iron(II) complex radical by another iron(III) ion molecule in a step assisted by a nucleophilic attack by water. The rate law proposed by this mechanism generates an acid and water activity dependence of the form $a_{H_2O}^2/a_{H_3O^+}$ which was experimentally confirmed.

The temperature dependence of the reaction rate gives the parameters $\Delta H^\ddagger = 10.5 \pm 1$ kcal/mol and $\Delta S^\ddagger = -(8 \pm 2)$ eu obtained by maintaining $a_{H_2O}^2/a_{H_3O^+}$ essentially constant. The participation of two water molecules and an activation entropy of −8 eu are found in several acid-catalyzed organic reactions reviewed by Bunnett.[23] The kinetic data presented in this paper corroborate the mechanism[3] proposed for this complex reaction and point to an interesting correlation between water participation and entropy of activation common to acid-catalyzed organic reactions, which can be explored further.

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Kinetics and Mechanism of the Formation, Acid-Catalyzed Decomposition, and Intramolecular Redox Reaction of Oxygen-Bonded (Sulfito)pentaamminecobalt(III) Ions in Aqueous Solution[1]

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Dissolved sulfur dioxide reacts almost instantaneously with aqueous $Co(NH_3)_5OH^{2+}$ ion to form the oxygen-bonded sulfito complex ion $Co(NH_3)_5OSO_2^+$. This unstable product rapidly loses SO_2 when acidified, restoring the aquopentaammine species. However, at higher pH values, a relatively slow intramolecular redox decomposition can be observed, which produces $Co(aq)^{2+}$ and SO_4^{2-} in a 2:1 ratio. This is a stepwise process, probably involving the SO_3^- radical ion. The kinetics of the very rapid SO_2-uptake reaction was studied within the ranges $3.7 < pH < 7.7$, $10\ °C < t < 34\ °C$, and $0.01\ M <$ [total sulfite] < 0.06 M. The formation of the complex ion $Co(NH_3)_5OSO_2^+$ is a second-order process for which $k = (2.6 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$ at 10 °C, $\Delta H^\ddagger = 9.8 \pm 0.3$ kcal mol^{-1}, and $\Delta S^\ddagger = 14.0 \pm 0.4$ cal deg^{-1} mol^{-1}. The rather slow redox reaction was studied over the ranges $3.4 < pH < 6.7$, $15\ °C < t < 35\ °C$, and $0.02\ M <$ [total sulfite] < 0.10 M. The rate-determining step appears to be an inner-sphere one-electron transfer between the Co(III) center and the ligand sulfite, with a rate constant (extrapolated to 10 °C) of $k = (1.3 \pm 0.3) \times 10^{-3}\ s^{-1}$, $\Delta H^\ddagger = 26.9 \pm 1.2$ kcal mol^{-1}, and $\Delta S^\ddagger = 23.1 \pm 4.2$ cal deg^{-1} mol^{-1}. The rate of the moderately rapid SO_2-elimination process, studied in absence of excess sulfite, is directly proportional to $[H^+]$ within the range $3.3 < pH < 4.6$ and has a rate constant at 10 °C of $(2.2 \pm 0.4) \times 10^6\ M^{-1}\ s^{-1}$.

Introduction

Significant contributions have been made in recent years toward the understanding of the formation reactions and reactivity properties of S-bonded sulfito complex ions. Salts of $Co(NH_3)_5SO_3^+$ can only be prepared and purified in solutions containing free ammonia,[3] since this complex reacts with water (especially in acidic medium) to form *trans*-$Co(NH_3)_4(OH_2)(SO_3)^+$. The latter reaction has led to impurities in earlier reported preparations of the (sulfito)pentaamminecobalt(III) complex.[4-6] The extraordinarily strong trans-labilizing influence of the S-bonded sulfito ligand in octahedral Co(III) species has been studied in several laboratories. The studies have included complexes containing ammonia,[7-11] ethylenediamine,[12-16] cyanide,[17,18] and dimethylglyoximate[19-21] as the N-bonded ligands. It has also been reported[8,9] that the tetraammine(sulfito)cobalt(III) complexes undergo redox decomposition to Co^{2+} and the free radical HSO_3 in acidic medium, at rates of approximately $10^{-4}\ s^{-1}$ at 25 °C. More recently the preparation of some S-bonded sulfur dioxide complexes has been described.[22,23]

On the contrary, very little has been reported on the formation and reactivity of O-bonded sulfito complexes. Stranks

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[1] A preliminary report of this work was presented at the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 1979. See Abstract No. INOR 383.

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and co-workers[12] suggested that the reaction of sulfite with *trans*-$Co(en)_2(OH)(OH_2)^{2+}$ proceeds via addition of SO_2 to the oxygen of the aquo ligand followed by rapid intramolecular rearrangement of the O- to the S-bonded sulfito complex, although they were unable to detect the O-bonded intermediate. Thacker and Higginson[24] reported the rapid formation of a (sulfito)cobalt(III) inner-sphere complex during the reduction of diaquo(nitrilotriacetato)cobalt(III) ions by sulfite, which may well have been an O-bonded sulfito intermediate as suggested above.[12] To our knowledge, the only fully documented example of the possible formation of an O-bonded sulfito complex has been reported for the equilibrium system[25]

$$Cr(OH_2)_6^{3+} + HOSO_2^- \rightleftarrows Cr(OH_2)_5(OSO_2)^+ + H_3O^+$$

The formation of this sulfito complex is extremely rapid and must therefore occur without the breakage of a Cr(III)–O bond.

We have been involved in various studies of CO_2 uptake by various cobalt(III) and rhodium(III) complexes during which O-bonded carbonato complexes are formed by the addition of CO_2 to a hydroxy ligand. It is generally agreed that such reactions because of their rapidity must occur without M–O bond breakage.[26,27] With this in mind, we decided to investigate the possible formation of O-bonded sulfito complexes that may proceed via SO_2-uptake by metal–hydroxo complexes, similar in nature to the CO_2-uptake process. We now report the results of the first of such studies, which has focused on the pentaamminecobalt(III) system.

