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Kinetics and Mechanism of the Formation, Substitution, Isomerization, and Acid-Catalyzed Aquation Reactions of *trans*-(Sulfito-*O*)cyanotetraamminecobalt(III) in Aqueous Solution

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Received November 28, 1984

Dissolved SO_2 reacts rapidly with *trans*-$Co(NH_3)_4(CN)OH^+$ to form *trans*-$Co(NH_3)_4(CN)OSO_2$, which on immediate acidification loses SO_2 to produce *trans*-$Co(NH_3)_4(CN)OH_2^{2+}$. The kinetics of the formation and acidification reactions were studied as a function of [total S], pH, and temperature, from which it follows that $k(SO_2 \text{ uptake}) = (1.04 \pm 0.07) \times 10^8$ M^{-1} s^{-1} at 25 °C, $\Delta H^* = 41 \pm 6$ kJ mol^{-1}, and $\Delta S^* = 50 \pm 20$ J K^{-1} mol^{-1} and $k(\text{acidification}) = (2.5 \pm 0.3) \times 10^6$ M^{-1} s^{-1} at 25 °C, $\Delta H^* = 61 \pm 1$ kJ mol^{-1}, and $\Delta S^* = 83 \pm 4$ J K^{-1} mol^{-1}. The *trans*-$Co(NH_3)_4(CN)OSO_2$ species undergoes a subsequent slow linkage isomerization reaction to produce *trans*-$Co(NH_3)_4(CN)SO_3$, for which $k = (1.6 \pm 0.4) \times 10^{-3}$ s^{-1} at 40 °C and is independent of pH and [total S]. The results are discussed in comparison with those of closely related systems to emphasize the influence of the cyano ligand on the mentioned reactions.

Introduction

Oxidation of S(IV) to S(VI) in aqueous solution is generally known to be catalyzed by traces of transition-metal ions such as Mn^{2+}/Mn^{3+}, Fe^{2+}/Fe^{3+}, Co^{2+}/Co^{3+}, and Cu^{2+}.[1–6] This reaction route represents a viable pathway for the oxidation of dissolved SO_2 to sulfate in atmospheric water droplets during the acid-rain process. Despite numerous detailed kinetic investigations,[7–9] the intimate nature of the metal ion–S(IV) interaction is not well-understood. It is in this respect that the classical Werner type complexes of Co(II) and Co(III) can be employed as model species to investigate this interaction.[8,10]

In the above-mentioned studies S-bonded metal bisulfito or sulfito complexes are suggested as precursors in such catalytic processes. Our earlier studies,[10,11] however, clearly demonstrated that, in the case of nonlabile metal centers, SO_2 uptake by a metal hydroxy species to produce an O-bonded sulfito complex is a significantly more effective process than substitution by HSO_3^- or SO_3^{2-} to produce the corresponding S-bonded species. Furthermore, the subsequent intramolecular redox reaction in the case of the pentaamminecobalt(III) complex is approximately 10^2 faster for the O-bonded than for the S-bonded species.[10,12] The stability of the O-bonded sulfito complex strongly depends on the nature of the other ligands coordinated to the metal center.[13] For instance, in the case of the tetren (tetraethylenepentamine) complex, the O-bonded species was found to be redox inert and an intramolecular linkage isomerization to the S-bonded species was observed.[14,15] Very similarly, preliminary investigations indicated that the introduction of a cyanide ligand trans to the O-bonded sulfito ligand in the tetraamminecobalt(III) complex surpressed the intramolecular redox reaction in favor of a linkage isomerization (O- to S-bonded) reaction.

Our interest in the fundamental nature of such processes, for the reasons outlined above, has encouraged us to investigate the kinetics and mechanism of the formation and reactivity of the *trans*-$Co(NH_3)_4(CN)OSO_2$ species in detail,[16] and we report our main findings in this paper.

Experimental Section

Materials. $Co(NH_3)_4(CN)SO_3 \cdot 2H_2O$ was prepared as described in the literature.[17] Chemical analyses[18] and UV-visible absorption spectra were in good agreement with the theoretically expected values and those reported elsewhere,[19] respectively. This complex shows a temperature-, pH-, and oxygen-sensitive redox reaction ($k \approx 10^{-5}$ s^{-1} at 41 °C and pH 4–8). $[Co(NH_3)_4(CN)H_2O]Cl_2$ was prepared by treating the sulfito complex with concentrated HCl as described elsewhere,[20] resulting in satisfactory chemical analyses[18] and UV–visible spectral data.[21] Chemicals of analytical reagent grade and doubly distilled water (saturated with argon to remove dissolved oxygen) were used throughout this study. Solid $Na_2S_2O_5$ was used as a source of sulfite, which dissociates very rapidly in aqueous solution to produce dissolved SO_2, HSO_3^-, and SO_3^{2-}.[10,13,22,23] McIlvaine phosphate–citric acid buffers,[24] the ionic strength of which had been adjusted with $NaClO_4$, were employed to stabilize the pH.

