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THE AQUATION OF THE NITROPENTAMINE COBALT(III)
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The Aquation of the Nitropentamminecobalt(III)
Ion in Sulfuric Acid Solutions

By Arlo D. Harris, Robert Stewart, David Hendrickson,
and William L. Jolly

We have previously observed that, in concentrated sulfuric acid, the nitropentamminecobalt(III) ion is converted to the bisulfatopentamminecobalt(III) ion via the aquopentamminecobalt(III) ion.¹ This result was rather surprising in view of the low activity of water in concentrated sulfuric acid and in view of the fact that the original nitro complex possesses no cobalt-oxygen bond. Therefore, in order to obtain information about the mechanism of the reaction, we have studied the kinetics of the reaction as a function of the sulfuric acid concentration, and have used oxygen-18 as a tracer to determine the source of the oxygen atom in the aquopentamminecobalt(III) ion.

Experimental Section

Syntheses.- The kinetic measurements were made using $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ which had been prepared by the method described by Schlessinger.² The

solutions in sulfuric acid were undoubtedly highly ion-paired, but for simplicity we shall write $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ for the reactant. A sample of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ was prepared by the method of Jorgensen.³

N.M.R. Procedure.- In sulfuric acid solutions more concentrated than 57%, the kinetics was studied using an A-60 proton magnetic resonance spectrometer¹ to follow the concentration of $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$. (In more dilute solutions of sulfuric acid, the solvent proton peak interferes seriously with the $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ peak and makes quantitative n.m.r. analysis impossible.) The solutions were initially about 0.15 M in $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$. Generally the n.m.r. tubes were kept in the probe throughout the run. For reactions with half-lives greater than 15 minutes, the samples were kept in an external bath at the temperature of the probe ($31 \pm 0.5^\circ$) when the spectra were not being run.

Spectroscopic Procedure.- In sulfuric acid solutions less concentrated than 57%, the kinetics was studied by following the concentration of $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ spectrophotometrically, using a Cary 14 spectrophotometer. The spectra were determined with a 1-cm quartz cell, using the absorbance at 325 m μ (corrected for the solvent blank) as a measure of the $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ concentration. Inasmuch as the extinction coefficients at 325 m μ for the species $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, and $\text{Co}(\text{NH}_3)_5\text{SO}_4^+$ are 1650, 28, and 21 l.cm.mole⁻¹, respectively, a negligible error was made by neglecting the absorbance due to the products. The solutions were initially about 10^{-3} M in $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$, and throughout the runs, they were maintained at $25.0 \pm 0.2^\circ$. Nitrogen (pre-equilibrated with sulfuric acid of the same concentration as that used in the run) was bubbled through the solutions in an effort to remove any volatile nitrogen compounds formed in the reaction. At acid

concentrations greater than 57%, log A-vs.-time plots showed upward curvature rather than straight line behavior because of formation of the NO^+ ion.⁴ The strong absorption of the NO^+ ion, relative to that of the $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ ion, made quantitative spectrophotometric studies impossible in the more concentrated sulfuric acid solutions.

Sulfuric Acid Preparation. - The sulfuric acid solutions used in the n.m.r. study were prepared by dilution of reagent grade 96% acid. The concentrations were determined by titration of weighed samples with standard base. The sulfuric acid solutions used in the spectrophotometric study were prepared by mixing weighed amounts of water and constant-boiling⁵ sulfuric acid (98.48%).

Isotopic Studies. - The solvent samples used for the isotopic studies were prepared by mixing 0.8 ml. of 30% O^{18} enriched water⁶ with 4.2 ml. of 100% sulfuric acid. The solution was allowed to reach isotopic equilibrium by storing at 50° for at least 48 hours. About 0.3 g. of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ was dissolved in 5 ml. of the solvent at about 27° . After 15 minutes (corresponding approximately to a maximum in the yield of the aquo complex), the solution was poured into 10 ml. of ice-cold concentrated HBr solution. The cooled mixture was stirred for five minutes, and the resulting mixed precipitate of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_5\text{HSO}_4]\text{Br}_2$ was collected by suction filtration and washed with 5 ml. of ice-cold conc. HBr, 5 ml. of ice water and two 5 ml. portions of ice-cold anhydrous methanol. The mixture consisted of approximately 60% $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3$, 20% $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ and 20% $[\text{Co}(\text{NH}_3)_5\text{HSO}_4]\text{Br}_2$. The dried solid was submitted to Dr. Geoffrey E. Dolbear of Stanford University, who kindly converted the water to CO_2 and mass-spectrometrically determined the O^{18} content.