Experimental Section

Materials. $[Co(NH_3)_5OH_2](ClO_4)_3$ was prepared according to standard procedures[28] by treating $[Co(NH_3)_5CO_3]NO_3$ with concentrated $HClO_4$ and recrystallizing from 0.1 M $HClO_4$. Chemical analyses[29] were in agreement with the theoretical values and the UV–visible spectra (measured by use of a Cary 118 or Cary 15 spectrophotometer) were close to those reported in the literature.[30,31] All chemicals used were of reagent grade, and the laboratory-distilled water was further purified by passage through a mixed-bed ion-exchange column. Solid $Na_2S_2O_5$ was used as the source of sulfite; this salt is very stable but hydrates very rapidly and completely when dissolved in water to yield sulfite (see below).

Determination of the Acid-Dissociation Constants. The value for the acid-dissociation constant of $Co(NH_3)_5OH_2^{3+}$ (K_3) was determined at 25 °C and an ionic strength of 1.0 M ($NaClO_4$) by titrating a 2 × 10^{-3} M complex solution with 0.1 M NaOH. The pH measurements were made with a Beckman Research Model pH meter and a reference electrode filled with saturated NaCl solution. We found pK_3 to be 6.30 ± 0.05, which is in good agreement with values reported elsewhere,[26,32] and its lack of temperature dependence in the range of our experiments was confirmed. The pK values for the acid dissociations of "H_2SO_3" (see below) were determined by acidifying solutions of $Na_2S_2O_5$ with $HClO_4$ and titrating with NaOH in the way outlined above.

Rate Measurements. All rate measurements were made at an ionic strength of 1.0 M ($NaClO_4$) and over acidity and temperature ranges as shown in Results and Discussion. The "equilibrium method", previously designed to study CO_2-uptake reactions,[26] was employed in a similar way to study the SO_2-uptake process. In this procedure appropriate amounts of solid aquopentaamminecobalt(III) perchlorate were dissolved in 1 M $NaClO_4$, and of solid $Na_2S_2O_5$ in McIlvaine phosphate–citric acid buffers[33] of which the ionic strength had also been adjusted to 1.0 M with $NaClO_4$. These solutions were introduced separately into the storage syringes of an automated Durrum Model 110 stopped-flow assembly, and the runs were made in the usual manner, with the [Co(III)] set at 1 × 10^{-3} M in all kinetics experiments. The SO_2-elimination process was studied by acidifying solutions of the O-bonded (sulfito)pentaamminecobalt(III) species with $HClO_4$ or with the above-mentioned buffers.[33] This complex was prepared in situ by dissolving the appropriate amounts of $[Co(NH_3)_5OH_2](ClO_4)_3$ and $Na_2S_2O_5$ in the molar ratio 1:2 in 1 M $NaClO_4$, adjusting the pH to approximately 5.5 and storing at 0 °C (see Results and Discussion). The rates of the SO_2-uptake and -elimination processes were determined at 330 nm, where the difference in absorbance between reactant and product is at a maximum (see Table I and Results and Discussion). pH measurements were performed immediately after the kinetic runs using a water-jacketed sample holder thermostated at the reaction temperature. The observed pseudo-first-order rate constants were calculated in the usual way by using a least-squares program and are reported as the mean of at least six kinetic runs.

Table I. UV–Visible Absorption Spectra of Some Co(III) Species

complex species	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
$Co(NH_3)_5OH_2^{3+}$	490, 343	49.0, 47.0	this work
	491	49.0	30
	491	48.0	27
	491	48.6	34
sulfito intermediate[a]	518, 330	~88, ~2100[b]	this work
$Co(NH_3)_5SO_3^+$	456	150	this work[c]
	456	147	8
	457, 278	148, 17 800	3
	456, 278	148, 19 500	9
	456, 278	150, 18 900	11
trans-$Co(NH_3)_4(OH_2)(SO_3)^+$	472	145	this work[c]
	472	159	8
	473, 273	120, 6460	3
trans-$Co(NH_3)_4(SO_3)_2^-$	~430, 327 (sh)	490, 29 500	9
cis-$Co(NH_3)_4(SO_3)_2^-$	452, 295, 264	200, 20 900, 20 000	9
	454	210	10

[a] "Sulfito intermediate" is assigned the structure $Co(NH_3)_5$-OSO_2^+ (see Results and Discussion). [b] Error limits are ~5% due to interference of redox reaction (see Results and Discussion). [c] Prepared as described in ref 3.

The O-bonded (sulfito)pentaamminecobalt(III) complex undergoes a slow redox reaction which was followed in the thermostated-cell compartment of the Cary UV–visible spectrophotometer. For these reactions, solutions similar to those used in the SO_2-uptake experiments were thermostated at the reaction temperature and rapidly mixed in a thermostated 1-cm cuvette with the aid of a syringe. It was found that the pH of such reaction mixtures was not altered by the presence or absence of $[Co(NH_3)_5OH_2]^{3+}$ ion, so these measurements were usually made on the sulfite-containing buffer solution prior to mixing by using a water-jacketed sample holder thermostated at the reaction temperature. The redox reaction was studied at 330 and 520 nm (see Table I and Results and Discussion), and the observed first-order rate constants 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. These plots proved to be linear for at least 2 half-lives.

Results and Discussion

Qualitative Observations. Some preliminary experiments illustrated the sequence of the overall reaction process. Bubbling in SO_2 gas or adding $Na_2S_2O_5$, $NaHSO_3$ or Na_2SO_3 to buffered solutions of $Co(NH_3)_5OH_2^{3+}$ at a pH between 4 and 7 resulted in an instantaneous color change from light to dark red. The latter solution slowly ($t_{1/2} \approx 50$ s) fades at room temperature to produce an almost colorless, light pink solution. The color changes were followed spectrophotometrically in the UV–visible region, and the amount of dark red intermediate formed was found to depend on the sulfite concentration and

