CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Study of the Hydrolysis of Sulfamatopentaamminecobalt(III) in Acidic Aqueous Solution

BY E. SUSHYNSKI, A. VAN ROODSELAAR, AND R. B. JORDAN*

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The hydrolysis kinetics of sulfamatopentaammineco balt(III) in aqueous acid has been studied. It is found that the complex undergoes an inital reaction with rate constant $k = 1.1 \times 10^{-3}$ sec^{-1} (25° 1 M LiClO$_4$), with $\Delta H^{\ddagger} = 24.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = 10.9$ cal mol^{-1} deg^{-1}. From the spectral change associated with this reaction and the fact that the product is rapidly hydrolyzed in 0.1 M NaOH it is assumed that this first reaction produces an equilibrium mixture of N- and O-bonded sulfamato complexes in acid solutions. Subsequent hydrolysis of this equilibrium mixture yields $(NH_3)_5CoOH_2^{3+}$ and follows the rate law $-d \ln [\text{complex}]/dt = k_2' + k_2''[H^+]$ in 1 M LiClO$_4$ over the temperature range 27–59.3°. For k_2' $\Delta H^{\ddagger} = 24.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.4$ cal mol^{-1} deg^{-1}, while for k_2'' $\Delta H^{\ddagger} = 20.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.5$ cal mol^{-1} deg^{-1}. It has not been possible to associate either k_2' or k_2'' with the hydrolysis of a specific species. The kinetics of the alkaline hydrolysis of the proposed O isomer was studied by stopped-flow techniques and found to have the rate law $-d \ln [\text{complex}]/dt = k'[OH^-]/(1 + K_b[OH^-])$ with $k' = 20$ M^{-1} sec^{-1} and $K_b = 5.1$ M^{-1} at 25.6° in 1 M NaClO$_4$. The K_b is associated with removal of an NH$_2$ proton from the O-bonded sulfamato complex.

Introduction

In a previous study[1] of the hydrolysis of sulfamatopentaamminecobalt(III) in alkaline solution, it was concluded that one term in the rate law was due to the reaction of $(NH_3)_5CoNH_2SO_3^{2+}$ with hydroxide ion. This conclusion rested in part on a comparison of hydrolysis rates in alkaline and acidic solutions. This study reports details of the kinetic study in acidic solution. It was originally supposed that in acid solution the reaction proceeded according to the equation

$$(NH_3)_5CoNH_2SO_3^{2+} + H_2O \xrightarrow{H^+} (NH_3)_5CoOH^{3+} + SO_3NH_2^-$$

However, observations subsequent to the initial work have revealed that a faster reaction precedes the main hydrolysis step. For reasons presented in this work, it is believed that the initial reaction involves an N- to O-bonded linkage isomerism of the sulfamate ligand with subsequent and/or parallel hydrolysis to produce $(NH_3)_5CoOH_2^{3+}$.

Experimental Section

Preparation and Analysis of Reagents.—The $(NH_3)_5CoNH_2SO_3(ClO_4)_2$ was prepared by a somewhat different but not necessarily better method than reported previously.[1] An aqueous solution (250 ml) containing sulfamic acid (20 g) and carbonatopentaamminecobalt(III) nitrate (4 g) was adjusted to a pH of 2.6 with sodium hydroxide and allowed to stand at ambient temperature for 4 weeks. The crystals which formed from the solution were collected and carefully washed with enough water to remove the reddish coloration and leave a yellow product. This product was redissolved in the minimum amount of sodium carbonate solution, filtered, and then acidified with concentrated perchloric acid. The solid product formed immediately and was collected and washed with water and methanol.

Anal. Calcd for $(NH_3)_5CoNH_2SO_3(ClO_4)_2$: N, 19.10; H, 3.90. Found: N, 20.11; H, 3.97. The visible and ultraviolet spectra of the product agreed with those previously reported[1] in both acidic and aqueous solutions.

It has also been found that the sulfamato complex can be prepared from $(NH_3)_5CoCl^{2+}$ and $AgNH_2SO_3$ in dimethyl sulfoxide. The product was precipitated from the anhydrous solvent with *sec*-butyl alcohol[2] and recrystallized as described above. This method of preparation was attempted in order to prepare the O-bonded isomer but did not yield the desired product and is generally less convenient than the methods already described.

