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Kinetics and Mechanisms of the Formation, Substitution, and Aquation Reactions of Sulfur-Bonded (Sulfito)amminecobalt(III) Complexes in Aqueous Solution[1]

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The formation kinetics of $Co(NH_3)_5SO_3^+$ and *trans*-$Co(NH_3)_4(SO_3)_2^-$ was studied at pH >9 as a function of temperature, pressure, $[SO_3^{2-}]$, and pH in ammonia buffer solutions. The data can be summarized by $k_{obsd} = k'[H^+] + k''[SO_3^{2-}]$, and the rate and activation parameters for k' and k'' are as follows: $(15.5 \pm 0.7) \times 10^5$ and 0.20 ± 0.04 M^{-1} s^{-1} at 45 °C, 37 ± 5 and 21 ± 2 kcal mol^{-1}, 87 ± 16 and 5 ± 7 cal K^{-1} mol^{-1}, and 8.1 ± 1.5 and 18.6 ± 1.5 cm^3 mol^{-1} at 35 °C, respectively. The k' and k'' terms represent contributions from the rate-determining hydrolysis and formation reactions of $Co(NH_3)_5SO_3^+$, respectively, which occur via dissociative reaction modes. The $Co(NH_3)_5SO_3^+$ species undergoes subsequent rapid substitution to produce *trans*-$Co(NH_3)_4(SO_3)_2^-$ for which k_{obsd} is independent of $[SO_3^{2-}]$. The kinetic parameters are as follows: $k = (1.21 \pm 0.05) \times 10^{-2}$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 23.8 \pm 1.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = 12.6 \pm 3.3$ cal K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = 13.7 \pm 0.7$ cm^3 mol^{-1} at 25 °C. These data are considered as strong evidence for a D mechanism in which the five-coordinate $Co(NH_3)_4SO_3^+$ species is formed in the rate-determining step. $Co(NH_3)_5SO_3^+$ undergoes acid-catalyzed aquation to form *trans*-$Co(NH_3)_4(SO_3)OH_2^+$, for which $k_{obsd} = k'''[H^+]$, where $k''' = (5.2 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 21.9 \pm 1.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 10.3 \pm 3.5$ cal K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = 6.0 \pm 1.2$ cm^3 mol^{-1}. This reaction is suggested to proceed via a D or I_d mechanism.

Introduction

The formation reactions and reactivity properties of sulfur-bonded (sulfito)cobalt(III) complexes have been studied by various groups in recent years. These studies emphasized the extraordinarily strong trans-labilizing influence of the S-bonded sulfite ligand in complexes containing ammonia,[2-6] ethylenediamine,[7-11] cyanide,[12,13] and dimethylglyoximate[14-16] as N-bonded ligands. As a result the complex $Co(NH_3)_5SO_3^+$ can only be prepared and purified in solutions containing free ammonia,[17] due to the reaction

$$Co(NH_3)_5SO_3^+ + H_2O \rightleftharpoons trans\text{-}Co(NH_3)_4(OH_2)SO_3^+ + NH_3 \quad (1)$$

which led to impurities in earlier reported[18-20] preparations.

Table I. UV-Visible Absorption Spectra of Some Sulfito Complexes

complex species	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	ref
$Co(NH_3)_5OH_2^{3+}$	490, 345	48.5, 45.0	this work
	490, 343	49.0, 47.0	21
$Co(NH_3)_5OSO_2^+$	513, 328	95, 2320	this work
	518, 330	~88, ~2100	21
$Co(NH_3)_5SO_3^+$	456, 278	148, 19 500	this work
	457, 278	148, 17 800	17
	456, 278	150, 18 900	6
	456, 278	148, 19 500	4
	456	150	21
trans-$Co(NH_3)_4(OH_2)SO_3^+$	272	6500	this work
	473, 273	120, 6460	17
	472	159	3
	472	145	21
trans-$Co(NH_3)_4(SO_3)_2^-$	326	29 480	this work
	430 (sh), 327	490, 29 510	4
cis-$Co(NH_3)_4(SO_3)_2^-$	295, 264	20 950, 20 000	this work
	452, 295, 264	200, 20 890, 19 500	4

Recent reports[21,22] on the formation and decomposition reactions of oxygen-bonded (sulfito)ammine trivalent transition-metal complexes of the type $M(NH_3)_5OSO_2^+$ (M = Co(III), Rh(III), Cr(III)) have added a new dimension to the chemistry of sulfito complexes. Such species are produced rapidly via SO_2 uptake by the corresponding metal hydroxo complexes.[21-23] On acidification, O-S bond breakage occurs[23] and the $M(NH_3)_5OH_2^{3+}$ species is formed along with SO_2. Both reactions (uptake and loss of SO_2) are rapid and nonsubstitutionally controlled. Furthermore, the O-bonded Co(III) sulfito complex[21] undergoes an intramolecular redox reaction that is approximately 10^2 times faster than for the corresponding S-bonded species. The Rh(III) and Cr(III) complexes[22] exhibit subsequent isomerization and/or further

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(1) A preliminary report of this work was presented at the 8th AIRAPT/19th EHPRG Conference, Uppsala, Sweden, Aug 1981. See Abstract No. N. 1.6.
(2) Halpern, J.; Palmer, R. A.; Blakley, L. M. *J. Am. Chem. Soc.* **1966,** *88,* 2877.
(3) Thacker, M. A.; Scott, K. L.; Simpson, M. E.; Murray, R. S.; Higginson, C. E. *J. Chem. Soc., Dalton Trans.* **1974,** 647.
(4) Scott, K. L. *J. Chem. Soc., Dalton Trans.* **1974,** 1486.
(5) Richards, L.; Halpern, J. *Inorg. Chem.* **1976,** *15,* 2571.
(6) Elder, R. C.; Heeg, M. J.; Payne, M. D.; Trkula, M.; Deutsch, E. *Inorg. Chem.* **1978,** *17,* 431.
(7) Murray, R. S.; Stranks, D. R.; Yandell, J. K. *J. Chem. Soc. D* **1969,** 604.
(8) Stranks, D. R.; Yandell, J. K. *Inorg. Chem.* **1970,** *9,* 751.
(9) Yandell, J. K.; Tomlins, L. A. *Aust. J. Chem.* **1978,** *31,* 561.
(10) Raston, C. L.; White, A. H.; Yandell, J. K. *Aust. J. Chem.* **1978,** *31,* 993.
(11) Raston, C. L.; White, A. H.; Yandell, J. K. *Aust. J. Chem.* **1978,** *31,* 999.
(12) Chen, H. H.; Tsao, M. S.; Gaver, R. W.; Tewari, P. H.; Wilmarth, W. K. *Inorg. Chem.* **1966,** *5,* 1913.
(13) Tewari, P. H.; Gaver, R. W.; Wilcox, H. K.; Wilmarth, W. K. *Inorg. Chem.* **1967,** *6,* 611.
(14) Hague, D. N.; Halpern, J. *Inorg. Chem.* **1967,** *6,* 2059.
(15) Palmer, J. M.; Deutsch, E. *Inorg. Chem.* **1975,** *14,* 17.
(16) Seibles, L.; Deutsch, E. *Inorg. Chem.* **1977,** *16,* 2273.
(17) Siebert, H.; Wittke, G. *Z. Anorg. Allg. Chem.* **1973,** *399,* 43.
(18) Werner, A.; Grüger, H. *Z. Anorg. Chem.* **1898,** *16,* 398.
(19) Babaeva, A. V.; Baranovskii, I. B. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1962,** *7,* 404.
(20) Babaeva, A. V.; Kharitonov, Y. Y.; Baranovskii, I. B. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1962,** *7,* 643.
(21) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980,** *19,* 880.
(22) van Eldik, R. *Inorg. Chim. Acta* **1980,** *42,* 49.
(23) van Eldik, R.; von Jouanne, J.; Kelm, H. *Inorg. Chem.* **1982,** *21,* 2818.

substitution reactions, where the latter originates from the trans-labilization effect of the sulfite ligand.