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the pH of the solutions. The maximum buildup of intermediate occurs at pH >5.5 (see later results) and its spectrum, recorded at 5 °C to minimize the decomposition process, is given in Table I along with spectra of several S-bonded sulfito complexes. It is seen that the spectrum of our intermediate sulfito species differs considerably from that of any of the S-bonded sulfito complexes.[34] Furthermore, the decomposition of the intermediate to Co(II) (see later results) is at least 10 times faster than the redox decomposition of the corresponding S-bonded complex.[8] In addition to these observations, it was found that the formation of the intermediate is a reversible process. Acidification of such solutions (pH <2) immediately after they had been prepared caused an instantaneous color change, and the resulting spectra are in exact agreement with that of $Co(NH_3)_5OH_2^{3+}$. If the acidification of the intermediate is performed after the lapse of some time, the resulting spectrum indicates that the initial concentration of $Co(NH_3)_5OH_2^{3+}$ is only regained partially, since partial decomposition of the intermediate to Co(II) occurs. On the contrary, the immediate result of acidification of the S-bonded $Co(NH_3)_5SO_3^+$ complex is a relatively small spectral change to that of *trans*-$Co(NH_3)_4(OH_2)(SO_3)^+$. The above observations are all in agreement with the formation in our experiments of an O-bonded $Co(NH_3)_5OSO_2^+$ intermediate which may either lose SO_2 on acidification or undergo a slower intramolecular redox reaction on standing. The intermediate could not be isolated as a pure solid complex due to its redox properties, which also seem to occur in the solid state. Similar arguments to those given above were used[25] to support the concept of the formation of the O-bonded Cr(III)–sulfito complex referred to in the Introduction. The rates of the formation and acid-decomposition reactions of $Co(NH_3)_5OSO_2^+$ (SO_2 uptake and elimination) differ significantly from each other and from that of the redox process, so it is possible to study the three reactions separately.

The SO_2-Uptake and -Elimination Processes. Before a detailed discussion of the SO_2 uptake process is presented, it is important to review the chemistry of the $SO_2/HSO_3^-/SO_3^{2-}$ system. SO_2 gas dissolves readily in water to give a reaction mixture called "sulfurous acid", which consists mainly of dissolved and loosely hydrated molecular sulfur dioxide.[35,36] "Sulfurous acid" shows two characteristic dissociations which can be expressed as eq 1 and 2. pH titrations of 0.04 M

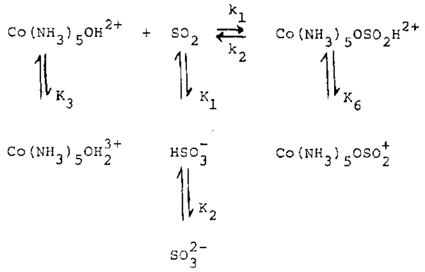
$$\text{“}H_2SO_3\text{”} \rightleftarrows H^+ + HSO_3^- \quad K_1 \tag{1}$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \quad K_2 \tag{2}$$

"H_2SO_3" (see Experimental Section) at 25 °C and ionic strength 1.0 M led to the values $pK_1 = 1.90 \pm 0.05$ and $pK_2 = 6.3 \pm 0.1$. The value of pK_1 is in very good agreement with values reported for similar conditions in the literature.[37] It has been reported by other authors[38] that pK_1 shows a concentration dependence, illustrating the complex nature of eq 1 which can be represented by the scheme[39]

$$SO_2 + H_2O \rightleftarrows SO_2\cdots H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \tag{3}$$

Scheme I



However, the sulfite concentration range employed in this study is such that no meaningful variation in pK_1 occurs. K_1 is, furthermore, somewhat temperature dependent, and an average value of $\Delta H_1 = -4.3$ kcal mol^{-1} was estimated from sets of data recorded elsewhere.[38,40]

It has been reported[41] that pK_2 is concentration independent, and our value is in close agreement with values in the literature.[41,42] From the temperature dependences of K_2/K_1[43] and K_1 (see above), it follows that K_2 is independent of temperature over the range involved in this investigation. A similar situation exists for the temperature dependences of the acid-dissociation constants of carbonic acid.[26] At high concentrations of bisulfite ion, a disulfite species[44] is formed according to the equilibrium[35,45]

$$2HSO_3^- \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} S_2O_5^{2-} + H_2O \quad K_4 \tag{4}$$

for which $K_4 = 7 \times 10^{-2}$ M^{-1} at 25 °C.[46] Solid $Na_2S_2O_5$, as used in this investigation, dissociates very rapidly in aqueous solution[47] according to eq 4 (the rate constants were found to be $k_4 = 7 \times 10^2$ M^{-1} s^{-1} and $k_{-4} = 1 \times 10^4$ s^{-1}, respectively) and exists as ≥99% HSO_3^- at $[Na_2S_2O_5] \leq 0.05$ M.

The rates of hydration and dehydration of sulfur dioxide according to eq 5 have been studied by several groups. A recent investigation[47] using an oxygen-exchange technique led to the values $k_5 = 1.0 \times 10^8$ s^{-1} and $k_{-5} = 2.5 \times 10^9$ M^{-1} s^{-1} at 25 °C and 0.9 M ionic strength. Significantly different results were reported earlier by using ultrasonic absorption[48] and ^{35}S tracer[49] techniques. The quoted value of k_{-5} is probably too small by a factor of at least 10, since most reactions of this type have rate constants between 10^{10} and 10^{11} M^{-1} s^{-1}. Moreover, in our experiments we found no peculiarities in the kinetics of the high-pH SO_2-uptake experiments (see below) which would have been expected to arise if the

$$SO_2 + H_2O \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} H^+ + HSO_3^- \tag{5}$$

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(34) A recent report on the photochemistry of the N- and S-bonded tris-chelate compound $Co(en)_2(S(O)_2CH_2CH_2NH_2)$ (Adamson, A. W.; Houlding, V. H.; Maecke, H., paper presented at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1979; see Abstract No. INOR 453) is of interest in this connection. The product of the irradiation is thought to be the O-bonded isomer $Co(en)_2(OS(O)CH_2CH_2NH_2)$. The wavelength maxima (nm) observed (Maecke, H., personal communication) are as follows (absorbances in parentheses, M^{-1} cm^{-1}): S-bonded 432 (220), 282 (14 200), 210 (15 500); O-bonded 511 (136), 325 (4100), 208 (16 500). These shifts are seen to parallel closely our findings for the O-bonded sulfito intermediate (see Table I).