Sodium hydroxide and sodium perchlorate solutions were prepared as reported previously.[1] A standard lithium perchlorate solution (~2 M) was prepared by dissolving LiClO$_4$ (G. R. Smith Co.) in water and was standardized as described previously.[2] Perchloric acid solutions were prepared by dilution of 60% HClO$_4$ and normalized using standard techniques. All reagents were prepared in water redistilled from alkaline permanganate in an all-glass apparatus.

Kinetic Measurements.—Most kinetics were studied using what will be called the continuous method in which the absorbance change of a solution was followed at 265 nm on either a Bausch and Lomb 505 or Precision spectrometer. The temperature was controlled by a water-circulation system described elsewhere.[2] The reaction was initiated by adding the solid complex to an appropriate mixture of lithium perchlorate and perchloric acid in a 5-cm path length spectrophotometer cell at the required temperature. The studies at 40–60° were done using a similar method in a 1-cm cell. The latter could not be used at 25° because the complex was too slow to dissolve at the required concentration.

In a few runs the first reaction was followed by a quenching method. In this case the complex (~0.006 g) was dissolved in 1 ml of water and the solution was diluted to 10 ml with 1.0 M HClO$_4$. Aliquots (1 ml) of this solution were taken periodically and added to 1 ml of 1.0 M NaOH and this solution was diluted to 5.0 ml. The spectra of these alkaline samples were recorded at 296 nm, a peak in the spectrum of $(NH_3)_5CoNHSO_3^+$. At least eight samples were taken over a time period of 80 min with the reaction solution at room temperature (24–25°).

The stopped-flow kinetic studies were performed on an Aminco-Morrow system equipped with a deuterium lamp. A solution containing ~5 mg of sulfamato complex, 1 ml of 1 M perchloric acid, and an appropriate volume of 2 M sodium perchlorate was diluted to 25 ml and allowed to stand for 60–80 min. Then this solution was mixed with an equal amount of a sodium hydroxide-sodium perchlorate solution in the stopped-flow system and the absorbance change at 260 nm was recorded. All runs were done at 25.6° with the final ionic strength adjusted to 1.0 M with sodium perchlorate.

Reaction Product Analysis.—The sulfamate complex could hydrolyze with N–S bond breaking to give $Co(NH_3)_6^{3+}$ or by the Co–N bond breaking to give $Co(NH_3)_5OH_2^{3+}$. It was found that $(NH_3)_5CoOH_2^{3+}$ is completely decomposed to insoluble cobalt oxide in 1 hr at 50° in 0.1 M NaOH, while $Co(NH_3)_6^{3+}$ is unaffected by this treatment. Blank experiments were carried out on synthetic mixtures of 4×10^{-3} M $Co(NH_3)_6^{3+}$ and 6×10^{-3} M $(NH_3)_5CoOH_2^{3+}$ treated as described above. The cobalt oxide was removed by filtration on a Millipore filter and the visible spectrum of the filtrate was recorded. The results indicated a quantitative recovery of $Co(NH_3)_6^{3+}$ and that solutions initially containing 1×10^{-3} M $Co(NH_3)_6^{3+}$ would yield readily detectable amounts of $Co(NH_3)_6^{3+}$.

The product of the hydrolysis reaction was determined by allowing a 0.01 M solution of $(NH_3)_5CoNH_2SO_3^{2+}$ to react in 1.0 M

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

[2] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **93**, 625 (1971).

perchloric acid at 50° for about 10 hr. This solution was then treated with sodium hydroxide, filtered, and tested spectrophotometrically for $Co(NH_3)_6^{3+}$ as described in the preceding paragraph.

Results and Discussion

The hydrolysis of sulfamatopentaamminecobalt(III) in acid was studied initially in the temperature range 40–60°. The absorbance decreased at 265 nm as expected for the production of $(NH_3)_5CoOH_2^{3+}$. The product analysis indicated that the reaction proceeded at least 95% to form $(NH_3)_5CoOH_2^{3+}$, with no detectable amount of $Co(NH_3)_6^{3+}$ being formed. Therefore the reaction appeared to go *via* Co–N bond breaking.