Instrumentation. UV-visible absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer. pH measurements were made with a Radiometer PHM 64 meter and a reference electrode filled with 3 M NaCl solution. Kinetic measurements at ambient pressure were performed in the thermostated (±0.2 °C) cell compartment of the above spectrophotometer and on an Aminco stopped-flow system. An on-line computer was employed to analyze the absorbance–time plots recorded with the stopped-flow instruments.

Rate Measurements. All rate measurements were made at an ionic strength of 0.5 M ($NaClO_4$ medium), over an acidity range of $3 \leq pH \leq 7$ and a temperature range of 13–40 °C. The buffer concentration was kept constant at 3×10^{-2} M (pH 6.3) throughout the study. Some experimental details are included in the following section. In general, rate constants were measured under pseudo-first-order conditions and the

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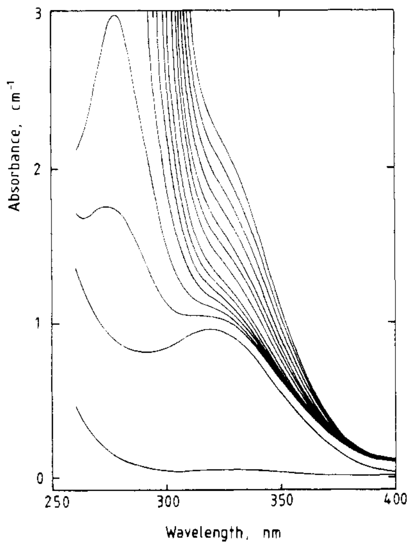

Figure 1. Spectral evidence for the formation and subsequent isomerization of *trans*-$Co(NH_3)_4(CN)OSO_2$. Conditions: [Co(III)] = 1×10^{-3} M; [total S] = 2×10^{-3} M; pH 7.8; temperature 40 °C; Δt = 2 min.

corresponding first-order plots were linear for at least 2–3 half-lives of the reaction. Rate constants for the fast (stopped-flow) reactions are reported as the mean value of between 6 and 8 independent measurements, whereas those for the slower reactions were averaged over two to three determinations. Data fitting was performed with the aid of a standard least-squares program. pH measurements were performed either before or immediately after the kinetic runs, depending on the reactivity of the system.

Results and Discussion

Qualitative Observations. As mentioned in the Experimental Section, the *trans*-$Co(NH_3)_4(CN)SO_3$ complex, hereafter referred to as $R(CN)SO_3$, undergoes a spontaneous slow redox decomposition. The rate of this reaction can be suppressed by increasing the buffer concentration to the mentioned level, i.e. by stabilizing the pH of the solution since ammonia is released when Co^{2+} is formed. However, this background reaction was observed under various conditions and must be taken into account during the investigation of relatively slow reactions involving this complex ion. This redox reaction is of the same order of magnitude as those found for other S-bonded sulfito complexes,[10,12,25,26] but considerably slower than the redox reaction of O-bonded sulfito complexes mentioned before.

Addition of $Na_2S_2O_5$ or Na_2SO_3 to a buffered solution of $R(CN)OH_2^{2+}$ at a pH between 4 and 8 resulted in an instantaneous change in the UV spectrum, producing an absorption at 318 nm. Immediate acidification regenerated the aquo complex, demonstrating the reversibility of the reaction. On the basis of our experience with related systems,[10,11,13,27] we conclude that the instantaneous spectral change is due to the rapid formation of $R(CN)OSO_2$, which on acidification will lose SO_2 to produce the aquo complex. In the present case two subsequent slower reactions are observed following the formation of the O-bonded sulfito species as seen from the recorded spectra in Figure 1. New absorption maxima occur at 278 and 327 nm (see Figure 2), which can be ascribed to the formation of $R(CN)SO_3$ and $R(SO_3)_2^-$, respectively. The identification of the different sulfito species is simplified by their very characteristic UV–visible spectra as summarized in Table I. At longer reaction times the absorption at 327 nm reaches a maximum and starts to decrease while the peak at 278 nm continuously increases in intensity (see Figure 3). A similar observation was made before[12] and can be ascribed to the spontaneous or catalyzed oxidation of free sulfite causing a shift in the equilibrium between the disulfito and cyano–sulfito species. Similar spectral changes were observed when sulfite was added to a solution of $R(CN)SO_3$, which resulted in the formation of $R(SO_3)_2^-$ followed by the same spectral changes during the reproduction of $R(CN)SO_3$. At even longer reaction times the

