NH_3)_4}{Co^{III}}} \cdots OH_2]$$

will cause the O^{16}/O^{18} ratio in the product to be related to X.

The hydrolysis reactions are amenable to an investigation of the kind we have undertaken because the exchange of the hydroxo product with the solvent is very slow.[9] However, the scope of the method is limited because decomposition of the product complex interferes, particularly for those which react slowly.

Experimental

$Co(NH_3)_5Cl_3$ and $Co(NH_3)_5Br_3$ were prepared using the methods of Hynes, Yanowski, and Shiller[10] and of Diehl, Clark, and Willard,[11] respectively. These compounds were washed in methanol and dried at 110° overnight. They were converted to the corresponding perchlorates by solution in 3 *M* sulfuric acid at 1 and 15°, respectively, followed by addition of ice cold concentrated perchloric acid. The crude perchlorates were purified by solution in ice-cold water and reprecipitation with cold perchloric acid. The solids were washed with methanol and dried under vacuum for 24 hr. $[Co(NH_3)_5Br](ClO_4)_2$ contains about $^2/_3$ of a molecule of water of crystallization which slowly exchanges with the complexed bromide. It was therefore used immediately after preparation. Later it was found that the water could be expelled quite safely by heating the complex at 110°. *Anal.* Calcd. for $[Co(NH_3)_5Cl](ClO_4)_2$: ionizable Cl, 9.37; NH_3, 22.5. Found: ionizable Cl, 9.24; NH_3, 22.4. Calcd. for $[Co(NH_3)_5Br](ClO_4)_2 \cdot 1.5H_2O$: Br, 18.4; NH_3, 19.6. Found: Br, 18.3; NH_3, 19.5.

The methods of preparation of $[Co(NH_3)_5NO_3](ClO_4)_2$ and $[Co(NH_3)_5SO_4]ClO_4$ have been described elsewhere.[12] The products to be used here were separated, washed only with methanol, and then dried under vacuum for 24 hr. $[Co(NH_3)_5F](NO_3)_2$ was prepared using the method of Basolo and Murmann,[13] except that precipitation was effected with sodium nitrate. It was converted to perchlorate by solution in 3 *M* ice-cold sulfuric acid as described above. The perchlorate salt was reprecipitated from ice-cold water, washed in methanol, and dried under vacuum. *Anal.* Calcd. for $[Co(NH_3)_5F](ClO_4)_2$: NH_3, 22.4. Found: NH_3, 22.3.

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NaOH (0.1 *N*) free from CO_2 was prepared from standard samples contained in ampoules. Redistilled water was kept in a stoppered flask for all experiments. No change in isotopic composition was detected over a period of 4 months.

In each run 250 ml. of a 1.012 *M* solution of complex was prepared, containing varying quantities of sodium hydroxide and, in some cases, additional salts. Chloro, bromo, and nitrato complexes were left to react for 40 min., sulfato for 60 min., and fluoro for 150 min. at 25.0°. Then 250 ml. of ice-cold concentrated hydrobromic acid (and in the case of the fluoro complex, solid potassium bromide) was added. After a short time a precipitate of $[Co(NH_3)_5H_2O]Br_3$ separated. Thereafter the procedure of Posey and Taube[7] was followed, in which complexed water was expelled and equilibrated with carbon dioxide. The isotopic composition of the carbon dioxide was determined in Dr. R. N. Clayton's mass spectrometer, a 6-in. double-collecting instrument built after the designs of Nier[14] and of McKinney, McCrea, Epstein, Allen, and Urey.[15] The isotopic composition of the complexed water was calculated from that of the carbon dioxide using the formula of Dostrovsky and Klein.[16] The weight of water involved in equilibration was obtained by assuming stoichiometric decomposition of $[Co(NH_3)H_2O]Br_3$ and that of carbon dioxide using a gas buret.

The initial concentration of OH^- was varied only over a limited range, from 0.012 to 0.02 *M* OH^-. High concentrations of OH^- had to be avoided, and even at the level used, some degradation of the hydroxopentaammine occurred. The precipitates of $[Co(NH_3)_5H_2O]Br_3$ did, however, give satisfactory analyses in each case. *Anal.* Calcd. for $[Co(NH_3)_5H_2O]Br_3$: NH_3, 21.2. Found: NH_3, for X = Cl^-, 21.2; Br^-, 21.0; NO_3^-, 21.2; SO_4^{-2}, 21.0; F^-, 21.8.

The accuracy of the determinations of isotopic composition may be limited by impurities in the gas admitted to the mass spectrometer. Contamination by ethanol, diethyl ether, and other substances which yield mass of 46 on ionization had to be avoided.

