a lower steric requirement for chloropalladation. However, the differences in rate are much less than the rate differences for chloropalladation and acetoxypalladation[8a] of vinylic chlorides and acetates. In this case chloropalladation was much less affected by steric hindrance. The different steric effects in the exchange of allylic and vinylic groups almost certainly reflect the fact that the exchanging group in the vinylic exchange is on the olefinic carbons thus causing vinylic exchange to be more susceptible to steric factors.

One point that deserves comment is whether the value of K_1' $(=k_1/k_{-1})$ in eq 12 has an appreciable value under the reaction conditions. One way to detect K_1' is to measure the rate constant over a broad range of trifluoroacetate concentrations. Of course this is complicated in the present case because of the formation of inactive monomeric π complexes (eq 6). However, a more complete study of the effect of allylic ester concentration on rate was carried out in the work on allylic ester exchange.[8b] It was found that if correction is made for eq 6, using a value of K_2 determined by an ultraviolet spectral study, the rate of exchange of allyl propionate was first order in allyl propionate over a range of allyl propionate concentrations from 0.02 to 0.5 M. Since allyl propionate and allyl trifluoroacetate would be expected to have similiar values of K_1', the concentrations of **5** under the reaction conditions will almost certainly be too small to be detected.

Experimental Section

Materials.—Preparation and analysis of Pd(II) stock solutions have been described previously[2-4] as have the preparations of the crotyl and 3-butene-2-ol trifluoroacetates.[8c] Similar procedures were used for the preparation of the methallyl trifluoroacetate (bp 97–97.5° (760 mm)).

Kinetic Runs.—Runs were made on a 1-ml scale by procedures described previously.[2,3] All analyses were by vapor-phase chromatography (vpc). For most runs a 6-ft 20% Carbowax 20 M on ABS (70–80 mesh) column programmed from 80 to 200° at 7.5°/min was used. Helium flow rate was 60 ml/min. For some runs a 20-ft 20% Lac 446 on Chromosorb W (60–80 mesh) at 80° was used. Helium flow rate was 100 ml/min.

Acknowledgment.—The author gratefully acknowledges helpful discussions with Professors H. Taube and H. Goering as well as the technical assistance of Mr. F. Kriss.

CONTRIBUTION FROM THE NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND 20910, AND THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA, WASHINGTON, D. C. 20017

Stoichiometry and Kinetics of the Decomposition of Some Cobalt(III) Ammines in Molten Ammonium Bisulfate and Concentrated Sulfuric Acid[1]

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Received December 9, 1971

The decomposition reactions of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5SO_4^+$ in molten NH_4HSO_4 and of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5HSO_4^{2+}$, and *cis*-$Co(NH_3)_4(HSO_4)_2^+$ in *ca.* 97% H_2SO_4 have been studied. Complete decomposition of all the complexes studied involves reduction of Co(III) to Co(II) and oxidation of NH_3 or NH_4^+ to N_2. However, proton magnetic resonance (pmr) spectra of partially reacted Co(III) complexes in *ca.* 97% H_2SO_4 reveal that at least three NH_3 ligands of $Co(NH_3)_6^{3+}$, at least two NH_3 ligands of $Co(NH_3)_5HSO_4^{2+}$, and at least one NH_3 ligand of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ are replaced by HSO_4^- ligands prior to the more rapid redox steps. The spectrophotometrically measured first-order rate constants for the replacement of the first NH_3 ligand are $(5.2 \pm 0.4) \times 10^{-5}$ sec^{-1} for $Co(NH_3)_6^{3+}$ and $(3.4 \pm 0.1) \times 10^{-4}$ sec^{-1} for $Co(NH_3)_5SO_4^+$ in molten NH_4HSO_4 at 153°; $(2.0 \pm 0.1) \times 10^{-4}$ sec^{-1} for $Co(NH_3)_6^{3+}$ and $(3.6 \pm 0.2) \times 10^{-4}$ sec^{-1} for $Co(NH_3)_5HSO_4^{2+}$ at 152.6°; and $(7.5 \pm 0.5) \times 10^{-4}$ sec^{-1} for *cis*-$Co(NH_3)_4(HSO_4)_2^+$ at 151.7° in *ca.* 97% H_2SO_4. The activation energies for the replacement of the first NH_3 lie in the range 38–42 kcal mol^{-1} for all complexes studied, and the rates of these substitution reactions are not affected appreciably by the addition of Co^{2+}, by the addition of fuming H_2SO_4 to the H_2SO_4 solvent, or by the addition of $(NH_4)_2SO_4$ to the NH_4HSO_4 solvent.

Introduction

In the course of a search for suitable electrolytes and cathode materials for molten salt batteries we have found that some cobalt(III)–ammonia complexes decompose slowly enough in molten ammonium bisulfate to allow their reactions to be studied in this solvent. For example, the orange color of $Co(NH_3)_6^{3+}$ persists for at least 1 hr after dissolution of $[Co(NH_3)_6][HSO_4]_3$ in molten NH_4HSO_4 at *ca.* 155°. However, if the temperature of the solution is raised to *ca.* 200°, evolution of a gas is observed, the color of the solution changes rapidly to pale blue, and the spectrum is found to be that characteristic of Co^{2+} in this solvent. These observations have prompted us to investigate the stoichiometry and kinetics of the decomposition of the hexaamminecobalt(III) ion in molten ammonium bisulfate. Although the overall decomposition reaction obviously involves reduction of cobalt(III), the high sensitivity of the rate to temperature suggested that the slow step in the reaction might be a substitution reaction. Indeed we have found that several substitution steps precede the redox step in the decomposition of $Co(NH_3)_6^{3+}$ in molten NH_4HSO_4, and very similar behavior has been observed with 95–100% H_2SO_4 as the solvent. The decomposition reaction of $Co(NH_3)_5HSO_4^{2+}$ has been studied also in both solvents, and the decomposition of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ has been

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(1) Based on the Ph.D. dissertation of R. A. Sutula, The Catholic University of America, Jan 1971. Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; see Abstracts, No. INOR 33.

studied in *ca.* 97% H_2SO_4, since the pentaammine and tetraammine complexes are expected intermediates in the decomposition of $Co(NH_3)_6^{3+}$.

In aqueous solutions the loss of the first NH_3 in the base hydrolysis of $Co(NH_3)_6^{3+}$ is catastrophic,[2] the other NH_3 molecules being lost much more rapidly than the first in the transformation of $Co(NH_3)_6^{3+}$ to Co_2O_3. Similar results were anticipated for $Co(NH_3)_6^{3+}$ in molten NH_4HSO_4; *i.e.*, it was expected that the loss of the second and succeeding NH_3 molecules from $Co(NH_3)_6^{3+}$ would be more rapid than the loss of the first NH_3, since each substitution of SO_4^{2-} or HSO_4^- for NH_3 would make the charge on the complex less positive.