During these studies on O-bonded sulfito complexes[21,22] it became clear that a number of aspects concerning the chemistry of S-bonded sulfito complexes (of Co(III) in particular) should be further investigated, since some of the earlier reported data are rather preliminary and qualitative in nature. Although the strong trans-labilizing effect generally observed in such species gives preference to a dissociatively activated reaction mode,[2,5,7-11] arguments in favor of an interchange type mechanism have recently been emphasized.[9] The determination of volumes of activation and reaction volumes from the pressure dependence of rate and equilibrium constants, respectively, has contributed to the elucidation of such mechanisms.[24-26] This encouraged us to study the mechanisms of some reactions of S-bonded Co(III) sulfito complexes, namely, the photolysis of $Co(NH_3)_5SO_3^+$, the formation of $Co(NH_3)_5SO_3^+$ and *trans*-$Co(NH_3)_4(SO_3)_2^-$, the formation of *trans*-$Co(NH_3)_4(SO_3)_2^-$ from $Co(NH_3)_5SO_3^+$, and the acid-catalyzed aquation of $Co(NH_3)_5SO_3^+$, at normal and elevated pressures.

Experimental Section

Materials. The following complexes were prepared as described in the literature: $[Co(NH_3)_5OH_2](ClO_4)_3$;[21,27] $Co(NH_3)_5OSO_2^+$;[21] $[Co(NH_3)_5SO_3]ClO_4$;[17] *trans*-$[Co(NH_3)_4(OH_2)SO_3]Cl$;[17] *trans*-$Na[Co(NH_3)_4(SO_3)_2]$;[4] *cis*-$Na[Co(NH_3)_4(SO_3)_2]$.[4,28] Chemical analyses[29] were in good agreement with the theoretical values.[30] UV–visible absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer under conditions where the complex ions are stable (see Results and Discussion) and correlate well with those reported elsewhere (see Table I). All chemicals used were of analytical reagent grade, and doubly distilled water was used throughout the investigation.

Rate Measurements. All rate measurements were made at a constant ionic strength, controlled by the addition of $NaClO_4$. Various NH_3–NH_4^+ buffer solutions (0.05–2.0 M) were employed to stabilize the pH of test solutions. pH measurements were made with a Radiometer PHM 64 meter.

The studied reactions were followed spectrophotometrically with different instrumental setups depending on the nature of the reaction under investigation. An instrument developed for the measurement of photochemical quantum yield[31] was employed to study the photolysis of $Co(NH_3)_5SO_3^+$. Kinetic runs at normal pressure were recorded on a Perkin-Elmer 555 spectrophotometer equipped with a thermostated (±0.1 °C) cell compartment. Kinetic runs under pressure were performed in a thermostated (±0.1 °C) high-pressure cell[32] coupled to a Zeiss PMQ II spectrophotometer. For the study of faster reactions, an Aminco and a recently constructed[33] high-pressure stopped-flow system were employed. The observed first-order rate constants, k_{obsd}, were calculated from plots of ln $(A_t - A_\infty)$ vs. t, where A_t and A_∞ are the absorbances at time t and infinity, respectively.

Results and Discussion

Photolysis of $Co(NH_3)_5SO_3^+$. Transition-metal complexes can in general undergo three types of photochemical reactions,[34,35] viz., oxidation–reduction, substitution, and isomerization. Most Co(III) complexes undergo photoredox reactions, during which an electron is transferred from a ligand to the central metal atom, followed by the decomposition of the unstable Co(II) species.[36] In addition to this process, Balzani and co-workers[37] reported the occurrence of a simultaneous linkage-isomerization reaction during the photolysis of $Co(NH_3)_5NO_2^{2+}$ to produce $Co(NH_3)_5ONO^{2+}$. This isomerization reaction[37,38] is the reverse of that found thermally, viz., isomerization from $Co(NH_3)_5ONO^{2+}$ to $Co(NH_3)_5NO_2^{2+}$.[39] In a recent study, Adamson and co-workers[40] reported a similar photo-linkage-isomerization process for $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$, during which the O-bonded sulfinato complex is formed. These studies suggest the possibility that $Co(NH_3)_5SO_3^+$ of isomerize photochemically to produce the O-bonded $Co(NH_3)_5OSO_2^+$ species, the existence of which has been illustrated recently.[21,23]

Aqueous solutions of $Co(NH_3)_5SO_3^+$ were irradiated under various experimental conditions. In the presence of 2×10^{-3} M ammonia buffer at pH 9.1, irradiation at 302.2 nm results in strong absorbance decreases at 278 and 456 nm and the formation of isosbestic points at 252 and 316 nm. No significant thermal decomposition occurs under these conditions. Spectral analyses at 330 nm revealed no evidence for the formation of $Co(NH_3)_5OSO_2^+$, and the formation of Co(II) could be proved quantitatively.[41]

The photolysis of $Co(NH_3)_5OSO_2^+$ was investigated in some further experiments. This species was prepared in citric acid–phosphate buffer solutions (pH ~6) by reacting $Co(NH_3)_5OH_2^{3+}$ with $S_2O_5^{2-}$.[21] Irradiation at 302.2 nm results in a decrease in absorbance at 330 nm, for which the observed "rate constant" coincides exactly with that measured for the thermal redox reaction under these conditions.[21] It follows that the O-bonded sulfito complex does not undergo a photoredox reaction, in contrast to that found for the S-bonded species. The possibility, therefore, does exist that the $Co(NH_3)_5SO_3^+$ complex undergoes photoisomerization to produce $Co(NH_3)_5OSO_2^+$, which decomposes rapidly to Co(II) and SO_4^{2-} according to the thermal reaction path.

Finally, solutions of $Co(NH_3)_5SO_3^+$ in citric acid–phosphate buffers at pH ~6 were irradiated at various wavelengths. The observed first-order "rate constants" have an average value of $(1.00 \pm 0.17) \times 10^{-3}$ s^{-1} at 9 °C and seem to be independent of the pH[42] and irradiation wavelength, i.e., light intensity. Furthermore, this value is in good agreement with an extrapolated value of 0.93×10^{-3} s^{-1} at 9 °C for the thermal redox reaction of $Co(NH_3)_5OSO_2^+$[21] and may suggest a common rate-determining step under these conditions.