Results and Discussion

The fractionation factor defined as

$$\frac{[O^{16}]/[O^{18}] \text{ in hydroxo product}}{[O^{16}]/[O^{18}] \text{ in solvent water}}$$

in the base hydrolysis of $Co(NH_3)_5{}^{III}X$ for different ligands, X, and for varying hydroxide ion concentrations is shown in Table I. Tables II and III show how these factors are affected by the addition of salts; none of the anions used enter the coordination sphere of the Co(III) complexes in alkaline solution. Accuracy is assessed at 1 in 5000 for chloro, bromo, and nitrato complexes, 1 in 1000 for sulfato, falling to 1 in 300 for the fluoro compound.

TABLE I
FRACTIONATION FACTORS FOR $Co(NH_3)_5{}^{III}X$[a]

	$[OH^-]$		
X	0.012 *M*	0.016 *M*	0.020 *M*
Cl^-	1.0056	1.0057	1.0056
Br^-	1.0056	1.0055	1.0056
NO_3^-	1.0056	1.0056	
F^-		0.9975	0.9995
SO_4^{-2} (a)	1.0033	1.0034	
SO_4^{-2} (b)	1.0081		

[a] $Co(NH_3)_5{}^{III}X$ = 0.012 *M*, temperature 25.0°; (a) and (b) represent different sources of SO_4^{-2}.

TABLE II
FRACTIONATION FACTORS FOR $[Co(NH_3)_5Cl]^{++}$ IN THE PRESENCE OF INERT SALTS

	Salt concentration		
Salt	0.02 *M*	0.06 *M*	0.09 *M*
KCl	1.0055		
KBr	1.0055		
K_2SO_4		1.0051	
$NaClO_4$		1.0053	1.0052

TABLE III
FRACTIONATION FACTORS FOR $[Co(NH_3)_5Br]^{++}$ IN THE PRESENCE OF INERT SALTS[a]

	Concentration	
Salt	0.02 *M*	0.06 *M*
KCl	1.0055	
$NaClO_4$		1.0053

[a] $Co(NH_3)_5Br^{++}$ = 0.012 *M*.

Several points emerge: (1) The "salt" effect is very small. As far as one can tell, bearing in mind the accuracy of the results, the effect is directly related to the concentration of the anion and is greater for a divalent than for a monovalent species. In the two cases tested, the nature of X made no difference. The effect is small enough for the anion X produced during hydrolysis of $Co(NH_3)_5{}^{III}X$ not to affect the later stages of the reaction. The change of fractionation factor with salt concentration is real, thus demonstrating that the factor is sensitive to a mild external influence. It is likely therefore that the fractionation factor would be even more sensitive to an internal influence such as that of replacing Cl^- by NO_3^- in the first coordination sphere if these ions were still in place when the $Co(III)-OH_2$ (or OH^-) bond is being made. This deduction is supported by the findings of Posey and Taube[8] on the aquation of $[Co(NH_3)_5X^{++}]$ ions in the presence of various metal ions, where, if a change takes place as the halide ion is varied, it is large, *ca.* 0.3% (Ag^+ catalyst), and a value below the limit of precision, *ca.* 0.02% (Hg^{++} catalyst).

(2) Chloro, bromo, and nitrato complexes at any fixed concentration of alkali show equal fractionation factors. This is compatible with the common intermediate of the SN1 CB mechanism, but cannot easily be reconciled with either the SN2 or SN2 CB scheme.

(3) The fluoro complex exhibits a different fractionation factor from the other complexes, which indicates that hydrolysis does not involve the intermediate $[Co(NH_3)_4NH_2]^{++}$. Some form of SN2 or SN2 CB mechanism is therefore implied.

(4) The fractionation factors all lie within 1% of 1.00. The equilibrium constant for the reaction

$$H_2O^{16} + O^{18}H^- = H_2O^{18} + O^{16}H^-$$

has been estimated to be 1.040 ± 0.003 at 25°.[17] Therefore, if kinetic isotope effects are ignored, the fractionation factor observed in an SN2 reaction where the attacking species is OH^- ought to be 1.040 compared with 1.000 in SN1 CB or SN2 CB systems where the oxygen atoms of the hydroxo product are derived from H_2O. The purely kinetic effect will modify this "chemical

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factor" of 1.040 or 1.000 as follows. In the SN2 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 SN1 CB mechanism a similar though smaller discrimination in favor of H_2O^{16} would be expected. In an SN2 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 SN2 mechanism.

In total, the results suggest an SN1 CB mechanism leading to a common intermediate for $X = Cl^-$, Br^-, or NO_3^-; when $X = F^-$, an SN2 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 SN2 mechanism is rendered unlikely by the results: suppose the splitting at the Co–O bond occurs by an SN2 mechanism with a 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 SN1 CB to an SN2 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 SN2 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.

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

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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

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[2] To whom inquiries should be addressed.

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