Experimental Section

Materials.—$[Co(NH_3)_6]Cl_3$ was prepared by the method of Schlessinger.[3] The chloride salt was dissolved in the minimum amount of 97% H_2SO_4 and stirred vigorously for 3 hr to remove HCl. The solution was mixed with an equal volume of ethanol at ice temperature, and the orange crystals which formed were washed with ethanol and then recrystallized from 97% H_2SO_4 by the addition of ethanol to ensure complete removal of chloride. The purified salt was washed with absolute ethanol and dried under high vacuum. Analysis showed the salt so prepared to be a mixture of sulfate and bisulfate salts with the relative content of the two anions varying with the conditions of precipitation, but the N/Co mole ratio was constant at 6.0. The visible spectrum of an aqueous solution of the salt had maxima at 472 and 336 nm with a ratio of peak heights (A_{472}/A_{336}) of 1.18. The peak positions are in good agreement with the report of Kuroya,[4] but the ratio of peak heights is substantially higher than the value 1.06 obtained from Kuroya's data. The proton magnetic resonance (pmr) spectrum of a solution of the compound in 97% H_2SO_4 showed only one peak in the region in which the ammine protons of cobalt(III) complexes resonate. The observed spectrum is consistent with the spectrum of $Co(NH_3)_6^{3+}$ reported by Jolly, *et al.*,[5] who observed no splitting of the ammine proton resonance lines by interaction with the nitrogen nucleus.

$[Co(NH_3)_5OH_2]Br_3$ was prepared by the method of Schlessinger.[6] The bromide salt was dissolved in the minimum amount of ice-cold water, and an equal volume of ice-cold 97% H_2SO_4 was added slowly while the solution was maintained below 5°. Red-orange $[Co(NH_3)_5H_2O]_2[SO_4]_3$ precipitated upon the addition of an equal volume of ice-cold absolute ethanol. The product was recrystallized twice from water by the successive addition of 97% H_2SO_4 and absolute ethanol, care being taken to keep the solution near ice temperature to prevent anation. The absorption spectrum of a solution of the product in 1 *M* $HClO_4$ had maxima at 490 and 345 nm with a ratio of peak heights (A_{490}/A_{345}) of 1.06. The peak positions and ratio of peak heights are in good agreement with the spectrum of $Co(NH_3)_5H_2O^{3+}$ reported by Kiss and Czegledy.[7]

$[Co(NH_3)_5SO_4]HSO_4$ was prepared by the procedure of Fialkov and Panasyuk.[8] The crude product was purified by ion-exchange chromatography, as suggested by Po and Jordan.[9] The $Co(NH_3)_5SO_4^{2+}$ ion was eluted from the column of Bio-Rad AG 50W-X8 resin with 1 *M* H_2SO_4 and was precipitated from the effluent by the addition of *ca.* 4 volumes of absolute ethanol. The precipitate was washed with ethanol and then ether and was dried *in vacuo*. The product appeared to be homogeneous in that successive portions of the column effluent had the same spectrum, as did the various fractions obtained by fractional recrystallization from dilute H_2SO_4 by the addition of ethanol. The absorption spectrum of the product in 1 *M* $HClO_4$ had maxima at 514 and 353 nm with a peak height ratio (A_{514}/A_{353}) of 1.25. The positions of the absorption maxima were in fair agreement with those reported for $Co(NH_3)_5SO_4^+$ by Po and Jordan,[9] but the ratio of peak heights was not. From Po and Jordan's reported extinction coefficients for the observed maxima at 517 and 357 nm, we calculate a ratio of peak heights (A_{517}/A_{357}) of 1.88. *Anal.* Calcd for $[Co(NH_3)_5SO_4]HSO_4$: Co, 17.5; N, 20.8; total SO_4^{2-}, 57.0; free SO_4^{2-}, 28.4. Found: Co, 17.2; N, 20.5; total SO_4^{2-}, 56.8; free SO_4^{2-}, 28.4. Titration to pH 7 required 0.977 equiv of base per mole (337 g) of $[Co(NH_3)_5SO_4]HSO_4$. When solutions of $[Co(NH_3)_5SO_4]HSO_4$ in distilled water were adsorbed onto columns of Dowex 50 resin in the H^+ form, the column effluent, which should have contained both the HSO_4^- and the H^+ displaced from the resin by $Co(NH_3)_5SO_4^+$, required 1.89 equiv of base per mole (337 g) of $[Co(NH_3)_5SO_4]HSO_4$ used. The cobalt complex on the resin eluted as a single band with 1 *M* $HClO_4$, and SO_4^{2-}/Co mole ratios of 0.99 and 1.04 were found for the complex eluted in two separate experiments. From these results we conclude that the compound could not have contained more than 5% of any cobalt complex other than $Co(NH_3)_5SO_4^+$. As further confirmation of this conclusion, the pmr spectrum of the compound in *ca.* 97% H_2SO_4 showed only two resonances with peak areas 4:1 in the region in which the ammine protons are expected to resonate. The pmr spectra will be discussed in detail below.

$[Co(NH_3)_4CO_3]_2SO_4$ was prepared by the procedure of Schlessinger.[10] $[(NH_3)_4Co(OH)_2Co(NH_3)_4][ClO_4]_4$ was a gift of Dr. M. M. deMaine and was converted to the sulfate salt by the addition of solid $(NH_4)_2SO_4$ to a nearly saturated aqueous solution. The sulfate salt was recrystallized twice from water by the addition of $(NH_4)_2SO_4$ to ensure complete removal of ClO_4^-. The facial isomer of $Co(NH_3)_3(NO_2)_3$ was prepared according to the procedure of Hagel and Druding.[11]

The NH_4HSO_4 (Fisher AR grade) used to prepare the molten NH_4HSO_4 solvent was found to have a melting range of 142–149°. The molten NH_4HSO_4 used as a solvent (henceforth designated simply NH_4HSO_4) was boiled for 1 min to remove water. The solvent so prepared was found by analysis to contain 1.00 mol of SO_4^{2-} and 1.00 mol of free acid (acid consumed on titration to pH 7) per mole (115 g). The density of this solvent measured by means of a hydrometer was 1.78 g/cm³ at 154°. The concentrated H_2SO_4 used as a solvent (henceforth simply H_2SO_4) was Mallinckrodt AR grade 95–98% H_2SO_4. The density of this solvent was found to be 1.71 g/cm³ at 154°.

Analyses.—Cobalt and nitrogen analyses of $[Co(NH_3)_5SO_4]HSO_4$ and of the mixed sulfate–bisulfate salts of $Co(NH_3)_6^{3+}$ were done by Aldrich Associates, Washington, D. C. In other cases cobalt was determined by EDTA titration of Co^{2+} after the ammine complex had been destroyed by base hydrolysis and the resulting Co_2O_3 had been reduced by boiling with 12 *M* HCl. Sulfate was determined gravimetrically as $BaSO_4$.[12] Where cobalt and sulfate were determined for the same solution, $BaCl_2$ was first added to precipitate $BaSO_4$, and the filtrate was treated with H_2SO_4 to remove the excess Ba^{2+} which would have interfered with the EDTA titration of Co^{2+}. Free sulfate, *i.e.*, sulfate not bound to Co(III), was determined by adsorbing the Co(III) species on a Dowex 50 resin column and then analyzing the effluent from the column for SO_4^{2-}. For total sulfate analyses the Co(III) complexes present were destroyed by base hydrolysis, and the Co_2O_3 which formed was destroyed by boiling with 12 *M* HCl before precipitation of $BaSO_4$.

Spectra.—Visible–ultraviolet absorption spectra were determined using a Cary Model 14R spectrophotometer equipped with a thermostated furnace in its sample compartment. The long-necked silica cuvettes were rinsed just before use with the solvent (NH_4HSO_4 heated to boiling or H_2SO_4 heated until fumes of SO_3 were visible). All spectra were recorded against air as the reference. The cell and solvent were allowed to stand in the furnace 30 min to ensure thermal equilibration before the spectrum of the solvent was recorded. A pinch of the salt under investigation was then added, and the mixture was stirred for 2 min to ensure complete dissolution of the sample. After the spectrum had been

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(2) J. H. Takemoto and M. M. Jones, *J. Inorg. Nucl. Chem.*, **32**, 175 (1970).