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Table II. Dependence of k_{obsd} on pH and [Total S] for SO_2 Uptake by $Co(NH_3)_5OH^{2+}$ at 10 °C

A. high pH values				B. low pH values			
pH	[total S], M	k_{obsd}, s^{-1}	$10^{-8}k_1$,[a] $M^{-1}\ s^{-1}$	pH	[total S], M	k_{obsd}, s^{-1}	$10^{-8}k_1$,[b] $M^{-1}\ s^{-1}$
5.46	0.04	283 ± 5	3.38 ± 0.06	5.20	0.04	361 ± 3	3.67 ± 0.03
5.54	0.02	143 ± 3	3.57 ± 0.07	5.26	0.02	163 ± 4	3.27 ± 0.08
5.60	0.01	66.1 ± 1.9	3.46 ± 0.10	5.26	0.01	102 ± 2	3.89 ± 0.08
5.72	0.04	198 ± 4	2.87 ± 0.06	4.76	0.04	333 ± 4	2.84 ± 0.03
5.82	0.02	90.4 ± 2.9	2.91 ± 0.09	4.76	0.04	342 ± 4	2.92 ± 0.03
5.90	0.01	38.8 ± 0.6	2.76 ± 0.04	4.80	0.02	153 ± 3	2.29 ± 0.04
5.76	0.04	182 ± 5	2.74 ± 0.07	4.80	0.01	96 ± 2	2.36 ± 0.05
6.16	0.04	70.5 ± 2.6	1.91 ± 0.07	4.44	0.04	341 ± 9	2.44 ± 0.06
6.28	0.04	55.7 ± 1.3	1.94 ± 0.04	4.50	0.02	196 ± 3	2.36 ± 0.04
6.54	0.04	36.9 ± 0.6	2.51 ± 0.04	4.46	0.01	128 ± 6	1.94 ± 0.09
6.63	0.04	27.5 ± 1.3	2.46 ± 0.11	4.04	0.04	379 ± 9	1.64 ± 0.04
6.78	0.04	14.3 ± 0.7	2.09 ± 0.10	4.01	0.02	324 ± 6	1.99 ± 0.04
7.68	0.04	0.41 ± 0.02	2.34 ± 0.08	4.00	0.01	303 ± 8	3.02 ± 0.08
6.62	0.06	33.4 ± 1.9	1.93 ± 0.11	3.74	0.04	700 ± 32	2.75 ± 0.12
6.66	0.05	23.8 ± 1.2	1.87 ± 0.09	4.40	0.04	352 ± 8	2.47 ± 0.06
6.76	0.04	15.3 ± 0.4	2.09 ± 0.05	4.46	0.02	210 ± 2	2.51 ± 0.02
6.90	0.03	9.24 ± 0.24	2.77 ± 0.07	4.46	0.01	135 ± 3	2.20 ± 0.05
7.08	0.02	3.59 ± 0.07	3.22 ± 0.06	4.08	0.04	540 ± 11	3.29 ± 0.07
			av 2.6 ± 0.6	4.06	0.02	333 ± 6	2.59 ± 0.05
				4.04	0.01	272 ± 14	2.60 ± 0.13
				4.02	0.04	400 ± 8	1.74 ± 0.03
				3.98	0.02	324 ± 5	1.69 ± 0.03
				3.96	0.01	281 ± 8	1.48 ± 0.04
				3.72	0.04	663 ± 22	2.25 ± 0.07
							av 2.5 ± 0.6

[a] Calculated from eq 7. [b] Calculated from eq 8 by using $k_2/K_6 = k'_2/[H^+] = 2.2 \times 10^6\ M^{-1}\ s^{-1}$ (Table III).

equilibrium of eq 5 were to become rate limiting. In any case, it is clear that hydration of SO_2 is several orders of magnitude faster than the corresponding uncatalyzed hydration of CO_2.[26]

In some preliminary SO_2-uptake experiments, the reproducibility of the reactions and the stability of the reagent solutions (see Experimental Section) were checked by performing kinetic runs with the same solutions over a period of 8 h. At pH 6.1, [total S] = 0.04 M, and 25 °C the average value of k_{obsd} was 254 ± 4 s^{-1} within this extended time period. Furthermore, removal of dissolved oxygen by bubbling nitrogen through the solutions prior to mixing had no influence on the value of k_{obsd}. The kinetics of the SO_2-uptake process was studied over the ranges $3.7 < pH < 7.7$ and $0.01 \leq [\text{total S}] \leq 0.06$ M at 10 °C for which the results are summarized in Table II. During these kinetic experiments it was observed that the overall absorbance increase and infinite time value was constant for SO_2 uptake at pH >5.5. However, at pH <5.5 these quantities decreased with decreasing pH down to the point (pH <3.7) where the extent of reaction becomes negligible. However, the value of k_{obsd} steadily increased as the pH was lowered. These observations are interpreted as evidence for an equilibration process in which the rate of the reverse step (SO_2 elimination) becomes significant and contributes appreciably to the value of k_{obsd} at pH <5.5.

A mechanism for the SO_2 uptake/elimination process consistent with the rate observations and based on our previous proposals for the CO_2 reactions[26] is presented in Scheme I. The slower subsequent redox decomposition of the O-bonded sulfito complex produced in this step will be discussed in a succeeding section. For simplicity, the hydrogen ions participating in the acid–base equilibria are omitted from the scheme and all the *K*'s are defined as *acid-dissociation* constants. The rate law for the sulfito complex formation and decomposition based on Scheme I is

$$k_{\text{obsd}} = k_1\left\{\frac{K_3}{K_3 + [H^+]}\right\}\left\{\frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right\} \times [\text{total S}] + k_2\left\{\frac{[H^+]}{[H^+] + K_6}\right\} \quad (6)$$

At low [H$^+$], where no contribution by the reverse SO_2-elimination process takes place (i.e., at pH >5.5) eq 6 reduces to

$$k_{\text{obsd}} = k_1\left\{\frac{K_3}{K_3 + [H^+]}\right\}\left\{\frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right\}[\text{total S}] \quad (7)$$

Since K_1, K_2, and K_3 are known, k_1 was calculated[50] for all high-pH data by using eq 7 and the values are recorded in Table IIA. It is seen that a fairly constant value for k_1 is obtained over the range of k_{obsd} values from 0.41 to 283 s^{-1} (a factor of about 7000). Furthermore, the calculated k_1 varies very little as [total S] is varied, confirming the second-order nature of the SO_2-uptake reaction. An average value of $(2.6 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$ at 10 °C was estimated for k_1 from this set of data. Alternatively, a graphical test can be made of the data of Table IIA by utilizing eq 7 in the simplified reciprocal form (using the known K_1 and K_2 values to calculate [SO_2]):

$$[SO_2]/k_{\text{obsd}} = 1/k_1 + [H^+]/k_1K_3$$

A plot of the left-hand term of the equation vs. [H$^+$] should yield a straight line of slope $1/k_1K_3$ and intercept $1/k_1$. While there is obviously considerable scatter in such a plot (see Figure 1), the test is successful in that the derived values of the constants are $k_1 \approx 2 \times 10^8\ M^{-1}\ s^{-1}$ and $K_3 \approx 10^{-6}$ M, in good agreement with the calculated average value given in Table IIA of $(2.6 \pm 0.6) \times 10^8\ M^{-1}\ s^{-1}$ and the known value of $K_3 = 5.0 \times 10^{-7}$ M.