Results

The pseudo-first order rate constants ($k = -\text{dln}[\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}]/\text{dt}$) were obtained from linear plots of the logarithm of the $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ concentration vs. time. In most experiments, the rate was followed for at least two half-lives. The values of k are given in Table I as a function of the concentration of sulfuric acid. At sulfuric acid concentrations from 0.94% to 55.74%, k is, within the precision of the data, constant. The average value, $(6 \pm 2) \times 10^{-7} \text{ sec}^{-1}$, is about 50 times larger than the rate constant extrapolated from the 70-100° data of Lalor⁷ for the same reaction in dilute acid solutions. For sulfuric acid concentrations above 57%, k may be calculated, within the precision of the data, from the relation $k = (4 \pm 2) \times 10^{-11} (h_0) \text{ sec}^{-1}$, where h_0 is the antilog of $-\text{H}_0$, the Hammett acidity function.⁸ We conclude that in the concentrated acid solutions a reaction path which is first-order in hydrogen ion activity predominates.⁷

Isotopic analysis of three different samples of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3$, isolated from the reaction of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ with ca. 90% sulfuric acid containing about 4% oxygen-18, showed that the coordinated water contained about 0.2% O^{18} , essentially the fraction present in normal oxygen samples. We therefore conclude that the oxygen of the coordinated water molecule came principally from the coordinated NO_2^- ion.

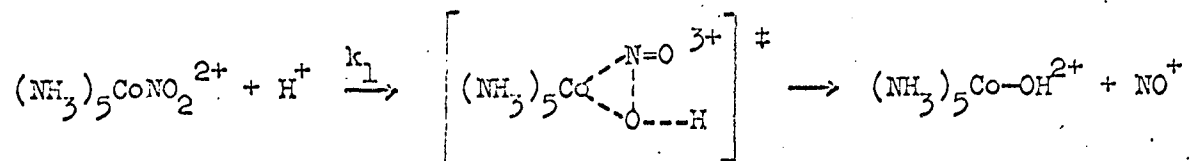
Discussion. - The mechanism for the conversion of the nitro complex to the aquo complex in concentrated sulfuric acid solutions must account for the first-order dependence on hydrogen ion activity and the fact that one of the NO_2^- oxygen atoms ends up in the coordinated water molecule.

We suggest the rate-determining step indicated below.

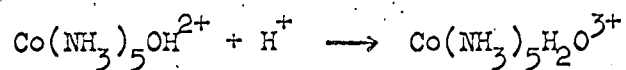
Table I.

Rate Constants for Aquation of
 $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ in Sulfuric Acid Solutions

Wt. % H_2SO_4	k , sec^{-1}	t , $^\circ\text{C}$
0.94	8.1×10^{-7}	25
5.43	6.2×10^{-7}	25
9.79	9.4×10^{-7}	25
18.15	4.1×10^{-7}	25
33.71	4.3×10^{-7}	25
45.20	5.1×10^{-7}	25
50.51	5.9×10^{-7}	25
55.74	7.6×10^{-7}	25
59.78	2.6×10^{-6}	31
64.82	1.1×10^{-5}	31
70.07	4.5×10^{-5}	31
75.74	1.8×10^{-4}	31
79.32	7.7×10^{-4}	31
85.27	3.0×10^{-3}	31

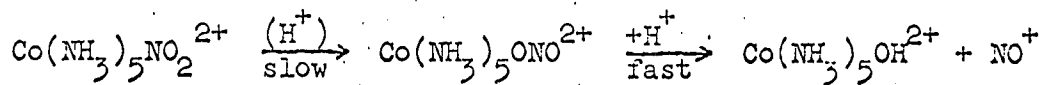


The proton may be considered as assisting the displacement of the nitrosyl ion. This step would be followed by a rapid protonation of the hydroxy intermediate,



In dilute sulfuric acid solutions, the aquo complex is the final product. In concentrated sulfuric acid solutions, the aquo complex is converted at a finite rate to the bisulfato complex.¹

Pearson *et al.*⁹ have studied the reverse reaction in weakly acidic solution; they found that the nitrosation of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ yields the nitrito complex as an intermediate. In our studies there was no evidence for the formation of this species. Indeed, when a sample of nitrito complex was dissolved in 70% sulfuric acid, the initial solution contained only the aquo complex and a smaller amount of nitro complex (the latter presumably was present as an impurity in the nitrito complex). However, we cannot rule out the possibility of a nitrito intermediate. Possibly in strongly acid solutions the nitro complex undergoes an acid-catalyzed isomerization to the nitrito complex, which then is rapidly converted to the aquo complex.



One bit of evidence against such a mechanism is the fact that in dilute solutions the nitrito-nitro conversion is retarded, rather than accelerated,

by the presence of acid.¹⁰

Murmann and Taube¹¹ observed that the conversion of the aquo complex to the nitrito complex in weakly acidic solutions proceeds without breaking the cobalt-oxygen bond, and that the nitrito-nitro conversion proceeds without exchange of oxygen atoms with the solvent. These findings are consistent with either of the above mechanisms and make the results of our isotopic study appear quite reasonable.

Acknowledgments.- We wish to thank Dr. Geoffrey E. Dolbear and Professor Henry Taube for determining the O¹⁸ contents of our $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3$ samples. This research was partly supported by the U. S. Atomic Energy Commission.

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