(3) G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962, p 176.

(4) H. Kuroya, cited in "Gmelins Handbuch der anorganischen Chemie," Kobalt, Teil B, Verlag Chemie, Weinheim, 1964, p 328.

(5) W. L. Jolly, A. D. Guthrie, and T. S. Briggs, *Inorg. Chem.*, **4**, 1064 (1965).

(6) Reference 3, p 209.

(7) A. V. Kiss and D. V. Czegledy, *Z. Anorg. Allg. Chem.*, **235**, 407 (1938).

(8) Y. A. Fialkov and V. D. Panasyuk, *Russ. J. Inorg. Chem.*, **2**, 1007 (1957).

(9) L. L. Po and R. B. Jordan, *Inorg. Chem.*, **7**, 526 (1968).

(10) Reference 3, p 233.

(11) R. B. Hagel and L. F. Druding, *Inorg. Chem.*, **9**, 1496 (1970).

(12) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 465.

recorded, the sample was heated carefully over a flame to decompose the Co(III) complex to Co(II). After cooling, the cell was weighed and its contents were dissolved in water for analysis. The molar extinction coefficients were calculated from the measured absorbances (corrected for solvent absorbance), the weight of solvent used and its density, and the cobalt analysis of the sample.

Proton magnetic resonance spectra were obtained on a Varian HA-100 spectrometer at 30° with tetramethylsilane as an external standard. In those experiments in which pmr spectra were recorded at various stages of the decomposition reactions, *ca.* 5 g of the salt under investigation was dissolved in 50 ml of H_2SO_4 contained in a flask suspended in a wax bath at 154 ± 1°. At appropriate intervals 5-ml aliquots were removed and quenched by cooling to *ca.* 15°. Some samples contained a precipitate, probably $CoSO_4$, which was removed by centrifugation. The spectra of samples containing Co^{2+} generally contained a number of spinning side bands. All samples were run at several spinning rates to allow the genuine sample resonances to be distinguished from the spinning side bands, the positions of which varied with spinning rate.

Overall Reaction Stoichiometry.—To determine the stoichiometry of complete decomposition of the various cobalt(III) complexes in the two solvents, samples of the complex salts were mixed with carefully degassed solvent in an evacuated flask at 154°. The decomposition reactions were allowed to proceed for 24 hr, a period of time after which no further change was detected in spectrophotometric runs. The gaseous reaction products were passed through a series of traps so as to divide them into those not condensable at liquid nitrogen temperature, those condensable at liquid nitrogen temperature but not at Dry Ice temperature, and those condensable at Dry Ice temperature. The quantity of gas in each fraction was determined by pressure measurement in a calibrated volume, and the composition of the gas mixture was determined mass spectrometrically. Finally, the quantity of Co^{2+} formed in the decomposition reaction was determined by chemical analysis.

Kinetics Measurements.—The progress of the decomposition reactions was followed spectrophotometrically as the decrease of absorbance at the long-wavelength absorption maximum of the complex being studied. To initiate reaction, the sulfate or bisulfate salt of the complex was added to the solvent, prepared as described above and already at thermal equilibrium with the thermostated block in the spectrophotometer. The solution was stirred with a preheated glass rod for 45 sec to 2 min, depending on the temperature, to ensure complete dissolution of the complex salt. To ensure a large absorbance change during the reaction, the quantity of complex salt used was such as to give an initial absorbance slightly greater than 1. The temperature of the cell contents was measured periodically by means of a glass-encapsulated thermocouple immersed in the solvent. The temperature change caused by the addition of the complex salt and stirring rod to the cell was only about ±0.3°, and thermal equilibrium was established again within *ca.* 2 min. Temperature differences as large as 2° between the bottom and top portions of the melt were recorded for cells containing the rather viscous NH_4HSO_4 a few degrees above its melting point, and the regulation of temperature for runs in this melt at *ca.* 153° was ±0.9°. The regulation of temperature in NH_4HSO_4 improved at higher temperatures, being ±0.2° at 162° and ±0.4° at 172°. The regulation of cell temperature for the runs in H_2SO_4 ranged from ±0.2° at 152° to ±0.35° at 181°.

The decomposition of $Co(NH_3)_6{}^{3+}$ in H_2SO_4 at 152° was followed also by retrieval of unreacted $Co(NH_3)_6{}^{3+}$ by precipitation as $[Co(NH_3)_6][ClO_4]_3$. Aliquots were removed periodically from the reaction mixture and were quenched by rapid cooling. One-half volume of 70% $HClO_4$ was added to the solution, upon which $[Co(NH_3)_6][ClO_4]_3$ precipitated quantitatively. The precipitate was washed with cold 1 *M* $HClO_4$ and then dissolved in 0.1 *M* $HClO_4$ for spectrophotometric determination of the $Co(NH_3)_6{}^{3+}$ present.

Results

Optical Spectra.—Absorption spectral data for several complexes of interest are given in Table I. As could have been anticipated from the results of Jolly, *et al.*,[5] substitution of sulfate (or bisulfate) for coordinated water on cobalt(III) is quite rapid in both molten NH_4HSO_4 and concentrated H_2SO_4 at *ca.* 150°. The conversions of $Co(NH_3)_5H_2O^{3+}$ to $Co(NH_3)_5HSO_4{}^{2+}$ and of both $Co(NH_3)_4CO_3{}^{+}$ and $(NH_3)_4Co(OH)_2Co(NH_3)_4{}^{4+}$ to *cis*-$Co(NH_3)_4(HSO_4)_2{}^{+}$ are essentially complete within the time required to dissolve the sulfate salts of these ions at temperatures above 150°. Thus the spectra of solutions prepared from $Co(NH_3)_5SO_4{}^{+}$ and from $Co(NH_3)_5H_2O^{3+}$ are identical, and the spectra of solutions prepared from $Co(NH_3)_4CO_3{}^{+}$ and from $(NH_3)_4Co(OH)_2Co(NH_3)_4{}^{4+}$ are identical.[13,14]

TABLE I

ABSORPTION MAXIMA OF COBALT SPECIES[a]

Complex ion	Solvent H_2SO_4	 NH_4HSO_4	 H_2O
$Co(NH_3)_6{}^{3+}$	485 (66 ± 2)	480 (62 ± 1)	472
	343 (55 ± 2)	341 (52 ± 1)	336
$Co(NH_3)_5SO_4{}^{+}$ [b]	522 (60 ± 1)	520 (62 ± 1)	514
	352 (51 ± 1)	352 (50 ± 1)	353
cis-$Co(NH_3)_4(HSO_4)_2{}^{+}$	535 (69 ± 3)		
	370 (50 ± 2)		
Co^{2+}	555 (12 ± 1)	568 (22 ± 1)	

[a] First number given is wavelength (nm) of an absorption maximum. Number following in parentheses is molar extinction coefficient (M^{-1} cm^{-1}) at this maximum at *ca.* 150°. [b] Probably exists as $Co(NH_3)_5HSO_4{}^{2+}$ in H_2SO_4.