At higher [H$^+$] (pH <5.5), the data as shown in Table IIB must be fitted with eq 6 since the reverse reaction now contributes to the total rate. However, since k_2 and K_6 are unknown, some SO_2-elimination experiments were performed, for which the results, obtained as already described, are summarized in Table III. The acidity range is limited by the mixing time (~0.001 s) of the stopped-flow instrument, so

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(50) pK_1 was estimated to be 1.74 at 10 °C from its value of 1.90 at 25 °C and $\Delta H_1 = -4.3$ kcal mol^{-1}.[38,40]

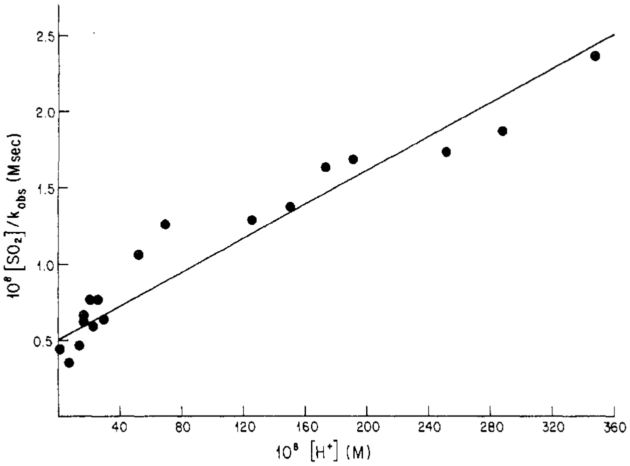


Figure 1. Plot of $[SO_2]/k_{obsd}$ vs. $[H^+]$ using data from Table IIA, showing least-squares best-fit curve.

Table III. pH Dependence of k_{obsd} for the Elimination of SO_2 from $Co(NH_3)_5OSO_2H^{2+}$ at 10 °C^a

pH	k_{obsd}, s^{-1}	k'_2,^{b,c} s^{-1}	$10^{-6}(k'_2/[H^+])$, M^{-1} s^{-1}
3.31	1200 ± 200	1170 ± 200	2.39 ± 0.41
3.84	338 ± 6	310 ± 11	2.15 ± 0.07
3.84	375 ± 13	347 ± 18	2.41 ± 0.12
3.90	376 ± 16	348 ± 21	2.76 ± 0.16
4.10	197 ± 3	169 ± 8	2.13 ± 0.10
4.14	197 ± 7	169 ± 12	2.33 ± 0.16
4.56	82.7 ± 1.3	55.3 ± 6.6	2.01 ± 0.24
4.61	64.6 ± 2.7	37.2 ± 8.0	1.52 ± 0.32
		av	2.2 ± 0.4

^{a} [Total S] = 4 × 10^{-3} M. ^{b} $k'_2 = k_2\{[H^+]/([H^+] + K_6)\} = (k_2/K_6)[H^+]$. ^{c} Calculated from eq 8 by using k_1 = (2.6 ± 0.6) × 10^8 M^{-1} s^{-1} (Table IIA).

that k_{obsd} values larger than 700 s^{-1} cannot be measured accurately. Equation 6 can be rewritten as eq 8 where k'_2 =

$$k_{obsd} = k_1\left\{\frac{K_3}{K_3 + [H^+]}\right\}\left\{\frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}\right\} \times [\text{total S}] + k'_2 \quad (8)$$

$k_2[H^+]/\{[H^+] + K_6\}$. With the value of k_1 = (2.6 ± 0.5) × 10^8 M^{-1} s^{-1} obtained from the SO_2-uptake data at pH >5.5 (Table IIA), k'_2 was calculated by means of eq 8 and its values are recorded in Table III. It is seen that k'_2 varies linearly with $[H^+]$, since a reasonably constant value for $k'_2/[H^+]$ is obtained. This can only be the case when $K_6 >> [H^+]$ such that $k'_2 = k_2[H^+]/K_6$ or $k'_2/[H^+] = k_2/K_6$. This is within reasonable expectation, since in the analogous carbonate system[26] the acid-dissociation constant of the bicarbonato complex was reported to be almost identical with that of the first dissociation constant of carbonic acid. Thus we expect K_6 to be close to K_1 in magnitude, which is indeed much larger than the $[H^+]$ values concerned. The average value of $k'_2/[H^+] = k_2/K_6$ (i.e., 2.2 × 10^6 M^{-1} s^{-1}) was used to calculate k_1 for the data at pH <5.5 in Table IIB, using eq 8. Once again a fairly constant value for k_1, independent of [total S], is obtained from these data, and its mean value of (2.5 ± 0.6) × 10^8 M^{-1} s^{-1} is indeed very close to that calculated from the data at pH >5.5. The overall mean value of k_1, calculated from all 42 data points in Table II, is (2.55 ± 0.6) × 10^8 M^{-1} s^{-1}. The validity of the above described data fit is further illustrated in Figure 2 where the data at [total S] = 0.04 M in Table II are plotted as a function of pH and compared with a curve calculated with the k_1 and k_2/K_6 values recorded above.

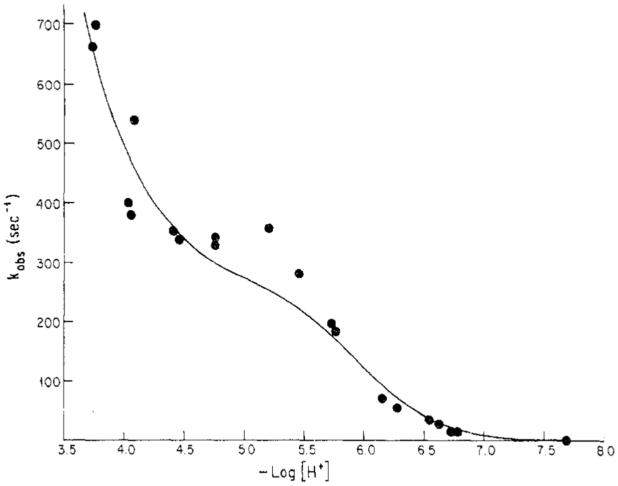


Figure 2. Plot of k_{obsd} vs. pH for the SO_2 uptake by $Co(NH_3)_5OH^{2+}$ at 10 °C and [total S] = 0.04 M. Points are from Table II; curve is calculated from eq 8 by using k_1 = 2.55 × 10^8 M^{-1} s^{-1} (Table II) and $k'_2/[H^+]$ = 2.2 × 10^6 M^{-1} s^{-1} (Table III).