Observation on First Reaction.—When the abovementioned study was extended to 25°, it was noticed that the absorbance at 265 nm underwent an initial small increase (~0.2 absorbance unit) before decreasing. A review of the data at 40–60° showed that the effect was present also but had been overlooked because it only caused the data at less than 5% reaction to deviate from the expected linearity of the semilogarithmic plot of absorbance change *vs.* time. A number of experiments and a kinetic study were then carried out in order to determine the nature of the first reaction causing the increase in absorbance.

Impurities in the system were first tested. The addition of sodium sulfamate or sulfamic acid had no effect on the initial reaction nor did the omission of lithium perchlorate from the reaction medium. If some $(NH_3)_5CoSO_4^+$ was present the absorbance should decrease, not increase, at 265 nm when the sulfato complex hydrolyzes. This was confirmed using an authentic sample of $(NH_3)_5CoSO_4(ClO_4)$.[1,3] Samples of the sulfamato complex prepared independently by each of the three authors, and of ages varying from 1 week to 6 years, all showed the same initial absorbance increase.

The possibility that a mixing or temperature effect might be causing the absorbance rise was checked by mixing a carefully equilibrated solution of the complex in lithium perchlorate and the perchloric acid solution. The same absorbance increase was observed. It was also found that mixing an initially alkaline (pH 8–9) solution of complex with excess perchloric acid also gave the absorbance increase.

An attempt was made to observe the first reaction using nmr. However, it was found that in dimethyl sulfoxide, the only solvent suitable for the nmr study, there was no change in the visible spectrum and of course no change was observed in the nmr spectrum.[4]

It was found that the cobalt(III) species, which was isolated essentially quantitatively by adding sodium perchlorate after 8–10 half-times of the first reaction, had the same nmr spectrum as the starting material. There was no indication of $(NH_3)_5CoOH_2^{3+}$ in this product, and when it was dissolved in aqueous acid, it again showed the initial rise in absorbance at 265 nm. It appears that the first reaction is reversed on precipitation or that the product is very soluble.

The results described thus far indicate that the initial absorbance increase at 265 nm is not due to a chemical impurity, or an experimental effect, and that sulfamate ion is not released. Before further experiments in this work are described, it will be useful to recall the results of the previous alkaline hydrolysis study. The latter results are summarized by the reactions

$$\begin{tikzcd}[column sep=large]
(NH_3)_5CoNH_2SO_3^{2+} + OH^- \arrow[r, "k = 100\ M^{-1}\ sec^{-1}"] \arrow[d, shift left, "pK_a = 5.7"] & {} \\
(NH_3)_5CoNHSO_3^{+} + OH^- \arrow[r, "k = 2.5 \times 10^{-7}\ M^{-1}\ sec^{-1}"] \arrow[u, shift left] & {} \\
(NH_3)_5CoOSO_3^{+} + OH^- \arrow[r, "k = 4.9 \times 10^{-2}\ M^{-1}\ sec^{-1}"] & {}
\end{tikzcd} \qquad (1)$$

All rate constants refer to the hydroxide ion catalyzed hydrolysis at 25° in 1 M $NaClO_4$. The sulfamate complex exists as the kinetically stable conjugate base $(NH_3)_5CoNHSO_3^+$ in alkaline solution. The latter hydrolyzes much more slowly than the sulfato complex in basic solution. It should also be noted that arguments advanced previously,[1] plus those of Armor and Taube[5] in connection with their preparation of $(NH_3)_5RuNH_2SO_3^{2+}$, all indicate that the starting material is in the N-bonded form.

The experiments described below were carried out to test the hypothesis that the initial absorbance rise in acidic solution is due to the production of the O-bonded sulfamato complex according to the equilibrium

$$(NH_3)_5CoNH_2SO_3^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NH_3)_5CoOSO_2NH_2^{2+} \qquad (2)$$

It was assumed that the O-bonded isomer would be kinetically similar to the sulfato complex. Thus, in alkaline solution the O isomer would hydrolyze readily while the N isomer would only convert to the stable conjugate base.