It is interesting to note that the spectra of the cobalt(III) complexes are not changed significantly by changing the solvent from NH_4HSO_4 to H_2SO_4. The rather large difference in the spectrum of Co^{2+} in the two solvents may be due to different proportions of tetrahedral and octahedral cobalt(II) species in the two solvents.

Reaction Stoichiometry.—The almost exclusive gaseous product of the complete decomposition of $Co(NH_3)_6{}^{3+}$, $Co(NH_3)_5H_2O^{3+}$, and $Co(NH_3)_5SO_4{}^{+}$ in molten NH_4HSO_4 was N_2. Complete decomposition of these three complexes in H_2SO_4 at 155° also gave N_2 as the principal gaseous product, but small amounts of NO and SO_2 were detected as well. If the principal net reaction involved the oxidation of NH_3 (or $NH_4{}^{+}$) to N_2 and reduction of Co(III) to Co(II), then 6 mol of Co(III) would be consumed per mole of N_2 evolved. From Table II it is seen that very nearly 6 mol of Co(III) was required per mole of N_2 evolved in the NH_4HSO_4 solvent and that about 7 mol of Co(III) was consumed per mole of N_2 evolved in the H_2SO_4 solvent.

TABLE II

STOICHIOMETRY OF DECOMPOSITION REACTIONS AT 155° FOR SOME COBALT(III) AMMINES

Compd	Moles of Co(III) reduced per mole of N_2 evolved In NH_4HSO_4	 In H_2SO_4
$[Co(NH_3)_6][HSO_4]_3$	6.04	6.99
$[Co(NH_3)_5SO_4][HSO_4]$	6.28	7.71
$[Co(NH_3)_5H_2O]_2[SO_4]_3$	5.97	7.10

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(13) The state of protonation of the sulfato complexes in the two solvents is unknown. It is likely that the bulk of the coordinated sulfato ligands are singly protonated in the highly acidic H_2SO_4 and unprotonated in NH_4HSO_4, so that the major form of the pentaammine complex would be $Co(NH_3)_5HSO_4{}^{2+}$ in H_2SO_4 and $Co(NH_3)_5SO_4{}^{+}$ in NH_4HSO_4.

(14) Although we have chosen to write the tetraammine species in H_2SO_4 as *cis*-$Co(NH_3)_4(HSO_4)_2{}^{+}$, with two bound sulfato ligands, a formulation which is equally consistent with all our observations is *cis*-$Co(NH_3)_4SO_4{}^{+}$, with sulfate serving as a bidentate ligand. An analogous ethylenediamine complex containing bidentate sulfate is known, namely, *cis*-$Co(en)_2SO_4{}^{+}$, and Duffy and Macdonald[15] have recently presented evidence indicating that *cis*- and *trans*-$Co(en)_2Cl_2{}^{+}$ and *cis*-$Co(en)_2C_2O_4{}^{+}$ are all converted to *cis*-$Co(en)_2SO_4{}^{+}$ in 100% H_2SO_4.

(15) J. A. Duffy and W. J. Macdonald, *J. Chem. Soc. A*, 1160 (1971).

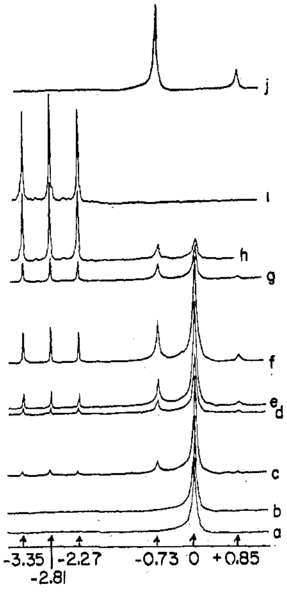

Figure 1.—The 100-MHz pmr spectra of a solution initially of *ca.* 0.2 *M* [$Co(NH_3)_6$][HSO_4]$_3$ in 95–98% H_2SO_4 at 30° (a) and after reaction for 5 (b), 35 (c), 65 (d), 75 (e), 105 (f), 135 (g), 255 (h), and 1440 (i) min at 154°. Spectrum (j) is that of a solution of *ca.* 0.3 *M* [$Co(NH_3)_5SO_4$]HSO_4 in 95–98% H_2SO_4 at 30°. The chemical shifts are relative to $Co(NH_3)_6{}^{3+}$.

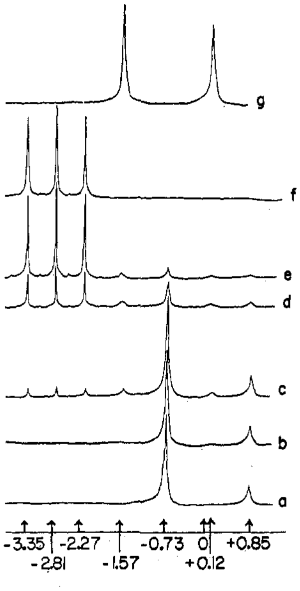

Figure 2.—The 100-MHz pmr spectra of a solution initially of *ca.* 0.3 *M* [$Co(NH_3)_5SO_4$]HSO_4 in 95–98% H_2SO_4 at 30° (a) and after reaction for 6 (b), 26 (c), 72 (d), 132 (e), and 1440 (f) min at 154°. Spectrum (g) is that of a solution of *ca.* 0.2 *M* *cis*-$Co(NH_3)_4(HSO_4)_2{}^+$, added as [$Co(NH_3)_4CO_3$]$_2SO_4$, in 95–98% H_2SO_4 at 30°. The chemical shifts are relative to $Co(NH_3)_6{}^{3+}$.

The overall reactions are extremely complex, as is seen from eq 1, which expresses the main net change for the

$$6Co(NH_3)_6{}^{3+} + 28HSO_4{}^- \longrightarrow N_2 + 6Co^{2+} + 34NH_4{}^+ + 28SO_4{}^{2-} \quad (1)$$

reaction of $Co(NH_3)_6{}^{3+}$ in molten NH_4HSO_4. The overall reaction involves at the very least six one-electron redox steps involving Co(III). The reaction also involves the breaking of six Co–NH_3 bonds per Co(III), so that a question of prime importance in unraveling the reaction mechanism is how many of these Co–NH_3 bonds are broken prior to the first redox step.

Evidence for Reaction Intermediates.—To determine to what extent intermediates formed by substitution of $SO_4{}^{2-}$ for NH_3 on Co(III) were involved in the decomposition reactions, pmr spectra were recorded for solutions in H_2SO_4 which had reacted for different times at 154°. One difficulty in interpreting the pmr results was that the paramagnetic Co(II) formed in the reactions caused the pmr peaks to shift relative to the external standard. For example, the pmr spectrum of a solution of [$Co(NH_3)_6$]$_2$[SO_4]$_3$ in H_2SO_4, prepared at 25° and containing no Co(II), had two peaks, one at 11.62 ppm due to the solvent and one at 3.54 ppm due to $Co(NH_3)_6{}^{3+}$, relative to the TMS external standard. The addition of enough $CoSO_4$ to saturate the solution shifted both peaks upfield by about 0.5 ppm. The extent of the shift caused by Co(II) was of course dependent on its concentration, but fortunately all peaks were shifted by the same amount in the presence of a given concentration of Co(II). It was therefore possible to use the H_2SO_4 peak as an internal standard for solutions containing Co(II). For convenience the pmr chemical shifts will be presented relative to the protons of $Co(NH_3)_6{}^{3+}$.