Table IV. Dependence of k_{obsd} on pH for the SO_2 Uptake by $Co(NH_3)_5OH^{2+}$ at 25 °C^a

pH	k_{obsd}, s^{-1}	$10^{-8}k_1$,^{b} M^{-1} s^{-1}
5.75	528 ± 22	5.45 ± 0.23
6.12	265 ± 6	4.58 ± 0.10
6.18	257 ± 5	5.00 ± 0.10
6.27	206 ± 4	4.84 ± 0.09
6.40	129 ± 3	4.16 ± 0.09
6.52	102 ± 2	4.53 ± 0.09
6.72	48.8 ± 1.5	4.04 ± 0.12
		av 4.7 ± 0.3

^{a} [Total S] = 0.04 M. ^{b} Calculated from eq 7.

Table V. Temperature Dependence of k_{obsd} for SO_2 Uptake by $Co(NH_3)_5OH^{2+}$

temp, °C	k_{obsd}, s^{-1}	pK_1^{a}	$10^{-8}k_1$,^{b} M^{-1} s^{-1}
10.04	48.4 ± 1.9	1.74	1.8 ± 0.1
14.96	74.7 ± 0.8	1.79	2.4 ± 0.1
19.61	114 ± 2	1.85	3.2 ± 0.1
24.51	170 ± 4	1.90	4.3 ± 0.1
25.00			4.7 ± 0.3^c
29.06	237 ± 7	1.94	5.4 ± 0.2
33.81	370 ± 10	1.99	7.6 ± 0.2

$\Delta H^{\ddagger}$ = 9.8 ± 0.3 kcal mol^{-1}
$\Delta S^{\ddagger}$ = 14.0 ± 0.4 cal deg^{-1} mol^{-1}

^{a} Calculated as outlined in ref 50. ^{b} Calculated from eq 7. ^{c} See Table IV.

It was not possible to measure the SO_2 elimination reaction with significant accuracy much above 10 °C due to the increasingly rapid redox decomposition of the sulfito complex under such conditions. The temperature dependence of this process was therefore not studied. However, SO_2-uptake experiments at higher temperatures could be carried out at pH ≥5.5, where there is little or no interference by the reverse elimination process. The results at 25 °C given in Table IV illustrate the reproducibility of k_1 at a fixed [total sulfite] over a narrow pH range above 5.7. A mean value of k_1 = (4.7 ± 0.3) × 10^8 M^{-1} s^{-1} is obtained. The magnitude of k_1 was determined at several other temperatures with the pH fixed at 6.3 and [total sulfite] at 0.04 M, and these results together with the derived activation parameters are summarized in Table V.

A comparison can now be made between the value of k_1 and its activation parameters with those reported for the analogous

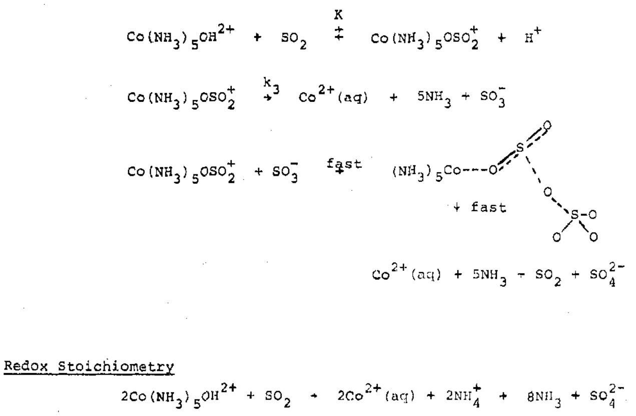
CO_2-uptake process[26] ($k_1 = 220$ M^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 15.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 3.6$ cal deg^{-1} mol^{-1}). The SO_2 uptake is approximately 10^6 times faster, accounted for by a combination of a lower value for $\Delta H^{\ddagger}$ and a higher value for $\Delta S^{\ddagger}$. A similar reactivity difference is found in the rates of hydration of SO_2 and CO_2 as mentioned earlier, and it also shows up in the solubility data for SO_2 and CO_2.[51] A direct comparison of the rates of SO_2 and CO_2 elimination is not possible since we could derive only a value for k_2/K_6 in this investigation. If, however, we make the assumption mentioned earlier that $K_6 \approx K_1 = 0.018$ M at 10 °C, it follows that $k_2 \simeq 4 \times 10^4$ s^{-1} at 10 °C. This is about 10^5 times greater than the value $k = 0.34$ s^{-1} for the loss of CO_2 from $Co(NH_3)_5OCO_2H^{2+}$ under such conditions,[52] again similar to the rate ratio found for the SO_2/CO_2 uptake comparison.

The kinetic results just discussed further confirm our earlier qualitative conclusion that an O-bonded (sulfito)pentaamminecobalt(III) complex is formed during the reaction of sulfite ion with $Co(NH_3)_5OH^{2+}$. The preparation of the S-bonded (sulfito)pentaamminecobalt(III) complex must be performed in ammonia-containing solutions.[3] The SO_2 concentration at such a high pH is so low that very little direct SO_2 uptake can occur so that the typically slow complete substitution of the hydroxo ligand by SO_3^{2-} leads to the S-bonded reaction product. The only O-bonded sulfito complex reported by these same investigators[53] is a species in which the –S–O– moiety acts as a bridge between two Co(III) centers. The results of our investigation also strengthen the preliminary conclusions of other workers mentioned in the Introduction,[12,24] in which SO_2 uptake by a hydroxycobalt(III) complex to form an O-bonded sulfito complex was proposed but in no way confirmed.

The Redox Decomposition of $Co(NH_3)_5OSO_2^+$. In the preliminary experiments it was observed that the O-bonded (sulfito)pentaamminecobalt(III) complex undergoes a relatively slow decomposition reaction during which the strongly colored solution fades almost completely. Analyses[8,54] of the final reaction mixture confirmed the presence of Co(II) at concentrations exactly equal to the initial concentrations of the Co(III) complex, and this finding was independent of reaction conditions. The identity of the sulfur-containing reaction product was determined as follows: Barium chloride is added to the final product solution, thus precipitating SO_4^{2-} and unreacted SO_3^{2-} but leaving $S_2O_6^{2-}$ in solution.[55,56] The $BaSO_3$ is removed from the precipitate by washing with HCl, and the remaining $BaSO_4$ is dried and weighed. The molar ratio of sulfate to cobalt in the system was found to be 0.5, thus showing that sulfate is the sole oxidation product in the reaction.