In the light of these suppositions, a solution of $(NH_3)_5CoNH_2SO_3^{2+}$ was allowed to react for 80 min in 0.1 M $HClO_4$ at 25°. The solution was then made 0.03 M in sodium hydroxide and allowed to stand for 40 min and then reacidified to 0.10 M in $HClO_4$. The absorbance of the reacidified solution was observed to increase at 265 nm with a half-time of ~10 min. This behavior is consistent with the proposal that the acidic solution after 80 min contained an equilibrium mixture of the O- and N-bonded isomers and that in 0.03 M NaOH the O-bonded form hydrolyzed to $(NH_3)_5CoOH^{2+}$. When the alkaline solution was reacidified, the $(NH_3)_5CoNH_2SO_3^{2+}$ again converted to the O-bonded isomer.

The series of experiments described above was repeated, except that the solution was made alkaline with Na_2CO_3 (pH ~9), and was then reacidified immediately. No increase in absorbance at 265 nm was observed in the reacidified solution. This result indicates that the O-bonded isomer did not hydrolyze in the brief period at pH 9 and that the reacidified solution contains the equilibrium mixture of N- and O-bonded isomers and therefore shows no absorbance increase.

These observations are consistent with the original hypothesis that the reaction described by eq 2 is causing the absorbance increase at 265 nm. Our explanation

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[3] The extinction coefficient of $(NH_3)_5CoSO_4(ClO_4)$ at 357 nm should be 54.8 M^{-1} cm^{-1}, not 34.8 M^{-1} cm^{-1} as given in ref 1.

[4] The nmr spectrum shows peaks for cis NH_3 (τ 6.47), trans NH_3 (τ 6.77), and sulfamate NH_2 (τ 3.46) relative to DMSO-d_6 at τ 7.48.

[5] J. N. Armor and H. Taube, *Inorg. Chem.*, **10**, 1571 (1971).

of the behavior of the O isomer in alkaline solution may be an oversimplification, however. There is also the possibility that the O isomer reconverts to the N-bonded conjugate base in strongly alkaline solution perhaps *via* the reaction sequence

$$\begin{array}{l}(NH_3)_5CoOSO_2NH_2^{2+} + OH^- \rightleftarrows \\ \qquad\qquad (NH_3)_5CoOSO_2NH^+ + H_2O \quad (3) \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad (NH_3)_5CoNHSO_3^+ \end{array}$$

especially since $(NH_3)_5CoNHSO_3^+$ is quite stable in alkaline solution. In order to check this possibility and to test further the proposed linkage isomerism, the kinetics of the first reaction were followed by the quench method described in the Experimental Section. In this method acidic samples are quenched by the addition of sodium hydroxide to make them basic. If the O isomer is destroyed by alkaline hydrolysis in the quenched kinetic samples, then the characteristic peak at 296 nm in the spectrum of $(NH_3)_5CoNHSO_3^+$ in the quenched solutions should decrease from sample to sample at the same rate as the initial rise in absorbance in the acidic medium. However, if the O-bonded isomer reconverts to the N-bonded isomer in sodium hydroxide, then no change in the 296-nm peak should be observed. The results of the quench method showed that the absorbance at 296 nm in the quenched solutions does decrease with a half-time of 10–15 min consistent with the kinetic results for the first reaction to be discussed subsequently. Unfortunately, because of sampling errors and the small absorbance change (~0.15 absorbance unit) the quench method did not yield very precise kinetic results but the observed change does occur over the expected time period and the absorbance levels off after 60–80 min as observed by the continuous method.

The final (after 80 min) and the initial absorbances in the quenched solutions can be used to calculate an equilibrium constant for eq 2 of ~0.3 at 24° in 0.90 *M* $HClO_4$. It must be allowed, however, that the quench method does not eliminate the possibility that some but not all of the O-bonded isomer may reisomerize in sodium hydroxide solution. Therefore the equilibrium constant is only a lower limit.

All of these results are consistent with the proposed linkage isomerism. It may also be noted that, if the analogy of the O-bonded sulfamato and sulfato complexes is extended to their ultraviolet spectrum, then the absorbance increase at 265 nm is consistent with formation of the O-bonded isomer; *i.e.*, the extinction coefficient of sulfato is greater than that of N-bonded sulfamato at 265 nm. However, it is admitted that the definitive proof of the O isomer would be its isolation as a solid product and in this all of our efforts have failed. Various starting materials and nonaqueous solvents all yielded the N-bonded sulfamato complex. It was also found that heating $((NH_3)_5CoOH_2)(NH_2SO_3)_3$ at 80° *in vacuo* yielded a salt of the sulfato complex. It is somewhat disheartening to note that the perchlorate salt precipitated from the equilibrium mixture proved to be the N-bonded isomer. This would indicate that a judicious choice of anion will be necessary in order to obtain the O-bonded isomer in the solid state.