Figure 1 shows pmr spectra recorded for solutions of $Co(NH_3)_6{}^{3+}$ in H_2SO_4 at 30° and after reaction for various periods of time at 154°. The top spectrum (j) of Figure 1 is that of a freshly prepared solution of $Co(NH_3)_5HSO_4{}^{2+}$. The peaks at −3.35, −2.81, and −2.27 ppm, which appeared as the sample reacted and eventually attained a constant amplitude, were due to the protons of $NH_4{}^+$ and appeared at the same positions as the new resonances found upon the addition of $(NH_4)_2SO_4$ to H_2SO_4. It is seen that new peaks also appeared at −0.73 and +0.85 ppm. The positions of the latter peaks matched very well the positions of the peaks for $Co(NH_3)_5HSO_4{}^{2+}$, and the ratio of integrated peak areas was 4:1, also as expected and observed for $Co(NH_3)_5HSO_4{}^{2+}$. The amplitude of the peak at 0 ppm due to $Co(NH_3)_6{}^{3+}$ decreased steadily as expected as decomposition occurred.

Figure 2 shows pmr spectra recorded for solutions of $Co(NH_3)_5HSO_4{}^{2+}$ in H_2SO_4 at 30° and after reaction for various periods of time at 154°. The top spectrum (g) is that of a solution of *cis*-$Co(NH_3)_4(HSO_4)_2{}^+$ in H_2SO_4, prepared by dissolving [$Co(NH_3)_4CO_3$]$_2SO_4$ in H_2SO_4 and allowing the solution to stand for 3 hr. It is seen that the peaks at −3.35, −2.81, and −2.27 ppm due to $NH_4{}^+$ again appeared and grew to a maximum, whereas the peaks at −0.73 and +0.85 ppm due to $Co(NH_3)_5HSO_4{}^+$ diminished steadily as the sample reacted. New peaks of about equal intensity appeared at +0.12 and −1.57 ppm. It is evident that the positions of the latter peaks match very well those of *cis*-$Co(NH_3)_4(HSO_4)_2{}^+$.

Figure 3 shows spectra of solutions of *cis*-$Co(NH_3)_4(HSO_4)_2{}^+$ recorded at room temperature and after reaction for various periods of time at 154°. The peaks due to *cis*-$Co(NH_3)_4(HSO_4)_2{}^+$ at −1.57 and +0.12 ppm diminished steadily, and the peaks at −3.35, −2.81, and −2.27 ppm due to $NH_4{}^+$ increased steadily, as decomposition occurred. One new peak at *ca.* −1.00 ppm appeared and then disappeared as the sample de-

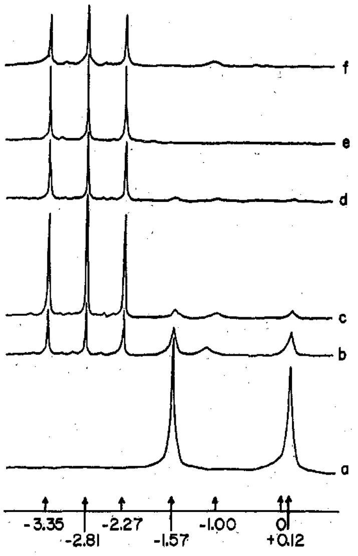

Figure 3.—The 100-MHz pmr spectra of a solution initially of *ca.* 0.2 *M* *cis*-$Co(NH_3)_4(HSO_4)_2^+$, added as $[Co(NH_3)_4CO_3]_2SO_4$, in 95–98% H_2SO_4 at 30° (a) and after reaction for 5 (b), 15 (c), 25 (d), and 45 (e) min at 154°. Spectrum (f) is that of a solution of 0.4 *M* $Co(NH_3)_3(NO_2)_3$ in 95–98% H_2SO_4 at 30°. The chemical shifts are relative to $Co(NH_3)_6^{3+}$.

composed. The position of this new peak matched fairly well the position of one peak in the spectrum (f) of a solution prepared by dissolving the facial isomer[11] of $Co(NH_3)_3(NO_2)_3$ in H_2SO_4 and purging the solution with argon until the evolution of oxides of nitrogen ceased. Although it is tempting to assign the peak at −1.00 ppm to *fac*-$Co(NH_3)_3(HSO_4)_3$, it is evident from the presence of NH_4^+ peaks in spectrum (f) that the *fac*-$Co(NH_3)_3(NO_2)_3$ underwent some reaction other than simple replacement of NO_2^- by HSO_4^-, so that this assignment is uncertain.

Figures 1–3 reveal a number of important facts concerning the mechanisms of decomposition of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5HSO_4^{2+}$, and *cis*-$Co(NH_3)_4(HSO_4)_2^+$ in H_2SO_4. For both $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5HSO_4^{2+}$ a substantial amount of the complex containing one less NH_3 per Co was formed in the course of the decomposition reaction, and this next lower ammine was the only cobalt(III)–ammonia complex intermediate for which evidence was found in the pmr spectra. Likewise one and only one intermediate, probably *fac*-$Co(NH_3)_3(HSO_4)_3$, was detected during the decomposition of *cis*-$Co(NH_3)_4(HSO_4)_2^+$. From a comparison of Figures 1–3, it is evident that the order of decreasing decomposition rates is *cis*-$Co(NH_3)_4(HSO_4)_2^+ > Co(NH_3)_5HSO_4^{2+} > Co(NH_3)_6^{3+}$.

Further evidence that substantial concentrations of intermediates build up during the decomposition of $Co(NH_3)_6^{3+}$ was obtained in those experiments in which unreacted $Co(NH_3)_6^{3+}$ was retrieved periodically. After removal of $Co(NH_3)_6^{3+}$, a solution which had reacted for 40 min at 152° in 97% H_2SO_4 had absorption maxima at 516 and 351 nm with a peak height ratio of $A_{516}/A_{351} = 1.24$, compared to maxima at 514 and 353 nm with $A_{514}/A_{353} = 1.25$ for $Co(NH_3)_5HSO_4^{2+}$. The presence of intermediates was indicated also by a large discrepancy between the Co^{2+} which had formed (measured as $CoCl_4^{2-}$) and the $Co(NH_3)_6^{3+}$ which had disappeared at various reaction times. For example, after 70 min in H_2SO_4 at 152°, 48% of the $Co(NH_3)_6^{3+}$ originally present had disappeared, whereas only 12% of the Co^{2+} ultimately formed had appeared. After 100 min of reaction, 62% of the $Co(NH_3)_6^{3+}$ had disappeared, whereas only 25% of the total Co was found as Co^{2+}. Thus 36–37% of the Co in these solutions must have been present as intermediates.

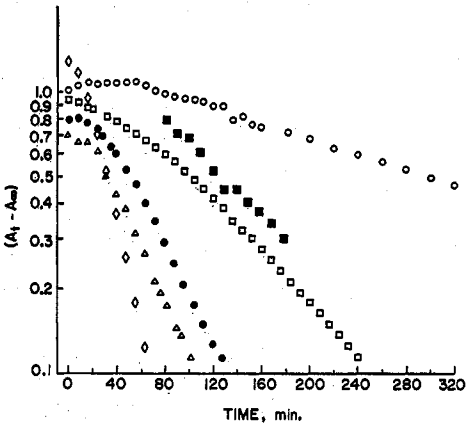

Figure 4.—Typical first-order rate plots based on absorbance–time data for the reactions of $Co(NH_3)_6^{3+}$ (○) and $Co(NH_3)_5SO_4^+$ (△) in molten NH_4HSO_4 and of $Co(NH_3)_6^{3+}$ (□), $Co(NH_3)_5HSO_4^{2+}$ (●), and *cis*-$Co(NH_3)_4(HSO_4)_2^+$ (◊) in 95–98% H_2SO_4 at *ca.* 153°. Rate plot for reaction of $Co(NH_3)_6^{3+}$ with H_2SO_4 at 152° (■), obtained by retrieving $Co(NH_3)_6^{3+}$ periodically, is shown with abscissa offset by 80 min.