Preliminary kinetic measurements indicated that the observed rate constant for the redox process is practically independent of pH and [total S] under conditions where the $Co(NH_3)_5OSO_2^+$ species is fully formed, i.e., at pH ≥5.5 and [total S] = 0.04 M. However, at lower pH where the sulfito complex is only partially formed (see results in previous section), k_{obsd} does depend on pH and [total S]. Several experiments were performed to establish the nature of the redox process. The following changes in reaction conditions had, within experimental error, no influence on the value of k_{obsd}: an increase in the [Co(III)] from 10^{-3} to 10^{-2} M; a change in wavelength at which the reaction was followed from 330 to 520 nm; the presence of NH_4^+ ions up to 1.0 M at pH 6; the presence of Co(II) ions up to 0.05 M; the presence of citric acid–phosphate buffers;[33] substituting $NaHSO_3$ or Na_2SO_3 for $Na_2S_2O_5$ as the source of sulfite; removal of dissolved oxygen by bubbling nitrogen through the reaction mixture; saturation of the reaction mixture with oxygen; the presence of mannitol up to 0.02 M.[57,58]

Scheme II



Detailed data on the kinetics of the redox process (measured at λ = 330 nm) were obtained as a function of temperature, pH, and [total sulfite], and these results are summarized in Table VI. In this study, the appearance of $Co(NH_3)_5OSO_2^+$ becomes an equilibration due to the rapidity of both SO_2 uptake and SO_2 elimination (Scheme I). A possible mechanism for the subsequent redox process is outlined in Scheme II, for which the appropriate rate law is

$$k_{obsd} = \frac{k_3K_3K[SO_2]}{K_3[H^+] + K_3K[SO_2] + [H^+]^2} \tag{9}$$

Values for k_3 can be computed from this expression since $[SO_2]$ can be calculated from the known [total sulfite] and the constants K_1 and K_2 already defined. The values of pK_1 are 1.79, 1.90, and 2.00 at 15, 25, and 35 °C, respectively (calculated as shown in ref 50), while both pK_2 and pK_3 are 6.3 over the limited temperature range of this study (see earlier discussion of these constants). The remaining constant $K = k_1K_6/k_2$ has a magnitude of 116 ± 34 at 10 °C, as calculated from the values derived above for k_1 and k_2/K_6. It is assumed that K is independent of temperature within the error limits quoted. The computed values for k_3 are given in Table VI and are seen to be reasonably constant at each temperature over the substantial ranges 3.4 < pH < 6.7 and 0.02 M < [total sulfite] < 0.10 M. The indicated activation parameters are $\Delta H^{\ddagger} = 26.9 \pm 1.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 23.1 \pm 4.2$ cal deg^{-1} mol^{-1}. These activation parameters are similar in magnitude to those frequently observed for various kinds of substitution reactions of pentaamminecobalt(III) complexes. This could suggest rate-determining loss of NH_3 as an alternative reaction path, which would indeed fit our data equally well. However, the magnitude of the $\Delta H^{\ddagger}$ values for ammonia release from a number of cobalt(III)–ammine complexes are consistently several kilocalories higher than those for internal reduction of cobalt(III) by even the rather robust aquo ligand.[59] We therefore favor direct reduction by the SO_3^{2-} ligand in the

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(51) The solubilities in water of SO_2 and CO_2 at 0 °C are 3.6 and 0.08 M, respectively: "Handbook of Chemistry and Physics", 49th ed.; CRC Press: Cleveland, 1968; pp B252, B189.

(52) Extrapolated from the data in: Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1968**, *90*, 6360.

(53) Siebert, H.; Wittke, G. *Z. Anorg. Allg. Chem.* **1974**, *406*, 282.

(54) Newton, A. M.; Swaddle, T. W. *Can. J. Chem.* **1974**, *52*, 2751.

(55) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience: New York, 1972; p 452.

(56) Reference 51: p B181.

(57) Fuller, E. C.; Crist, R. H. *J. Am. Chem. Soc.* **1941**, *63*, 1644.

(58) Byerley, J. J.; Fouda, S. A.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1975**, 1329.

(59) For a summation of data of this type, see Table III in: Hyde, K. E.; Harris, G. M. *J. Phys. Chem.* **1978**, *82*, 2204.

Table VI. Rate Data for the Redox Decomposition of $Co(NH_3)_5OSO_2^+$ as a Function of Temperature, pH, and [Total S]

15 °C			
pH	[total S], M	10^3k_{obsd},[a] s^{-1}	10^3k_3,[b] s^{-1}
3.69	0.04	1.12 ± 0.14	2.75
4.06	0.04	1.27 ± 0.06	2.06
4.47	0.04	1.36 ± 0.10	1.69
4.76	0.04	1.73 ± 0.07	1.95
5.12	0.04	1.81 ± 0.03	1.92
5.42	0.04	2.23 ± 0.02	2.30
5.72	0.04	2.44 ± 0.03	2.49
6.02	0.04	2.41 ± 0.10	2.44
6.33	0.04	2.37 ± 0.05	2.40
6.54	0.04	2.65 ± 0.07	2.69
6.66	0.04	2.76 ± 0.14	2.80
6.72	0.04	2.62 ± 0.10	2.66
4.40	0.04	1.35 ± 0.11	1.74
4.38	0.06	1.41 ± 0.01	1.69
4.37	0.08	2.01 ± 0.12	2.32
4.36	0.10	2.19 ± 0.13	2.47
5.49	0.02	2.55 ± 0.07	2.70
5.42	0.04	2.81 ± 0.15	2.90
5.40	0.06	2.96 ± 0.06	3.03
5.33	0.08	3.08 ± 0.09	3.14
5.26	0.10	2.89 ± 0.03	2.94
6.53	0.02	2.16 ± 0.09	2.22
6.36	0.04	2.65 ± 0.11	2.68
6.15	0.06	2.72 ± 0.07	2.74
6.09	0.08	2.80 ± 0.07	2.82
5.99	0.10	2.72 ± 0.01	2.73