Formation of $Co(NH_3)_5SO_3^+$ and *trans*-$Co(NH_3)_4(SO_3)_2^-$. The $[Co(NH_3)_5SO_3]ClO_4$ complex can only be synthesized[17] under well-controlled conditions, i.e., by reacting $Co(NH_3)_5OH^{2+}$ with SO_3^{2-} in the ratio 1:1 in the presence of a large excess of NH_3, due to the interference of reaction 1. At higher sulfite concentration ratios the $Co(NH_3)_5SO_3^+$ species undergoes rapid substitution to form a bis(sulfito) complex according to

$$Co(NH_3)_5SO_3^+ + SO_3^{2-} \overset{K_2}{\rightleftharpoons} trans\text{-}Co(NH_3)_4(SO_3)_2^- + NH_3 \quad (2)$$

for which $K_2 = 125$ at 25 °C.[43] This equilibrium is shifted in the direction of the mono(sulfito) species in the absence of an excess of SO_3^{2-} such that solvent composition has a marked

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(24) Palmer, D. A.; Kelm, H. *Z. Anorg. Allg. Chem.* **1979**, *450*, 50.
(25) Hyde, K. E.; Kelm, H.; Palmer, D. A. *Inorg. Chem.* **1978**, *17*, 1647.
(26) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 1520.
(27) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 172.
(28) Bailar, J. C., Jr.; Peppard, D. F. *J. Am. Chem. Soc.* **1940**, *62*, 105.
(29) Hoechst AG; Analytical Laboratory, Frankfurt/Main, FRG.
(30) Spitzer, U. Diplomarbeit, University of Frankfurt, 1980, p 14.
(31) Drews, W.; Schmidt, R.; Brauer, H.-D. *J. Photochem.* **1977**, *6*, 391.
(32) Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
(33) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131.
(34) Balzani, V.; Moggi, L.; Scandola, F.; Carassiti, V. *Inorg. Chim. Acta, Rev.* **1967**, *1*, 7.
(35) Endicott, J. F. *Isr. J. Chem.* **1970**, *8*, 209.
(36) Haim, A.; Taube, H. *Inorg. Chem.* **1963**, *2*, 1199.
(37) Balzani, V.; Ballardini, R.; Sabbatini, N.; Moggi, L. *Inorg. Chem.* **1968**, *7*, 1398.
(38) Scandola, F.; Bartocci, C.; Scandola, M. A. *J. Phys. Chem.* **1974**, *78*, 572.
(39) Murmann, R. K.; Taube, H. *J. Am. Chem. Soc.* **1956**, *78*, 4886.
(40) Mäcke, H.; Houlding, V.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6888.
(41) Newton, A. M.; Swaddle, T. W. *Can. J. Chem.* **1974**, *52*, 2751.
(42) Adamson, A. W. *Discuss. Faraday Soc.* **1960**, *29*, 163.
(43) Byrd, J. E.; Wilmarth, W. K. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 7.

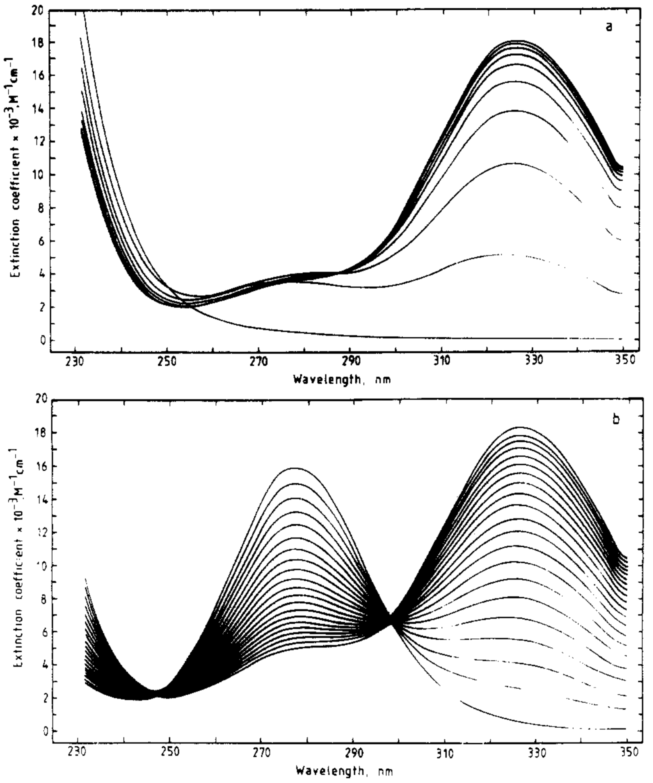

Figure 1. Repetitive-scan spectra illustrating the formation and decomposition of Co(III) sulfito complexes: (a) $Co(NH_3)_5OH^{2+}$ + SO_3^{2-} → $Co(NH_3)_5SO_3^+$/*trans*-$Co(NH_3)_4(SO_3)_2^-$, Δt = 10 min; (b) *trans*-$Co(NH_3)_4(SO_3)_2^-$ + NH_3 → $Co(NH_3)_5SO_3^+$ + SO_3^{2-}, Δt = 30 min. The conditions were as follows: [Co(III)] = 6.8 × 10^{-5} M; [Na_2SO_3] = 2.2 × 10^{-3} M; [buffer] = 0.1 M; ionic strength 0.5 M; temperature 316.2 K; pH 9.4.

influence on the absorption spectrum and stability of the *trans*-bis(sulfito) species.[4]

Some preliminary measurements[30] indicated that NH_3–NH_4^+ buffer solutions are capable of stabilizing the pH of solution containing cobalt sulfito complexes and sulfite ions over periods long enough to enable accurate kinetic measurements. The buffer concentration was varied depending on the pH and [SO_3^{2-}] of the test solutions. Under the usual pseudo-first-order reaction conditions, i.e., at least a 10-fold excess of sulfite ion, the formation of $Co(NH_3)_5SO_3^+$ from the reaction of $Co(NH_3)_5OH^{2+}$ with SO_3^{2-} will be immediately followed by the formation of *trans*-$Co(NH_3)_4(SO_3)_2^-$. This is clearly illustrated by the repetitive-scan spectra recorded in Figure 1. When [$Co(NH_3)_5OH_2$]$(ClO_4)_3$ and Na_2SO_3 are mixed in an ammonia buffer solution at pH ~9.4, the reactive species in solution are $Co(NH_3)_5OH^{2+}$[44] and SO_3^{2-}. The initial spectra (Figure 1a) show the formation of mainly *trans*-$Co(NH_3)_4(SO_3)_2^-$ (λ_{max} = 326 nm) and little $Co(NH_3)_5SO_3^+$ (λ_{max} = 278 nm). At longer reaction times (Figure 1b) the absorbance maximum at 326 nm slowly decreases and is accompanied by an absorbance increase at 278 nm. This occurs until the absorption at 326 nm has almost disappeared completely and a new maximum at 278 nm (i.e., for $Co(NH_3)_5SO_3^+$) is produced. This stage is ascribed to the oxidation of free sulfite ion under these conditions[45] and results in shifting equilibrium 2 to the left. If Na_2SO_3 is added to the reaction mixture at the point where a maximum buildup of $Co(NH_3)_5SO_3^+$ is observed, an instantaneous change in spectrum occurs and the original spectrum, corresponding to that of *trans*-$Co(NH_3)_4(SO_3)_2^-$, is obtained. The oxidation of sulfite can almost be prevented by working in an inert atmosphere (N_2 or Ar), and the second stage ascribed above is not seen under such conditions for reaction times of up to 14 h. However, passing oxygen through such inert solutions causes an almost instantaneous change in spectrum and the same spectral pattern as in the second stage (Figure 1b) is observed. During the final stage (not shown) the absorbance at 278 nm slowly decreases and an isosbestic point occurs at 254 nm. This process is ascribed to the redox reaction[3] of $Co(NH_3)_5SO_3^+$, during which Co^{2+} is produced.