Reaction Kinetics.—Figure 4 shows attempts to fit the absorbance–time data for the various complexes to first-order rate plots. The early part of the absorbance–time record for the reactions in NH_4HSO_4 was rather noisy, probably due to bubble formation. Large bubbles could be seen clinging to the walls of the spectrophotometer cells during the early part of the reaction in NH_4HSO_4. It is probably for this reason that the absorbance of some solutions of $Co(NH_3)_6^{3+}$ in NH_4HSO_4, such as that used to obtain the plot of Figure 4, increased slightly at first even though all possible products have lower extinction coefficients than the reactant.

All of the rate plots of Figure 4 are characterized by an induction period followed by a period of reasonably good first-order behavior. The behavior illustrated in Figure 4 is explained easily with the aid of the pmr results already discussed above. Let us first consider the decomposition of $Co(NH_3)_6^{3+}$ in H_2SO_4. It has been concluded from the pmr results and those experiments in which unreacted $Co(NH_3)_6^{3+}$ was retrieved periodically that substantial amounts of $Co(NH_3)_5HSO_4^{2+}$ accumulate during the decomposition of $Co(NH_3)_6^{3+}$ but that the accumulation of other cobalt(III)–ammonia complexes is negligible. Significant quantities of only three colored species are then expected to be present during the reaction, these species being $Co(NH_3)_6^{3+}$, $Co(NH_3)_5HSO_4^{2+}$, and Co^{2+}, with molar extinction coefficients of 66, 49, and 5 M^{-1} cm^{-1}, respectively, at 483 nm, the wavelength at which the reaction was followed. In the early stages of the reaction the main net change will be the conversion of $Co(NH_3)_6^{3+}$ to $Co(NH_3)_5HSO_4^{2+}$, with an absorbance change per mole of 17. The concentration of $Co(NH_3)_5HSO_4^{2+}$ will increase steadily until it attains a maximum, at which time the rates of formation and decomposition of $Co(NH_3)_5HSO_4^{2+}$ will be equal and the main net change will be the conversion of $Co(NH_3)_6^{3+}$ to Co^{2+}, with an absorbance change per mole of 61. The linear portion of the first-order rate plot for this reaction in Figure 4 would then correspond to that portion of the reaction during which $Co(NH_3)_5HSO_4^{2+}$ is at steady state. The steady-state approximation is not very good in this case, however, since $Co(NH_3)_5HSO_4^{2+}$ is not much more reactive than is $Co(NH_3)_6^{3+}$.

Analogous arguments can be used to explain the shapes of the other rate plots in Figure 4. There is an induction period at the beginning of each rate plot during which the main net change is the conversion of the parent complex to the next lower ammine, with a small change in extinction coefficient. The slope of the rate plot increases gradually as the rate of production of Co^{2+}, with its accompanying large change in extinction coefficients, increases.

As noted above, the disappearance of $Co(NH_3)_6^{3+}$ in H_2SO_4 was monitored more directly by the periodic precipitation of $[Co(NH_3)_6](ClO_4)_3$. A first-order rate plot based on this method is also shown in Figure 4. The linearity of this plot confirms that the reaction of $Co(NH_3)_6^{3+}$ in H_2SO_4 is first order. Further, the slope of this plot is seen to be only about 20% shallower than the slope of the linear portion of the rate plot based on the absorbance of the complete reaction mixture.

First-order rate constants for the loss of the first NH_3 from the various complexes were obtained by interpreting the absorbance–time data in terms of the model

$$A \xrightarrow{k_1} B \xrightarrow{k_2} Co^{2+} \qquad (2)$$

where k_1 and k_2 are first-order rate constants, A is the complex under study, and B is the next lower ammine, *e.g.*, B is $Co(NH_3)_5SO_4^+$ where A is $Co(NH_3)_6^{3+}$. If B is assumed to be a reactive intermediate, it can be shown easily that eq 3 holds once B is at steady state.

$$\frac{-d[A]}{dt} = \frac{d[Co^{2+}]}{dt} = k_1[A] \qquad (3)$$

To obtain approximate values of k_1 for the various complexes, first-order rate plots such as those shown in Figure 4 were constructed. The absorbance–time data for only the linear portion of these rate plots were then fitted to the rate equation $A_t = (A_0 - A_\infty)e^{-k_1t} + A_\infty$ using a nonlinear least-squares computer program. (A_t, A_0, and A_∞ are the instantaneous, zero-time,[16] and infinite-time absorbance values.)

In those cases in which an independent estimate of the decomposition rate of intermediate B was available, the first-order rate constants were further refined by fitting the whole absorbance–time curve to the scheme of eq 2, using a computer program for consecutive first-order reactions adapted from Wiberg.[17] This program first calculated the initial concentration of the parent complex A from the initial absorbance and the known extinction coefficient and then chose the values of k_1 and k_2 which in combination with the known extinction coefficients gave the best fit to the absorbance–time data. In Figure 5 the absorbance–time data (circles) for a typical run are compared to the curve generated by the computer. The fit is obviously quite good. Two independent evaluations of the rate constant for the loss of the first NH_3 from $Co(NH_3)_5HSO_4^{2+}$ in H_2SO_4 were obtained in this manner, since this rate constant was obtained as k_2 in runs starting with $Co(NH_3)_6^{3+}$ and as k_1 in runs starting with $Co(NH_3)_5HSO_4^{2+}$.

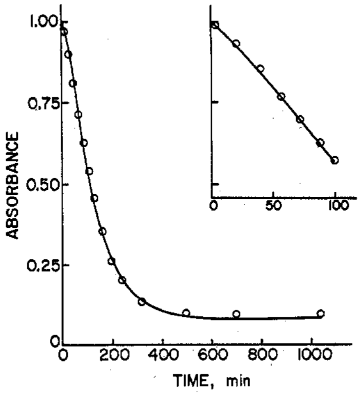

Figure 5.—Comparison of absorbance–time data (circles) for the reaction of $Co(NH_3)_6^{3+}$ in H_2SO_4 at 153° to the computer-generated absorbance–time curve (solid line). The curve was calculated treating the conversion of $Co(NH_3)_6^{3+}$ to $Co(NH_3)_5HSO_4^{2+}$ and of $Co(NH_3)_5HSO_4^{2+}$ to Co^{2+} as consecutive first-order reactions using the rate constants of Table III and the extinction coefficients of Table I. Insert shows the expanded plot for the first 100 min of reaction.