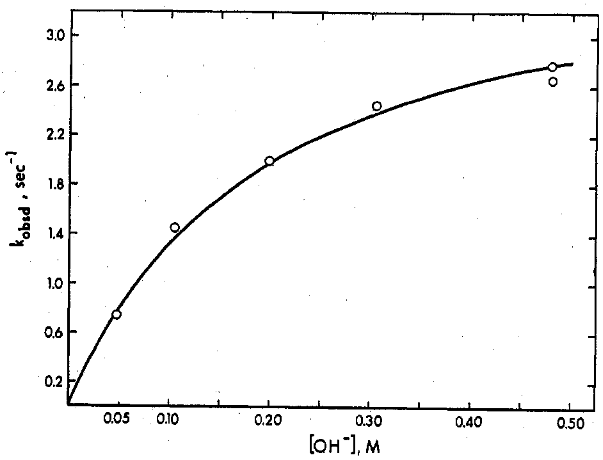


Figure 1.—Variation of k_{obsd} with hydroxide ion concentration for the alkaline hydrolysis of O-bonded sulfamatopentaamminecobalt(III), 25.6°, μ = 0.1 *M* $(NaClO)_4$. The smooth curve is calculated from eq 2 with $k' = 20\ M^{-1}\ sec^{-1}$ and $K_b = 5.1\ M^{-1}$.

Stopped-Flow Studies in Alkaline Solutions.—The proposal for the behavior of the sulfamato complex described above predicts that the O-bonded isomer will hydrolyze in moderately strong sodium hydroxide solution. In order to test this prediction the acidic equilibrium mixture was made alkaline with sodium hydroxide in a stopped-flow system. Based on the assumed similarity of the electronic spectra of the O-bonded sulfamato and sulfato complexes it was predicted that the hydrolysis of O-bonded sulfamato in alkaline solution would be observable at 260 nm. This wavelength is near the minimum after the peak at 296 nm in the spectrum of $(NH_3)_5CoNHSO_3^+$.

Preliminary observations confirmed that an absorbance decrease does occur on mixing an equilibrated acidic solution of the complex with excess sodium hydroxide with a half-time of several tenths of 1 sec. The rate was studied as a function of hydroxide ion concentration at 25.6° and 1.0 *M* ionic strength to give the results shown in Figure 1. These data are consistent with the rate law

$$-\frac{d\ \ln\ [complex]}{dt} = k_{obsd} = \frac{k'[OH^-]}{1 + K_b[OH^-]} \quad (4)$$

A plot of k_{obsd}^{-1} *vs.* $[OH^-]^{-1}$ is linear and yields values for k' and K_b of 20 M^{-1} sec^{-1} and 5.1 M^{-1}, respectively.

The qualitative observation of an absorbance decrease at 260 nm is consistent with the predicted behavior of the O-bonded sulfamato complex. The form of the rate law for the alkaline hydrolysis is consistent with the reaction scheme

$$\begin{array}{ccc} (NH_3)_5CoOSO_2NH_2^{2+} + OH^- & \overset{K_b}{\rightleftarrows} & (NH_3)_5CoOSO_2NH^+ + H_2O \\ k_1' \downarrow OH^- & & k_2 \downarrow \\ (NH_3)_5CoOH^{2+} + NH_2SO_3 & & (NH_3)_5CoNHSO_3^+ \end{array} \quad (5)$$

The observed rate law indicates that alkaline hydrolysis of $(NH_3)_5CoOSO_2NH^+$ is not observed. From eq 5, with the assumption that K_b is a rapid equilibrium it is easily shown that

$$k_{obsd} = \frac{(k_1' + k_2K_b)[OH^-]}{1 + K_b[OH^-]} \quad (6)$$

which is consistent with the observed rate law (eq 4).