Kinetic measurements on the formation of $Co(NH_3)_5SO_3^+$/*trans*-$Co(NH_3)_4(SO_3)_2^-$ were performed under inert atmosphere. The infinity spectrum of such reactions, i.e., at the end of the first stage in Figure 1, strongly depends on the [SO_3^{2-}] and pH, which controls the [NH_3] of the solutions. This illustrates the important role played by reaction 2 in the formation process. First-order plots were linear for at least 2–3 half-lives, and the values of k_{obsd} are summarized in Table II as a function of a number of variables. The data illustrate that k_{obsd} increases with increasing [SO_3^{2-}] according to the equation

$$k_{obsd} = k_A + k_B[SO_3^{2-}] \qquad (3)$$

The values of k_A and k_B were calculated according to a linear least-squares analysis and are included in the table. Kinetic measurements at lower [SO_3^{2-}] confirmed the validity of eq 3 down to [SO_3^{2-}] ≥ 5 × 10^{-4} M. However, below this concentration level deviations occur due to the movement away from the pseudo-first-order conditions. The determination of k_A is subjected to considerable error especially at low temperatures and higher pH. Nevertheless, the k_A data exhibit a meaningful pH dependence, which can according to the data in Table III be reasonably described by $k_A = k_A'[H^+]$, such that

$$k_{obsd} = k_A'[H^+] + k_B[SO_3^{2-}] \qquad (4)$$

The temperature dependence of k_A', i.e., $k_A/[H^+]$ in Table III, suggests that k_A' may be a composite quantity since the Arrhenius plot is strongly curved. On the other hand, k_B seems to be fairly pH independent and its mean values (Table III) were used to calculate ΔH^* and ΔS^* in the usual way. Omission of the low-temperature data points significantly increases the accuracy of the activation parameters for both k_A' and k_B.

The pressure dependence of k_{obsd} (Table IV) enables the calculation of volumes of activation, ΔV^*_{exptl}, for the k_A and k_B paths. An improved fit of the data can be obtained[46] by calculating the best fit for ln k_{obsd} vs. p at every [SO_3^{2-}] and using the so-corrected values of k_{obsd}, calculated at every pressure, in the estimation of k_A and k_B. Volumes of activation turn out to be 7.8 ± 0.1 and 18.9 ± 0.4 cm^3 mol^{-1} for k_A and k_B, respectively, indicating that the corresponding values in Table IV are reliable.

In general, an equation of the form of (3) or (4) can be interpreted as evidence for either two parallel processes or a forward and reverse step combination. The k_B path is independent of pH, depends linearly on the [SO_3^{2-}], and can only be associated with the formation of $Co(NH_3)_5SO_3^+$. This reaction is then followed by a non-rate-determining substitution to produce *trans*-$Co(NH_3)_4(SO_3)_2^-$ (see further discussion). The formation of $Co(NH_3)_5SO_3^+$ may occur via a D or an I_d mechanism (eq 5–8). The experimental data were measured

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(44) The pK_a of $Co(NH_3)_5OH_2^{3+}$ is 6.3 at 25 °C and 1.0 M ionic strength,[21] such that complete deprotonation occurs under these conditions.

(45) Halpern, J.; Taube, H. *J. Am. Chem. Soc.* **1950**, *72*, 3319.

(46) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.

$$\text{“D”:}\ \mathrm{Co(NH_3)_5OH^{2+}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Co(NH_3)_5{}^{3+} + OH^-}$$

$$\mathrm{Co(NH_3)_5{}^{3+} + SO_3{}^{2-}} \xrightarrow{k_4} \mathrm{Co(NH_3)_5SO_3{}^+} \tag{5}$$

$$\begin{aligned} k_{\mathrm{obsd}} &= k_4k_3[\mathrm{SO_3{}^{2-}}]/(k_{-3}[\mathrm{OH^-}] + k_4[\mathrm{SO_3{}^{2-}}]) \\ &= k_4k_3[\mathrm{SO_3{}^{2-}}]/k_{-3}[\mathrm{OH^-}] \text{ when } k_4[\mathrm{SO_3{}^{2-}}] << k_{-3}[\mathrm{OH^-}] \end{aligned} \tag{6}$$

$$\text{“I}_\mathrm{d}\text{”:}\ \mathrm{Co(NH_3)_5OH^{2+} + SO_3{}^{2-}} \overset{K_5}{\rightleftharpoons} (\mathrm{Co(NH_3)_5OH^{2+},SO_3{}^{2-}}) \xrightarrow{k_6} \mathrm{Co(NH_3)_5SO_3{}^+ + OH^-} \tag{7}$$

$$\begin{aligned} k_{\mathrm{obsd}} &= k_6K_5[\mathrm{SO_3{}^{2-}}]/(1 + K_5[\mathrm{SO_3{}^{2-}}]) \\ &= k_6K_5[\mathrm{SO_3{}^{2-}}] \text{ when } K_5[\mathrm{SO_3{}^{2-}}] << 1 \end{aligned} \tag{8}$$

at relatively low $[\mathrm{SO_3{}^{2-}}]$ (see Tables II and IV) and allow for the simplifications in eq 6 and 8. Furthermore, plots of k_{obsd} vs. $[\mathrm{SO_3{}^{2-}}]$ are linear under all conditions, indicating that these simplifications are justified. According to eq 6, k_B should depend inversely on $[\mathrm{OH^-}]$ for a D mechanism, which is not in line with the experimental data. Alternatively, since $\mathrm{OH^-}$ and $\mathrm{NH_3}$ exhibit very similar trans effects,[47] $\mathrm{Co(NH_3)_4OH^{2+}}$ could be the five-coordinate intermediate in reactions 5. This, however, would require k_B to depend inversely on $[\mathrm{NH_3}]$, i.e., $[\mathrm{OH^-}]$, which is once again in disagreement with the experimental data. We must, therefore, conclude that the direct reaction of sulfite ion with $\mathrm{Co(NH_3)_5OH^{2+}}$ proceeds via an $\mathrm{I_d}$ mechanism, for which $k_\mathrm{B} = k_6K_5$.

The magnitude of k_B (Table III) is considerably larger than reported for the interchange reactions of the $\mathrm{Co(NH_3)_5OH_2{}^{3+}}$ species in general.[26] In addition, k_B is of the same order as the rate constant for $\mathrm{SO_2}$ uptake when extrapolated to the present experimental conditions,[21] which may suggest a similarity in mechanism. It has been shown[23] that $\mathrm{SO_2}$ uptake by $\mathrm{Co(NH_3)_5OH^{2+}}$ to produce $\mathrm{Co(NH_3)_5OSO_2{}^+}$ proceeds without metal–oxygen bond breakage. This means that the interchange step (7) may involve such an interaction between the hydroxy and sulfite ions, followed by a rapid linkage-isomerization (O- to S-bonded) step. It is obvious that the experimental data cannot be interpreted along the basis of a simple $\mathrm{SO_2}$-uptake process, since that would require a completely different pH dependence of k_B.