The first-order rate constants for the loss of the first NH_3 from the various complexes are given in Table III. The values of the rate constants given in Table III have an internal consistency and a consistency with

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE LOSS OF THE FIRST NH_3 FROM VARIOUS COBALT(III) COMPLEXES

Complex ion	Temp, °C	10^4k, sec^{-1}	E_a, kcal mol^{-1}
	1. NH_4HSO_4 Solvent		
$Co(NH_3)_6^{3+}$ [a]	153.1 ± 0.9	0.52 ± 0.04	42 ± 2
	161.6 ± 1.0	1.44 ± 0.06	
	172.1 ± 0.9	4.3 ± 0.3	
$Co(NH_3)_5SO_4^{2+}$ [b]	153.4 ± 0.9	3.4 ± 0.1	40 ± 3
	161.4 ± 1.0	8.5 ± 0.8	
	172.0 ± 1.0	25 ± 2	
	2. H_2SO_4 Solvent		
$Co(NH_3)_6^{3+}$ [a]	152.6 ± 0.3	1.97 ± 0.04 1.73 ± 0.07[d]	40 ± 2
	161.0 ± 0.4	4.6 ± 0.2	
	171.1 ± 0.3	13.9 ± 0.7	
	181.0 ± 0.2	36 ± 2	
$Co(NH_3)_5HSO_4^{2+}$ [a]	152.6 ± 0.3	3.6 ± 0.2 3.6 ± 0.3[c] 3.0 ± 0.3[b] 3.6 ± 0.3[d]	38 ± 2
	161.0 ± 0.3	8.5 ± 0.5	
	171.1 ± 0.3	23 ± 1	
	181.0 ± 0.2	60 ±2	
cis-$Co(NH_3)_4(HSO_4)_2^+$ [b]	151.7 ± 0.4	7.5 ± 0.5 7.4 ± 0.4[d]	40 ± 2
	161.8 ± 0.5	20 ± 1	
	171.7 ± 0.4	61 ± 4	
	181.6 ± 0.4	169 ± 13	

[a] Rate constants determined using the modified Wiberg computer program for consecutive first-order reactions, except as noted. [b] Rate constants from the slope of the straight-line portion of first-order rate plots analogous to Figure 4. [c] Obtained from the computer fit of runs startingw ith $Co(NH_3)_6^{3+}$. [d] Solutions 0.02 M in added Co^{2+}.

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[16] Zero time was chosen to coincide with the beginning of the linear portion of the first-order rate plots shown in Figure 4.

[17] K. B. Wiberg, "Computer Programming for Chemists," W. A. Benjamin, New York, N. Y., 1965, p 181.

other evidence which justifies the assumptions on which they are based. For example, the value of k for $Co(NH_3)_5HSO_4^{2+}$ in H_2SO_4 at *ca.* 153° is the same within $\pm5\%$ whether it is calculated as k_1 starting with either $Co(NH_3)_5HSO_4^{2+}$ or $Co(NH_3)_5H_2O^{3+}$ or as k_2 starting with $Co(NH_3)_6^{3+}$. Further, the values of k for $Co(NH_3)_5HSO_4^{2+}$ so obtained are only about 20% higher than the value obtained treating the decomposition of $Co(NH_3)_5HSO_4^{2+}$ as a first-order reaction using the linear portion of the appropriate plot of Figure 4. The values given in Table III also further justify the assumption that the next lower ammine is the only intermediate which attains significant concentration in the decomposition of a particular complex. From the rate constants for H_2SO_4 at *ca.* 153° we calculate that the maximum concentration of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ attained during the decomposition of $Co(NH_3)_6^{3+}$ is only about 7% of the initial concentration of $Co(NH_3)_6^{3+}$. Further, the values of k given in Table III lead us to expect that the maximum concentration of the intermediate $Co(NH_3)_5HSO_4^{2+}$ formed during the decomposition of $Co(NH_3)_6^{3+}$ in H_2SO_4 will be about 27% of the initial concentration of $Co(NH_3)_6^{3+}$ and will be attained after about 1 hr at 153°. Based on Table III the maximum part of the original $Co(NH_3)_6^{3+}$ which is expected to be found as intermediates is then *ca.* 34% at 153°, which is consistent with the maximum of *ca.* 37% of total Co not accounted for as either $Co(NH_3)_6^{3+}$ or Co^{2+} during runs at 152°. The half-time for the decomposition of $Co(NH_3)_6^{3+}$ in H_2SO_4 based on Table III is 60 min at 152.6°, in good agreement with a half-time of 71 min at 152° based on the precipitation of $[Co(NH_3)_6](ClO_4)_3$.

Unfortunately the pmr spectra of Figures 1–3 do not provide good quantitative data concerning the concentrations of intermediates. The absolute intensities of the pmr signals were affected by the Co^{2+} present, and some samples had been centrifuged to remove precipitated $CoSO_4$, whereas this treatment was not necessary for other samples. Nevertheless, the pmr spectra provide at least semiquantitative support for the data of Table III. For example, from Figure 2 it appears that the half-time for the disappearance of $Co(NH_3)_5HSO_4^{2+}$ in H_2SO_4 at 154° lies somewhere between 26 and 72 min, whereas a half-time of 32 min is calculated from Table III. From Figure 1 the maximum concentration of $Co(NH_3)_5HSO_4^{2+}$ formed during the decomposition of $Co(NH_3)_6^{3+}$ in H_2SO_4 is certainly greater than 10% and less than 50% of the initial concentration of $Co(NH_3)_6^{3+}$, compared to 27% calculated from Table III.

The values of k for the decomposition of $Co(NH_3)_5SO_4^+$ in NH_4HSO_4 and of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ in H_2SO_4 are the least reliable values given in Table III, since they are based solely on a fit of the absorbance–time data (after the induction period) to a first-order rate equation. The long induction periods seen in the rate plots for these reactions (see Figure 4) imply that substantial concentrations of intermediates are involved. It is likely that the true value of the rate constant for the loss of the first NH_3 in these two cases is somewhat higher, possibly as much as 20% higher, than that listed in Table III.

Removing the last traces of water from the H_2SO_4 solvent by the addition of fuming H_2SO_4 and increasing the SO_4^{2-} concentration of the NH_4HSO_4 solvent by the addition of saturating quantities of $(NH_4)_2SO_4$ had no significant effect on the rate constants of Table III. The addition of Co^{2+} also had no significant effect on the rate constants.

Discussion

Although all of the Co(III) complexes which we have studied are reduced ultimately to Co(II), our results reveal almost nothing about the rates of the redox steps involved in the overall reactions. The only definite conclusion which our results allow concerning these redox steps is that they are substantially more rapid than the substitution steps which precede them. It can be concluded definitely that $Co(NH_3)_6^{3+}$ in both H_2SO_4 and NH_4HSO_4 and $Co(NH_3)_5HSO_4^{2+}$ in H_2SO_4 undergo substitution rather than redox reactions under the conditions of our experiments. Strong support for this conclusion is found in the pmr results for H_2SO_4 and in the kinetic data for both solvents. For example, the pmr results show that $Co(NH_3)_5HSO_4^{2+}$ formed in the decomposition of $Co(NH_3)_6^{3+}$ is approximately that expected if all of the $Co(NH_3)_6^{3+}$ decomposes to $Co(NH_3)_5HSO_4^{2+}$, rather than being reduced directly to Co^{2+}. Further evidence that all of the $Co(NH_3)_6^{3+}$ is converted to $Co(NH_3)_5HSO_4^{2+}$ is the finding that the same value of the rate constant for the decomposition of $Co(NH_3)_5HSO_4^{2+}$ is obtained from the absorbance–time data starting with $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5HSO_4^{2+}$.