The value of K_b (5.1 M^{-1}) may be converted to an acid dissociation constant (K_a) by multiplying by the self-ionization constant of water (1.7×10^{-14} M^2 in 1 M $NaClO_4$ at 25°[6]) to give $K_a = 8.5 \times 10^{-14}$ M or $pK_a = 13.1$. The O-bonded sulfamato complex is much less acidic than the N-bonded form (pK_a = 5.7[1]), as expected. Unfortunately, it is not possible to decide if the magnitude of the change in pK_a is reasonable since there are no comparable systems.

The relative contributions of k_1' and k_2K_b to k' are also difficult to assess. The rate constants for hydroxide ion catalyzed hydrolysis of N-bonded sulfamato ($(NH_3)_5CoNH_2SO_3^{2+}$) and the sulfato complex are ~100^7 and 0.049 M^{-1} sec^{-1}, respectively, at 25°. Therefore a value of 20 M^{-1} sec^{-1} for k_1' would not seem unreasonable. However, there is no way of estimating the magnitude of k_2 in eq 5. The failure to observe a term in the rate law due to hydrolysis of $(NH_3)_5OSO_2NH^+$ is reasonable if its hydrolysis rate is similar to that of the isoelectronic sulfato complex.

Kinetics of the First Reaction in Acidic Solution.—This reaction was followed by continuously monitoring the increase in absorbance at 265 nm in acidic solutions of $(NH_3)_5CoNH_2SO_3^{2+}$ until it had reached a constant value. The rate of the first reaction is about 20 times greater than the second (discussed below), in the 20–30° temperature range, so that the two processes can be treated independently.

Although the total absorbance change was rather small (~0.3 unit), linear kinetic plots for >80% reaction were obtained, and the results summarized in Table I show that the rate is independent of hydrogen ion concentration. If reaction 2 is the process being observed, then the observed rate constant is the sum of the forward and reverse constants.

TABLE I

KINETIC RESULTS FOR THE FIRST REACTION IN THE HYDROLYSIS OF $(NH_3)_5CoNH_2SO_3^{2+}$ (μ = 1.0 M, $LiClO_4$)

Temp, °C	[$HClO_4$], M	10^3k_{obsd}, sec^{-1}	Av 10^3k_{obsd}, sec^{-1} Obsd	Av 10^3k_{obsd}, sec^{-1} Calcd[a]
21.2	0.10	0.679	0.694	0.693
21.2	0.50	0.723		
21.2	1.00	0.679		
24.6	0.10	1.05	1.07	1.14
24.6	0.50	1.05		
24.6	1.00	1.10		
29.2	0.10	2.31	2.18	2.18
29.2	0.50	2.31		
29.2	1.00	1.92		

[a] Calculated from the transition-state theory equation with $\Delta H^{\ddagger}$ = 24.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 10.94 cal mol^{-1} deg^{-1}.

$$k_{obsd} = \frac{0.693}{\text{half-time}} = k_1 + k_{-1} \tag{7}$$

The apparent activation energy and entropy for k_{obsd} are 24.7 kcal mol^{-1} and 10.9 cal mol^{-1} deg^{-1}, respectively. In the absence of a reliable value for the equilibrium constant K_1 it is not possible to evaluate k_1 and k_{-1} separately nor to determine their activation parameters.

Kinetics of the Second Reaction in Acidic Solution.—The kinetic results for the absorbance decrease at 265 nm are summarized in Table II. The observed rate constant is given by

TABLE II

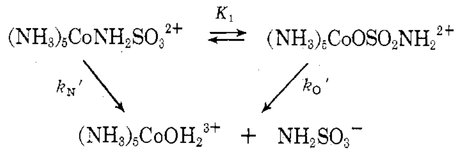
KINETIC RESULTS FOR THE SECOND REACTION IN THE HYDROLYSIS OF $(NH_3)_5CoNH_2SO_3^{2+}$ (μ = 1.0 M, $LiClO_4$)