The somewhat surprisingly high value of $\Delta\bar{V}^{*}_{\mathrm{exptl}}$ for k_B would rather favor a D instead of an $\mathrm{I_d}$ mechanism.[24-26] It must, however, be kept in mind that for the latter case[26]

$$\Delta\bar{V}^{*}_{\mathrm{exptl}} = \Delta\bar{V}(K_5) + \Delta\bar{V}^{*}(k_6)$$

and $\Delta\bar{V}$ for the formation of a 2+/2− ion pair may well be in the order of 10–12 $\mathrm{cm^3\ mol^{-1}}$.[48] This means that $\Delta\bar{V}^{*}(k_6)$ turns out to be 6–8 $\mathrm{cm^3\ mol^{-1}}$, which is indeed very reasonable for a dissociatively activated interchange mechanism.[26,49] The magnitude of ΔH^{*} and especially ΔS^{*} for k_B in Table III supports these conclusions.

We now turn to a discussion of the data for the k_A path. A first possibility is that k_A presents a parallel reaction path independent of $[\mathrm{SO_3{}^{2-}}]$. This means that $\mathrm{Co(NH_3)_5OH^{2+}}$ must undergo a rate-determining loss of $\mathrm{NH_3}$ or $\mathrm{OH^-}$ to produce a five-coordinate intermediate capable of reacting with $\mathrm{SO_3{}^{2-}}$ in a non-rate-determining step. Although such a reaction path is not unlikely, it is difficult to visualize such a process which would also be in line with the $[\mathrm{H^+}]$ or $[\mathrm{OH^-}]$ dependence of k_A. Alternatively, k_A can be ascribed to the contribution of a reverse reaction step. This was confirmed by a detailed study of the infinity spectra obtained during the corresponding kinetic measurements. These strongly depend on temperature, $[\mathrm{SO_3{}^{2-}}]$, pH, and $[\mathrm{NH_3}]$ and partly illustrate the influence of equilibrium 2. More significant, however, is that the sum of the concentrations of $\mathrm{Co(NH_3)_5SO_3{}^+}$ and *trans*-$\mathrm{Co(NH_3)_4(SO_3)_2{}^-}$, determined from the absorbances at

Table II. k_{obsd} for the Formation of $\mathrm{Co(NH_3)_5SO_3{}^+}$/*trans*-$\mathrm{Co(NH_3)_4(SO_3)_2{}^-}$ as a Function of Temperature, pH, and $[\mathrm{SO_3{}^{2-}}]$[a]

pH	temp, K	$10^3[\mathrm{SO_3{}^{2-}}]$, M	10^4k_{obsd},[b] $\mathrm{s^{-1}}$	10^4k_A,[c] $\mathrm{s^{-1}}$	$10k_\mathrm{B}$,[c] $\mathrm{M^{-1}\ s^{-1}}$
9.24	312.9	1.10	3.41	2.5 ± 0.3	0.9 ± 0.2
		1.38	4.05		
		1.84	4.09		
		2.13	4.37		
		2.54	4.99		
	317.9	1.10	11.8	9.2 ± 0.3	2.5 ± 0.2
		1.38	12.8		
		1.84	14.1		
		2.13	14.6		
		2.54	15.5		
	322.9	1.10	23.0	19.6 ± 0.6	3.3 ± 0.3
		1.38	24.5		
		1.84	26.1		
		2.13	26.4		
		2.54	28.1		
	327.4	1.10	37.5	32.8 ± 1.0	4.5 ± 0.5
		1.38	39.8		
		1.84	40.9		
		2.13	42.0		
		2.54	44.7		
9.39	314.3	1.25	2.14	0.3 ± 0.4	1.5 ± 0.2
		1.42	2.59		
		1.81	2.68		
		2.09	3.51		
		2.51	4.05		
	317.9	1.25	8.52	6.1 ± 0.3	2.0 ± 0.1
		1.42	9.08		
		1.81	9.92		
		2.09	10.2		
		2.51	11.2		
	322.6	1.25	20.3	16.0 ± 0.4	3.6 ± 0.2
		1.42	21.3		
		1.81	22.3		
		2.09	23.3		
		2.51	25.0		
	327.2	1.25	28.0	21.8 ± 0.8	5.2 ± 0.4
		1.42	29.6		
		1.81	31.4		
		2.09	32.2		
		2.51	35.0		
9.54	312.9	1.11	0.43	−0.2 ± 0.2[d]	0.68 ± 0.08[d]
		1.49	0.63		
		1.75	0.89		
		2.35	1.42		
		2.90	1.97		
	318.0	1.11	2.25	0.5 ± 0.3	1.6 ± 0.1
		1.49	2.98		
		1.75	3.62		
		2.35	4.20		
		2.90	5.31		
	323.2	1.11	13.7	10.6 ± 0.7	2.6 ± 0.3
		1.49	14.3		
		1.75	15.1		
		2.35	16.0		
		2.90	18.5		
	327.3	1.11	23.6	18.6 ± 0.4	4.2 ± 0.2
		1.49	24.8		
		1.75	25.6		
		2.35	28.6		
		2.90	31.0		

[a] Conditions: $[\mathrm{Co(NH_3)_5OH^{2+}}] = 4 \times 10^{-5}$ M; ionic strength 0.5 M; [buffer] = 0.1 M; wavelength 325 nm. [b] Mean value of at least three kinetic runs. [c] $k_{\mathrm{obsd}} = k_\mathrm{A} + k_\mathrm{B}[\mathrm{SO_3{}^{2-}}]$; see eq 3. [d] Calculated for the inclusion of one zero point.

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(47) Tobe, M. L. "Inorganic Reaction Mechanisms"; Nelson: London, 1972; p 55.

(48) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 471.

(49) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.

Table III. Rate Parameters for the Formation of $Co(NH_3)_5SO_3^+$/*trans*-$Co(NH_3)_4(SO_3)_2^-$

temp,[a] K	pH	$10^{-5}k_A/[H^+]$,[b] M^{-1} s^{-1}		$10k_B$, M^{-1} s^{-1}	
313.4	9.24	4.3 ± 0.5	4.3 ± 0.5	0.9 ± 0.2	1.0 ± 0.4
	9.39	*c*		1.5 ± 0.2	
	9.54	*c*		0.7 ± 0.1	
317.9	9.24	16.0 ± 0.5	15.5 ± 0.7	2.5 ± 0.2	2.0 ± 0.4
	9.39	15.0 ± 0.7		2.0 ± 0.1	
	9.54	*c*		1.6 ± 0.1	
322.9	9.24	34.1 ± 1.0	37 ± 3	3.3 ± 0.3	3.2 ± 0.5
	9.39	39.3 ± 1.0		3.6 ± 0.2	
	9.54	36.8 ± 2.4		2.6 ± 0.3	
327.3	9.24	57.0 ± 1.7	58 ± 6	4.5 ± 0.5	4.6 ± 0.5
	9.39	53.6 ± 2.0		5.2 ± 0.4	
	9.54	64.6 ± 1.4		4.2 ± 0.2	
$\Delta H^\ddagger$, kcal mol^{-1}		37 ± 5 (29 ± 4)[d]		21 ± 2 (17.7 ± 0.5)[d]	
$\Delta S^\ddagger$, cal K^{-1} mol^{-1}		87 ± 16 (60 ± 12)[d]		5 ± 7 (−6.2 ± 1.6)[d]	

[a] Mean value of temperatures in Table II. [b] $k_A' = k_A/[H^+]$ since $k_A = k_A'[H^+]$; see Results and Discussion. [c] Omitted; see Results and Discussion. [d] Data point at 313.4 K not included in calculation; see Results and Discussion.