$k_3 = (2.5 \pm 0.4) \times 10^{-3}\ s^{-1}$

25 °C			
pH	[total S], M	10^2k_{obsd},[a] s^{-1}	10^2k_3,[b] s^{-1}
3.42	0.04	0.49 ± 0.02	1.54
3.65	0.04	0.41 ± 0.01	0.92
3.80	0.04	0.67 ± 0.04	1.26
4.03	0.04	0.67 ± 0.03	1.02
4.21	0.04	0.98 ± 0.02	1.32
4.48	0.04	1.24 ± 0.07	1.47
4.47	0.04	1.39 ± 0.04	1.65
4.76	0.04	1.63 ± 0.06	1.79
5.07	0.04	1.44 ± 0.07	1.51
5.12	0.04	1.79 ± 0.18	1.87
5.56	0.04	1.57 ± 0.08	1.81
5.57	0.04	1.73 ± 0.10	1.76
5.94	0.04	1.55 ± 0.10	1.57
5.60	0.04	1.65 ± 0.06	1.68
6.24	0.04	1.70 ± 0.09	1.72
6.45	0.04	1.21 ± 0.03	1.22
6.49	0.04	1.34 ± 0.07	1.35
6.61	0.04	1.38 ± 0.03	1.39
6.69	0.04	1.39 ± 0.09	1.41
6.69	0.04	1.41 ± 0.20	1.43
4.43	0.02	0.64 ± 0.02	0.91
4.40	0.04	0.85 ± 0.01	1.04
4.39	0.06	0.94 ± 0.07	1.08
4.35	0.08	0.93 ± 0.08	1.05
4.38	0.10	1.06 ± 0.15	1.16
5.46	0.02	1.53 ± 0.06	1.60
5.37	0.04	1.78 ± 0.05	1.83
5.30	0.06	1.56 ± 0.09	1.59
5.25	0.08	1.50 ± 0.12	1.53
5.23	0.10	1.79 ± 0.08	1.82
6.51	0.02	1.01 ± 0.05	1.03
6.33	0.04	0.94 ± 0.08	0.95
6.18	0.06	1.24 ± 0.27	1.25
6.11	0.08	1.42 ± 0.04	1.43
5.98	0.10	1.46 ± 0.05	1.47

$k_3 = (1.4 \pm 0.3) \times 10^{-2}\ s^{-1}$

35 °C			
pH	[total S], M	10^2k_{obsd},[a] s^{-1}	10^2k_3,[b] s^{-1}
4.39	0.04	3.25 ± 0.25	3.84
4.71	0.04	4.13 ± 0.31	4.49
5.07	0.04	4.50 ± 0.20	4.68
5.39	0.04	5.45 ± 0.33	5.57
5.69	0.04	5.43 ± 0.78	5.50
6.01	0.04	4.62 ± 0.73	4.66
6.30	0.04	5.79 ± 0.12	5.84
6.50	0.04	4.76 ± 0.31	4.80
6.62	0.04	4.80 ± 0.69	4.84
6.69	0.04	4.85 ± 0.88	4.90
4.36	0.04	3.51 ± 0.38	4.19
4.35	0.06	4.50 ± 0.26	5.09
4.33	0.08	4.67 ± 0.63	5.15
4.31	0.10	5.19 ± 1.14	5.64
5.46	0.02	6.39 ± 0.22	6.64
5.39	0.04	6.57 ± 0.07	6.59
5.33	0.06	6.91 ± 0.88	7.02
5.28	0.08	6.56 ± 0.47	6.65
5.22	0.10	6.59 ± 0.72	6.67
6.47	0.02	5.78 ± 0.07	5.88
6.30	0.04	6.32 ± 0.27	6.37
6.17	0.06	6.32 ± 0.29	6.35
6.07	0.08	6.83 ± 0.38	6.86
5.98	0.10	6.98 ± 0.68	7.01

$k_3 = (5.6 \pm 1.0) \times 10^{-2}\ s^{-1}$

[a] Mean value of at least three kinetic runs. [b] Calculated from eq 9 (see Results and Discussion).

rate-determining step of Scheme II, with formation of the radical ion SO_3^- and Co^{2+}. The radical ion can be visualized[8] as undergoing a variety of subsequent reactions to produce SO_3^{2-}, SO_4^{2-}, or $S_2O_6^{2-}$. However, our barium salt precipitation tests rule out $S_2O_6^{2-}$ as an appreciable product. This has led us to postulate very effective scavenging of SO_3^- by $Co(NH_3)_5OSO_2^+$ ions, as illustrated in Scheme II, since other common free-radical scavengers such as Co(II), oxygen, and mannitol have been shown to have no observable influence on the redox rate.

A study has been made previously[8] of the redox reaction of the S-bonded isomer of our compound. In this process, the initial step has been assigned to the dissociation of NH_3 from the parent species to produce *trans*-$Co(NH_3)_4(OH_2)(SO_3)^+$. The parameters for this first reaction are $k = 1 \times 10^{-4}\ s^{-1}$ at 25 °C, $\Delta H^\ddagger = 26.5 \pm 0.1$ kcal mol^{-1}, and $\Delta S^\ddagger = 12.5 \pm 0.4$ cal deg^{-1} mol^{-1}. This is followed by the intramolecular redox reaction with a rate approximately 6 times as great as the initial step, suggesting a value not greater than $10^{-3}\ s^{-1}$ at 25 °C, which is to be compared with our value for redox decomposition of the oxygen-bonded complex, $k_3 = (1.4 \pm 0.3) \times 10^{-2}\ s^{-1}$. Clearly, there are substantial differences in the rates and mechanisms of these processes, notwithstanding the apparent (and perhaps coincidental) identity of the $\Delta H^\ddagger$ values for the rate-determining processes, so that the rate difference is entirely entropic in origin. A possible explanation may lie in the bridging ability of the oxygen atom in the O-bonded sulfito complex which may assist both the initial rate-determining electron-transfer step and the secondary electron-transfer reaction as outlined in Scheme II.

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Registry No. $Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $Co(NH_3)_5OSO_2^+$, 19394-96-8; $Co(NH_3)_5SO_3^+$, 53108-45-5; *trans*-$Co(NH_3)_4(OH_2)(SO_3)^+$, 48052-50-2; $Co(NH_3)_5OH^{2+}$, 16632-75-0; SO_2, 7446-09-5.