Temp, °C	[H^+], M	10^4k_{obsd}, sec^{-1} Obsd	10^4k_{obsd}, sec^{-1} Calcd[a,b]	Temp, °C	[H^+], M	10^4k_{obsd}, sec^{-1} Obsd	10^4k_{obsd}, sec^{-1} Calcd[a,b]
27	0.10	0.398	0.385	49.6	0.40	7.96	8.13
27	0.70	0.641	0.611	49.6	0.50	8.42	8.57
39.4	0.10	2.06	1.95	49.6	0.60	8.88	9.03
39.4	0.30	2.35	2.26	49.6	0.70	9.09	9.48
39.4	0.40	2.50	2.41	49.6	0.80	9.53	9.93
39.4	0.50	2.64	2.56	49.6	0.90	9.61	10.4
40.0	0.05	1.85	2.02	49.6	1.00	10.5	10.8
40.0	0.05	2.05	2.02	59.3	0.05	20.0	20.1
40.0	0.05	1.94	2.02	59.3	0.10	20.3	20.7
40.0	0.10	2.03	2.10	59.3	0.20	22.0	21.9
40.0	0.10	2.13	2.10	59.3	0.30	23.1	23.1
40.0	0.70	2.93	3.09	59.3	0.40	24.6	24.2
49.6	0.05	6.63	6.56	59.3	0.60	26.9	26.6
49.6	0.10	7.13	6.78	59.3	0.70	28.2	27.8
49.6	0.20	7.21	7.23	59.3	0.80	29.6	28.9
49.6	0.30	7.69	7.68	59.3	0.90	36.0	30.1

[a] Calculated from a least-squares fit to eq 6 which gave $\Delta H^{\ddagger}$ = $24.1_2 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger}$ = $1.4_0 \pm 3$ cal mol^{-1} deg^{-1} for k_2'; and $\Delta H^{\ddagger}$ = $20.5_0 \pm 2.0$ kcal mol^{-1} and $\Delta S^{\ddagger}$ = -10.5 ± 7 cal mol^{-1} deg^{-1} for k_2''. [b] The parameters in footnote *a* predict values of 2.63×10^{-5} sec^{-1} and 2.97×10^{-5} M^{-1} sec^{-1} for k_2' and k_2'', respectively, at 25.0°.

$$k_{obsd} = k_2' + k_2''[H^+] \tag{8}$$

Plots of k_{obsd} *vs.* [H^+] are linear as required by eq 8. However, the apparent rate constants k_2' and k_2'' are actually composite values if the reaction scheme is



$$\begin{tikzcd}[column sep=small] (NH_3)_5CoNH_2SO_3^{2+} \arrow[rr, shift left, "K_1"] \arrow[dr, "k_N'"'] & & (NH_3)_5CoOSO_2NH_2^{2+} \arrow[ll, shift left] \arrow[dl, "k_O'"] \\ & (NH_3)_5CoOH_2^{3+} + NH_2SO_3^- & \end{tikzcd} \tag{9}$$

where k_N' and k_O' are the apparent rate constants for hydrolysis of the N- and O-bonded isomers and K_1 is taken to be a rapid equilibrium at least relative to k_N and k_O. The latter is consistent with the fact that the first reaction is ~20 times faster than the second. It can then be shown that

$$k_{obsd} = \frac{k_N' + k_O'K_1}{K_1 + 1} \tag{10}$$

It is further possible that k_N' and k_O' may have acid-independent and -dependent contributions so that

$$k_N' = k_{N1} + k_{N2}[H^+] \tag{11}$$

$$k_O' = k_{O1} + k_{O2}[H^+] \tag{12}$$

Substitution of (11) and (12) into (10) and comparing the results to (8) show that

$$k_2' = \frac{k_{N1} + K_1k_{O1}}{K_1 + 1} \tag{13}$$

and

$$k_2'' = \frac{k_{N2} + K_1k_{O2}}{K_1 + 1} \tag{14}$$

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(6) L. G. Sillén and A. E. Murtell, Ed., *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

(7) The $\Delta S^{\ddagger}$ given for the constant k' in ref 1 should be +0.32, not −3.5 cal mol^{-1} deg^{-1}, and the value for k'' should be 49.6, not 46 cal mol^{-1} deg^{-1}.

Clearly the contributions to k_2' and k_2'' cannot be separated from a study of the hydrolysis of the total sulfamato complex. It was hoped that studies over a wide temperature range might yield a nonlinear temperature dependence of k_2' and k_2'' as would occur if the activation energies for the individual terms were much different. However, a nonlinear least-squares fit[8] of all the data in Table II to eq 8 with normal transition-state theory expressions for k_2' and k_2'' did not indicate any significant nonlinearity in the temperature dependence as can be seen by comparison of the calculated and observed values in Table II. Either the various terms have similar activation enthalpies or one of them is dominant but it cannot be determined which one it might be.