Table IV. k_{obsd} for the Formation of $Co(NH_3)_5SO_3^+$/*trans*-$Co(NH_3)_4(SO_3)_2^-$ as a Function of Pressure[a]

pressure, bar	$[SO_3^{2-}]$, M	10^4k_{obsd},[b] s^{-1}	10^5k_A, s^{-1}	10^2k_B, M^{-1} s^{-1}
10	1.63	1.82	9.5 ± 0.7	5.2 ± 0.3
	1.80	1.87		
	2.15	2.09		
	2.43	2.18		
	2.82	2.44		
250	1.63	1.58	9.3 ± 0.9	4.1 ± 0.4
	1.80	1.71		
	2.15	1.79		
	2.43	1.97		
	2.82	2.08		
500	1.63	1.39	7.5 ± 0.9	4.0 ± 0.4
	1.80	1.46		
	2.15	1.65		
	2.43	1.67		
	2.82	1.88		
750	1.63	1.29	7.7 ± 0.8	3.0 ± 0.4
	1.80	1.28		
	2.15	1.42		
	2.43	1.46		
	2.82	1.64		
1000	1.63	1.13	7.4 ± 0.6	2.4 ± 0.3
	1.80	1.19		
	2.15	1.25		
	2.43	1.29		
	2.82	1.44		
1250	1.63	0.97	6.2 ± 0.6	2.1 ± 0.3
	1.80	1.03		
	2.15	1.05		
	2.43	1.13		
	2.82	1.24		
$\Delta \bar{V}^\ddagger_{exptl}$, cm^3 mol^{-1}			8.1 ± 1.5	18.6 ± 1.5

[a] Conditions: $[Co(NH_3)_5OH^{2+}] = 4 \times 10^{-5}$ M; ionic strength 0.5 M; [buffer] = 0.1 M; wavelength 325 nm; temperature 307.7 K; pH 9.39. [b] Mean value of at least three kinetic runs.

278 and 326 nm (Table I), respectively, decreases significantly with decreasing $[SO_3^{2-}]$. This means that more $Co(NH_3)_5OH^{2+}$ is present in the solutions at lower $[SO_3^{2-}]$ and points toward a reverse process during which the reactants are produced. The mentioned spectra enabled the estimation of a constant for the $Co(NH_3)_5OH^{2+}$–$Co(NH_3)_5SO_3^+$ "equilibrium", viz., 350 ± 100 M^{-1} at pH 9.39 and 316 K. This is in good agreement with the value 328 ± 32 M^{-1} calculated for k_B/k_A from the data in Table II at these conditions. Since the exact nature of the reverse process (k_A path) is unknown, various possible reaction routes are to be considered.

The $Co(NH_3)_5SO_3^+$ species can undergo the series of reactions shown by eq 9–11. Reactions 9 and 10 constitute the

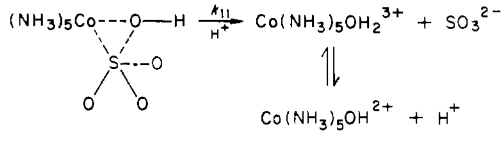
$$Co(NH_3)_5SO_3^+ \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Co(NH_3)_4SO_3^+ + NH_3 \qquad (9)$$

$$Co(NH_3)_4SO_3^+ + SO_3^{2-} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} trans\text{-}Co(NH_3)_4(SO_3)_2^- \qquad (10)$$

$$Co(NH_3)_4SO_3^+ + H_2O \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} trans\text{-}Co(NH_3)_4(SO_3)OH_2^+ \overset{K_{10}}{\rightleftharpoons} trans\text{-}Co(NH_3)_4(SO_3)OH + H^+ \qquad (11)$$

overall equilibrium (2). The strong trans-labilizing effect of the sulfite ligand introduces the dissociative reaction mode, in line with the exchange experiments performed by Richards and Halpern.[5] The five-coordinate $Co(NH_3)_4SO_3^+$ species reacts with H_2O or OH^- to produce *trans*-$Co(NH_3)_4(SO_3)OH_2^+$, for which pK_{10} was measured as 9.53 ± 0.02 at 23 °C. The latter is in good agreement with the value of 9.45 at 25 °C for the p*K* of *trans*-$Co(en)_2(SO_3)OH_2^+$.[8] Although OH^- is expected to react considerably faster with $Co(NH_3)_4SO_3^+$ than H_2O,[8,9] the concentration ratio is such that $k_9[H_2O] > k_9[OH^-]$. Rate data for the various steps included in reactions 9–11, reported in the literature[2,7–9] for this or the very closely related bis(ethylenediamine) system, illustrate that these reactions are considerably faster than those measured in this study. On the other hand, the isomerization reaction of *trans*-$Co(NH_3)_4(SO_3)_2^-$ to produce *cis*-$Co(NH_3)_4(SO_3)_2^-$ was found to be very slow, in agreement with earlier findings.[3] It follows that none of these steps can account for the k_A values reported in Tables II and IV.

One possibility, however, does remain, namely, that $Co(NH_3)_5SO_3^+$ undergoes an acid-catalyzed aquation process during which $Co(NH_3)_5OH^{2+}$ and SO_3^{2-} are produced. According to the mechanism outlined in (7) the reaction products of the formation process are $Co(NH_3)_5SO_3^+$ and OH^-, which may suggest the reverse reaction to depend on the $[OH^-]$ instead of the $[H^+]$. However, reaction 7 presents the overall chemical process, whereas the kinetic data predict the nature of the reaction mechanism, viz., an acid-catalyzed process. The magnitude of k_A' ($=k_A/[H^+]$) is such that it excludes a direct Co–S bond breakage step (see further discussion), and we suggest that this reverse process occurs during an intermediate stage in the interchange formation process as suggested above. That means that, before $Co(NH_3)_5SO_3^+$ is actually formed, it partially undergoes acid-catalyzed aquation. In this respect it is significant to point out that the magnitude of k_A' compares favorably with that reported[21] for the acidification of $Co(NH_3)_5OSO_2^+$, which does not involve M–O bond breakage.[23] Once $Co(NH_3)_5SO_3^+$ is produced, the trans-labilizing effect of SO_3^{2-} is so strong that it proceeds immediately to the reaction sequence outlined in reactions 9–11. During this suggested aquation process, sulfite ions are released and the process could probably be visualized as



(12)

The activation parameters in Tables III and IV favor a dissociative reaction mode, and the large positive ΔV^*_{intr} for the breakage of the Co- - -S bond may partially be canceled by a negative contribution from ΔV^*_{solv} due to the creation of charges on going to the reaction products. The pressure dependence of k_A must be interpreted with caution, since k_A