The similarity of the shape of the rate plots for the decomposition of *cis*-$Co(NH_3)_4(HSO_4)_2^+$ in H_2SO_4 and of $Co(NH_3)_5SO_4^+$ in NH_4HSO_4 to the shape of the rate plots for the other reactions suggests that these reactions, too, have as their slowest step the conversion of the parent complex to the next lower ammine. For *cis*-$Co(NH_3)_4(HSO_4)_2^+$ this conclusion is supported also by the appearance of a new pmr peak, probably due to $Co(NH_3)_3(HSO_4)_3$, during the decomposition reaction. At the very least the rate constants given in Table III for these two cases are upper limits for the rate constants of the substitution reactions, even if some direct reduction of these complexes to cobalt(II) occurs.

The trends in substitution rates revealed by our results are as anticipated in the Introduction. Each successive substitution of HSO_4^- or SO_4^{2-} for NH_3 increases the reaction rate; *i.e.*, in H_2SO_4 the order of increasing reactivity is $Co(NH_3)_6^{3+} < Co(NH_3)_5HSO_4^{2+} <$ *cis*-$Co(NH_3)_4(HSO_4)_2^+$. However, it is not the difference in reaction rates but rather the remarkable similarity in reaction rates which is surprising. The tetraammine complex, which probably exists as *cis*-$Co(NH_3)_4(HSO_4)_2^+$ in H_2SO_4, loses NH_3 at a rate which is at most 4 times as rapid as the loss of NH_3 from $Co(NH_3)_6^{3+}$ under the same conditions, even though the charge on the two complexes differs by 2 units. In contrast to this, the rate of loss of a Cl^- ligand from a cobalt(III)–ammine complex is usually changed by at least an order of magnitude by changing the charge on the complex by one unit.[18]

The reaction rates at the same temperature and also the activation energies for the two solvents are remarkably similar. At a given temperature the rate con-

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[18] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 3.

stants for all the reactions studied span a factor of less than 15. The relative rates for $Co(NH_3)_6^{3+}$ in the two solvents is in fact the reverse of what would be expected on the basis of the availability of nucleophiles. We estimate the molar concentration of undissociated H_2SO_4 in 95% H_2SO_4 to be 11.7 and that of the HSO_4^- ion to be 4.8 at 152°, whereas the major sulfate species in NH_4HSO_4 is HSO_4^- with an estimated molar concentration of 15.4 at 152°. The concentration of SO_4^{2-} ions is also expected to be much greater in NH_4HSO_4 than in H_2SO_4. The expected order of increasing nucleophilicity is $H_2SO_4 < HSO_4^- < SO_4^{2-}$. However, it is seen from Table III that $Co(NH_3)_6^{3+}$ reacts more rapidly in H_2SO_4, despite the lower availability of good nucleophiles in this solvent. It has been noted already that reaction rates were not affected significantly by the addition of fuming H_2SO_4 to the H_2SO_4 solvent or of $(NH_4)_2SO_4$ to NH_4HSO_4, although these additions alter substantially the concentrations of nucleophiles.

The activation energies for the two solvents and for the various complexes are also remarkably similar. All of the activation energies in Table III are, within experimental error, 40 kcal/mol.

It seems reasonable to conclude that for all of the complexes studied the replacement of the first NH_3 molecule is the slow step in the decomposition reaction, and this step is essentially unimolecular in character. We suggest that the critical act in the replacement of this NH_3 molecule is the stretching of the very robust Co–N bond to a critical distance, an act requiring about 40 kcal/mol of activation energy. Once the NH_3 ligand has been separated to this critical distance, it becomes protonated and its place in the first coordination sphere is taken by whatever sulfate species happens to be available in the second coordination sphere.

The very robust character of the cobalt(III)–ammonia bond is illustrated vividly by an extrapolation of our results to 25°. Assuming an activation energy of 38 kcal/mol, the rate of replacement of NH_3 at 153° is estimated to be 10^8 times as rapid as at 25°. The most labile of the complexes we have studied, *cis*-$Co(NH_3)_4(HSO_4)_2^+$, would lose its first NH_3 with a half-time of about 3000 years at 25°! The half-time for water exchange on $Co(NH_3)_5H_2O^{3+}$ is about 12 days at 25°, so that replacement of H_2O on a cobalt(III)–ammonia complex occurs about 10^5 times as rapidly as replacement of NH_3.

Qualitative support for the results and conclusions which we have reported here is found in recent work of Duffy and Macdonald.[15] These authors recorded the changes in spectra accompanying the decomposition of cobalt(III)–ammonia complexes to Co(II) in 100% H_2SO_4 and in molten $NaHSO_4$–$KHSO_4$ at temperatures up to 152°. They concluded as did we that ligand replacement precedes reduction and that reaction rates increase with decreasing number of NH_3 ligands. Further, their time interval of 40 min at 152° for 50% reduction in absorbance of the ${}^1T_{2g} \leftarrow {}^1A_{1g}$ absorption band of $Co(NH_3)_5HSO_4^{2+}$ is almost identical with the half-time calculated from our Table III for decomposition of this complex. However, their half-time of 240 min for 50% reduction in this band for $Co(NH_3)_6^{3+}$ is about 3 times longer than we found for the decomposition of this complex by retrieving unreacted $Co(NH_3)_6^{3+}$. This discrepancy exists because the ultraviolet absorption maximum of the intermediate $Co(NH_3)_5HSO_4^{2+}$ lies at nearly the same frequency as that of $Co(NH_3)_6^{3+}$, and the extinction coefficient of the intermediate is about 25% higher than that of $Co(NH_3)_6^{3+}$.

Our results have interesting implications concerning the mechanism of some other substitution reactions of cobalt(III) complexes. For example, it seems reasonable to expect the cleavage of cobalt(III)–nitrogen bonds in ethylenediamine complexes to occur at rates similar to the rates of cobalt–ammonia bond cleavage, with half-times on the order of years at 25°. An isomerization or racemization reaction of a cobalt(III)–ethylenediamine complex with a half-time of only a few hours at 25° is then not expected to occur by a mechanism in which one bond to ethylenediamine is first cleaved and then formed again.[19]

It is interesting to note that the decomposition of none of the complexes which we have studied is catalyzed by Co^{2+}, not even when the solutions were saturated with $CoSO_4$, as in the pmr experiments. Assuming that an enhancement of the decomposition rates by 20% upon the addition of Co^{2+} would have been detected, we can set upper limits for the second-order rate constants for electron-exchange reactions with Co^{2+} of about $1 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 153°.

An interesting question which our results leave unanswered is whether it is the NH_3 which is bound to Co(III) or ambient NH_4^+ which is oxidized in the first redox step of the overall decomposition reactions. Unfortunately we have not been able to start our experiments with the complex which undergoes reduction in preference to substitution. An interesting experiment which might shed light on this question would be to generate Co^{3+} not complexed with NH_3 in the H_2SO_4 solvent, either by electrolysis or by addition of $Co(CO_3)_3^{3-}$, and to mix the resulting solution with a solution containing NH_4^+.

Acknowledgments.—This research was done at the Naval Ordnance Laboratory under Tasks ORD 333-006/092-1/UF17-331-301 and MAT 03L-000/ZR-011-01-01. The authors are grateful to Dr. L. Kaplan and Miss E. G. Kayser for aid in obtaining the pmr spectra, to V. Sutula for doing the drawings and the data reduction, and to Dr. A. G. Hellfritzsch for helpful suggestions concerning the manuscript.

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[19] Such a mechanism was once suggested for the isomerization of the dichlorobis(ethylenediamine)cobalt(III) ion but was rejected on other grounds. See Chapter 3 of ref 18.