In the previous study[1] of the hydrolysis of the sulfamato complex in basic solution, a term in the rate law independent of $[OH^-]$ was observed. This term could be assigned either to the reaction of $(NH_3)_5CoNHSO_3^+$ with water or to the reaction of $(NH_3)_5CoNH_2SO_3^{2+}$ with hydroxide ion. The latter path was favored in the earlier work because a comparison of the ratio of the rate constants for reaction with hydroxide ion and water (results given here) was normal, *i.e.*, in the range of 10^4–10^6 M^{-1}. The detailed results given here show that the reaction of $(NH_3)_5CoNH_2SO_3^{2+}$ in aqueous acid is more complicated than supposed before. However, the observed rate constant for hydrolysis in acidic solution gives an upper limit for the aquation rate constant of the N-bonded isomer, so that the ratio of alkaline hydrolysis to aquation rates is $\geq 100/(2.6 \times 10^{-5})$ or 3.8×10^6 M^{-1}. Since this is a much more normal ratio than the value of 0.35 obtained if the alternative reaction path is assumed, then the arguments in ref 1 are still valid, and the alkaline hydrolysis of $(NH_3)_5CoNH_2SO_3^{2+}$ was observed in the previous work.

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CONTRIBUTION FROM THE INLAND WATERS BRANCH, DEPARTMENT OF THE ENVIRONMENT,
OTTAWA, ONTARIO, CANADA

A Laser Raman Study of Aqueous Copper Nitrate Solutions

BY A. R. DAVIS* AND C. CHONG

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Raman spectra of aqueous copper nitrate solutions have been recorded using an argon ion laser. Absorption of Raman scattered light by the deeply colored copper solutions has necessitated corrections to measured Raman intensities. Corrected Raman intensities have been used to calculate concentration equilibrium constants of the species present in solution. Good agreement has been obtained between concentration quotients calculated from intensity variations of the 722- and 1052-cm^{-1} Raman bands, both originating from the solvated nitrate ion. The validity of the calculated concentration quotient for $CuNO_3^+$, $K_{assoc} = 0.07 \pm 0.02$ at 25°, is illustrated in the agreement between measured and calculated Raman intensities of copper nitrate solutions.

Introduction

The use of Raman spectroscopy to study interactions in metal nitrate systems is now well established.[1] The Raman spectrum of saturated aqueous copper nitrate has been reported and noted to be more complex than that of the alkali metal nitrates.[2] Mathieu and Lounsbury interpreted Raman spectral results by assuming that the saturated solution has a structure similar to that of the hydrated crystal.[3] Whereas, Hester and Plane interpreted their results in terms of complex ion formation,[2] an isopiestic study of aqueous copper nitrate solution led Robinson, *et al.*, to suggest that there is probably no appreciable complex formation in aqueous copper nitrate.[4]

A study of the system by Bjerrum has detected a very weak hydroxynitrato species $(Cu(OH)_{1.5}(NO_3)_{0.5})$.[5] Two authors have studied the uv and visible spectrum of copper(II) nitrate dissolved in an acetone–water mixture. Plane has suggested that there is evidence for ion pairing.[6] Gazo has developed a photometric method of determining trace amounts of nitrate in acetone based on the formation of a complex species among the copper(II) ion, nitrate ion, and acetone.[7] The species is considered to be polymeric with the nitrate group acting as a bridge. An esr study of copper(II) ions in solutions has shown that the line width of the broad band observed was both concentration and anion dependent, above approximately 0.1 M.[8] The reduction in half-width of the copper(II) resonance with concentration has been related to the equilibrium between the solvated copper(II) ions and an ion pair involving copper(II) and nitrate ions.

There has, in general, been reasonable agreement between equilibrium constants obtained from Raman spectroscopy and other physical measurements.[9] Although no formation constants have been measured for complex nitrate–copper species, it may be concluded from measurements made that if the species exist they will be weak.[4] An objective of this study is to extend the previous Raman measurements and measure the formation constants of complex nitrate–copper species.

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