Table V. k_{obsd} for the Reaction $Co(NH_3)_5SO_3^+ + SO_3^{2-} \rightarrow$ *trans*-$Co(NH_3)_4(SO_3)_2^- + NH_3$ as a Function of $[SO_3^{2-}]$, Temperature, and Pressure[a]

temp, K	pressure, bar	$10^3[SO_3^{2-}]$, M	10^2k_{obsd},[b] s^{-1}
298.6	1	2.62	1.23
		3.15	1.19
		3.67	1.21
		4.08	1.18
		4.59	1.22
		5.00	1.23
293.5		3.86	0.58
295.5			0.89
298.3			1.22
300.9			2.01
308.8			5.41
313.4			8.40
$\Delta H^{\ddagger}$, kcal mol^{-1}			23.8 ± 1.0
$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}			12.6 ± 3.3
298.1	10	3.86	1.22
	100		1.20
	250		1.10
	400		1.00
	500		0.99
	600		0.92
	700		0.88
	800		0.77
	900		0.75
	1000		0.72
$\Delta V^{\ddagger}$, cm^3 mol^{-1}			13.7 ± 0.7

[a] Conditions: $[Co(NH_3)_5SO_3^+] = 4 \times 10^{-5}$ M; ionic strength 0.5 M; [buffer] = 0.1 M; pH 9.39; wavelength 325 nm. [b] Mean value of at least three kinetic runs.

Table VI. k_{obsd} for the Reaction $Co(NH_3)_5SO_3^+ + H^+ \rightarrow$ *trans*-$Co(NH_3)_4(SO_3)OH_2^+ + NH_4^+$ as a Function of $[H^+]$, Temperature, and Pressure[a]

temp, K	pressure, bar	$[H^+]$, M	10^2k_{obsd},[b] s^{-1}
297.8	1	0.1	0.72
		0.5	2.81
		1.0	5.83
		1.5	8.02
		2.0	10.6
289.7	1	1.5	2.54
293.4			5.59
297.8			8.02
301.3			14.4
308.8			32.7
313.4			54.1
$\Delta H^{\ddagger}$, kcal mol^{-1}			21.9 ± 1.1
$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}			10.3 ± 3.5
298.0	10	1.5	7.97
	250		7.25
	500		6.93
	750		6.94
	1000		6.02
$\Delta V^{\ddagger}$, cm^3 mol^{-1}			6.0 ± 1.2

[a] Conditions: $[Co(NH_3)_5SO_3^+] = 1.6 \times 10^{-3}$ M; ionic strength 2.0 M; wavelength 472 nm. [b] Mean value of at least three kinetic runs.

strongly depends on the pH of the solution, which may in turn vary with pressure due to the possible pressure dependence of the ammonia buffer system. In a similar way, the rather complex temperature dependence reported for k_A (Table III) could be due to a complicating temperature dependence of the pH of the buffer solutions and partially account for the unusually high values of ΔH^* and ΔS^*.

Formation of *trans*-$Co(NH_3)_4(SO_3)_2^-$ from $Co(NH_3)_5SO_3^+$. In an effort to throw more light on the reactivity behavior of $Co(NH_3)_5SO_3^+$, the kinetics of its reaction with SO_3^{2-} to produce *trans*-$Co(NH_3)_4(SO_3)_2^-$ under conditions similar to those given in Table II were studied at normal and elevated pressures. For this purpose $[Co(NH_3)_5SO_3]ClO_4$ was dissolved in the ammonia buffer and mixed with Na_2SO_3 solutions with use of a stopped-flow instrument. The results (Table V) indicate that this reaction is indeed fast and independent of $[SO_3^{2-}]$ with an average k_{obsd} value of $(1.21 \pm 0.05) \times 10^{-2}$ s^{-1} at 25 °C. This is in good agreement with the value of $(1.2 \pm 0.1) \times 10^{-2}$ s^{-1} at 25 °C reported by Halpern and coworkers[2] for the reaction of $Co(NH_3)_5SO_3^+$ with OH^-, CN^-, NO_2^-, and SCN^-. In addition, Deutsch and co-workers[6] reported a value of $(1.03 \pm 0.03) \times 10^{-2}$ s^{-1} at 25 °C for the formation of $Co(NH_3)_4SO_3^+$ from $Co(NH_3)_5SO_3^+$. The common rate-determining step must be the formation of the five-coordinate species $Co(NH_3)_4SO_3^+$, i.e., k_7 in reaction 9, such that

$$\begin{aligned} k_{obsd} &= k_8k_7[SO_3^{2-}]/(k_{-7}[NH_3] + k_8[SO_3^{2-}]) \\ &= k_7 \text{ when } k_8[SO_3^{2-}] >> k_{-7}[NH_3] \qquad (13) \end{aligned}$$

This is in line with the $[SO_3^{2-}]$ independence of k_{obsd} in Table V. The large positive values for ΔS^* and $\Delta \bar{V}^*_{exptl}$ underline the dissociative nature of the reaction mechanism. During the release of NH_3 no major changes in electrostriction are expected and $\Delta \bar{V}^*_{exptl}$ mainly represents ΔV^*_{intr} due to the breakage of the Co–NH_3 bond. If we assign a radius r to the leaving group and assume that it creates a cylindrical hole during the activation process, then $\Delta V^* = \pi r^2(\Delta l)$, where Δl is a crude estimate[50] of the extent to which the bond must be stretched in the transition state. With use of the partial molar volume of NH_3 (24.85 cm^3 mol^{-1})[51] and with a dead volume of 20% assumed, r turns out to be 2.0 Å with a corresponding Δl value of 1.4 Å. Using a simple harmonic oscillator model, Deutsch and co-workers[6] estimated a transition-state Co–N distance of 3.2 Å, which corresponds to a Δl value of 1.2 Å, in close agreement with our findings. The magnitude of $\Delta \bar{V}^*_{exptl}$ is in good agreement with values reported in the literature for similar dissociative processes.[24,25] Furthermore, these data reinforce the suggestions of Halpern et al.[2] in favor of a D mechanism and are not consistent with an I_d mechanism as suggested elsewhere.[9]

Acid-Catalyzed Aquation of $Co(NH_3)_5SO_3^+$. Scott and co-workers[3,4] observed that $Co(NH_3)_5SO_3^+$ and *trans*-$Co(NH_3)_4(SO_3)_2^-$ undergo an almost instantaneous aquation when treated with perchloric acid to produce *trans*-$Co(NH_3)_4(SO_3)OH_2^+$. We could measure this reaction for the $Co(NH_3)_5SO_3^+$ system by mixing solutions of the latter in ammonia buffer with perchloric acid in a stopped-flow apparatus. The results in Table VI indicate a linear $[H^+]$ dependence according to

$$k_{obsd} = k_{12} + k_{13}[H^+] \approx k_{13}[H^+] \qquad (14)$$

where $k_{12} = (0.3 \pm 0.2) \times 10^{-2}$ s^{-1} and $k_{13} = (5.2 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C.

The k_{12} term is ascribed to a "water-assisted" reaction path and is seen to be considerably smaller than k_7 measured in the previous section for the formation of $Co(NH_3)_4SO_3^+$. This may indicate that in weakly acidic medium the reaction is of the interchange type with water as entering ligand. Alternatively, the formation of $Co(NH_3)_4SO_3^+$ in basic medium may include some base-catalyzed component and so account for the difference in k_7 and k_{12}.

A more acceptable explanation lies in the difference in ionic strength employed during the determination of k_7 and k_{12}, viz., 0.5 and 2.0 M, respectively. A number of experiments were

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(50) Stranks, D. R.; Vanderhoek, N. *Inorg. Chem.* **1976**, *15*, 2645.
(51) Stokes, R. H. *Aust. J. Chem.* **1975**, *28*, 2109.

repeated over a limited acidity range at an ionic strength of 0.5 M. The corresponding results are $k_{12} = (0.9 \pm 0.2) \times 10^{-2}$ s^{-1} and $k_{13} = (5.9 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} at 25 °C, from which it follows that k_{12} is indeed very close to k_7.

The acid-catalyzed path, i.e., $k_{13}[H^+]$, completely outweighs the water-catalyzed processes (k_{12}) under the high-ionic-strength conditions and probably involves the acid-promoted breakage of the Co–NH₃ bond. For a mechanism of the type

$$Co(NH_3)_5SO_3^+ + H^+ \xrightarrow[\text{slow}]{k_{13}} Co(NH_3)_4SO_3^+ + NH_4^+ \xrightarrow[\text{fast}]{H_2O} \textit{trans}\text{-}Co(NH_3)_4(SO_3)OH_2^+ \quad (15)$$

$k_{obsd} = k_{13}[H^+]$. This process differs to some extent from that reported for the formation of *trans*-$Co(NH_3)_4(SO_3)_2^-$ from $Co(NH_3)_5SO_3^+$, where NH_3 was released in the rate-determining step (k_7 in reaction 9). The release of NH_4^+ is expected to be accompanied by a significantly smaller positive $\Delta\bar{V}^\ddagger_{exptl}$ value, due to the difference in the partial molar volumes of NH_3 and NH_4^+.[51,52] The activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) in Table VI are close to those reported for k_7 in Table V and point to the similarity in mechanisms. However, due to the lower $\Delta\bar{V}^\ddagger_{exptl}$ value, we cannot exclude the possibility of an I_d mechanism:

$$Co(NH_3)_5SO_3^+ + H_3O^+ \overset{K_{14}}{\rightleftharpoons} (Co(NH_3)_5SO_3^+,H_3O^+) \xrightarrow{k_{15}} \textit{trans}\text{-}Co(NH_3)_4(SO_3)OH_2^+ + NH_4^+ \quad (16)$$

In this case $k_{obsd} = k_{15}K_{14}[H^+]/(1 + K_{14}[H^+])$, which simplifies to $k_{obsd} = k_{15}K_{14}[H^+]$, since no significant curvature was observed in the plot of k_{obsd} vs. $[H^+]$ for the data in Table VI. A small negative value for $\Delta\bar{V}(K_{14})$ may contribute toward $\Delta\bar{V}^\ddagger_{exptl}$, since charge concentration occurs during the encounter complex formation reaction. The resulting positive value of $\Delta\bar{V}^\ddagger_{exptl}$ (Table VI) may indicate a positive contribution from the interchange process (k_{15}) and as such emphasize the dissociative nature of this reaction.

In conclusion, the results of this study clearly illustrate the strong dissociative nature of the reaction processes, especially when induced by the trans effect of the sulfito ligand.

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Registry No. $Co(NH_3)_5SO_3^+$, 53108-45-5; *trans*-$Co(NH_3)_4(SO_3)_2^-$, 62559-96-0; *trans*-$Co(NH_3)_4(SO_3)OH_2^+$, 48052-50-2.

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[52] Horne, R. A. "Water and Aqueous Solutions"; Wiley: New York, 1972; Chapter 13.

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Kinetics and Mechanism of the Formation of Violet Peroxychromate in Aqueous Solution

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The kinetics and mechanism of the formation of violet peroxychromate, $HCrO_6^-$, have been studied with use of a stopped-flow method. The rate law is $d[CrO_5(OH)^-]/dt = k[HCrO_4^-][H^+][H_2O_2]$ with a third-order Arrhenius rate constant of $k = 10^{7.8\pm0.5} \exp[(-5000 \pm 600\ \text{cal})/RT]$. A three-step mechanism is proposed which is similar to one previously suggested by Wilkins et al. for the formation of blue peroxychromate. Enthalpies and entropies of activation for the rate-determining step have been calculated and are found to be 6.6 ± 1.0 kcal and −14 ± 4 cal/K, respectively.

Introduction

When hydrogen peroxide is added to a strongly acidic aqueous solution of dichromate, the well-known blue diperoxychromium(VI) species $CrO(O_2)_2 \cdot H_2O$ rapidly forms:[1-3]

$$HCrO_4^- + 2H_2O_2 + H^+ \rightarrow CrO_5 \cdot H_2O + 2H_2O \quad (1)$$

The kinetics of formation of $CrO_5 \cdot H_2O$ have been extensively studied by Moore, Kettle, and Wilkins,[4] Orhanovic and Wilkins,[5] and Funahashi, Uchida, and Tanaka.[6] The reaction is third-order overall, being first order in each of the species H^+, H_2O_2, and $HCrO_4^-$. The rate constant at 0.1 M ionic strength is reported to be

$$k = 10^{7.6\pm0.2} \exp[(-4500 \pm 200\ \text{cal})/RT]\ M^{-2}\ s^{-1}$$

If the same reactants are mixed under less acidic conditions, pH 4–7, violet diperoxychromium(VI), $CrO_5(OH)^-$, is formed according to[7]

$$HCrO_4^- + 2H_2O_2 \rightarrow HCrO_6^- + 2H_2O \quad (2)$$

Finally, in alkaline solution the reaction yields still another product, the red-brown tetraperoxychromate(V), CrO_8^{3-}.

We have undertaken a study of the kinetics and mechanism of formation of violet peroxychromate in aqueous solution. In particular, we are interested in comparing the mechanism of this reaction with the closely related ones yielding the blue and red-brown peroxychromates. Since the reaction (2) like (1) is over in a matter of seconds, we have used stopped-flow techniques to study its kinetics. The progress of the reaction can be followed spectrophotometrically at 540 nm, where $HCrO_6^-$ has a strong absorption band ($\epsilon_{540} = 510$ M^{-1} cm^{-1} [8]). The rate law was determined with the method of initial rates. In the application of this method the effect of systematic variations in initial reactant concentrations on the initial reaction rates is used to determine the concentration dependence of each species in the rate law. Both the rate law and the third-order rate constant k have been determined at 15.0, 25.0, and 35.0 °C.

Experimental Section

All reagents were of the highest purity commercially available and were used without further purification. Potassium dichromate and

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[1] Glasner, A.; Steinberg, M. *J. Chem. Soc.* **1957**, 2569.
[2] Evans, D. F. *J. Chem. Soc.* **1957**, 4013.
[3] Tuck, D. G.; Walters, R. M. *Inorg. Chem.* **1963**, *2*, 3404.
[4] Moore, P.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 466.
[5] Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.
[6] Funahashi, S.; Uchida, F.; Tanaka, M. *Inorg. Chem.* **1978**, *17*, 2784.
[7] Griffith, W. P. *J. Chem. Soc.* **1962**, 3948.
[8] Bartlett, B. L.; Quane, D. *Inorg. Chem.* **1973**, *12*, 1925.

0020-1669/82/1321-4014$01.25/0