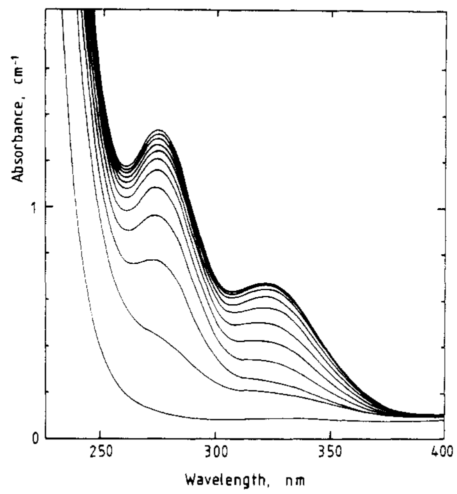

Figure 2. Spectral evidence for the formation of *trans*-$Co(NH_3)_4(CN)SO_3$ and *trans*-$Co(NH_3)_4(SO_3)_2^-$. Conditions: [Co(III)] = 5×10^{-4} M; [total S] = 1×10^{-3} M; pH 6.4; temperature 40 °C; Δt = 8 min.

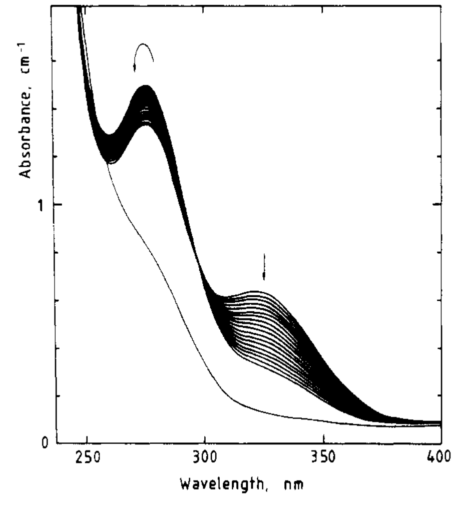

Figure 3. Spectral evidence for the formation of *trans*-$Co(NH_3)_4(CN)SO_3$ from *trans*-$Co(NH_3)_4(SO_3)_2^-$ followed by the redox decomposition of *trans*-$Co(NH_3)_4(CN)SO_3$. Conditions: [Co(III)] = 5×10^{-4} M; [total S] = 1×10^{-3} M; pH 6.4; temperature 40 °C; Δt = 8 min; final spectrum recorded after 15 h.

Scheme I

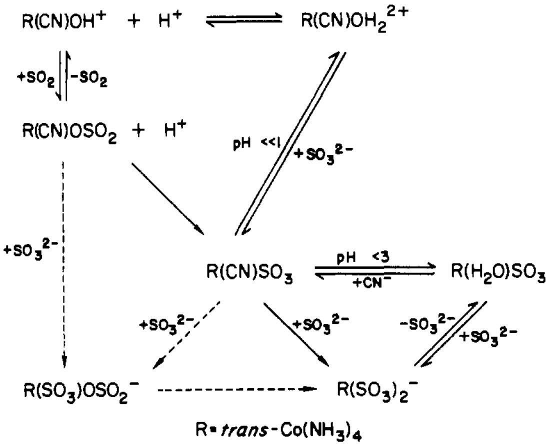

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Table I. UV–Visible Absorption Spectra of Some Cyano and Sulfito Complexes of Co(III)

complex species	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	ref
trans-$Co(NH_3)_4(CN)OH_2^{2+}$	450, 332	67, 54	this work
	453, 333	67, 53	21
cis-$Co(NH_3)_4(CN)OH_2^{2+}$	456, 333, 237	79, 65, 3020	30
trans-$Co(NH_3)_4(CN)OH^+$	465, 354	82, 72	this work
	465, 352	82, 72	21
trans-$Co(NH_3)_4(CN)OSO_2$	458, 318	~100, ~1000	this work
trans-$Co(NH_3)_4(CN)SO_3$	427, 278	~150, ~19 500	this work
	427	~145	19
$Co(NH_3)_5OSO_2^+$	513, 328	95, 2320	12
	518, 330	~88, ~2100	10
$Co(NH_3)_5SO_3^+$	456, 278	148, 19 500	12, 26
	457, 278, 364 (sh)	148, 17 780	28
	456, 278	150, 18 900	29
	456	150	10
	460		19
trans-$Co(NH_3)_4(SO_3)OH_2^+$	472	159	25
	472	145	10
	473, 273, 370 (sh)	120, 6460	28
	272	6500	12
trans-$Co(NH_3)_4(SO_3)_2^-$	430 (sh), 327	490, 29 510	26
	326	29 480	12
cis-$Co(NH_3)_4(SO_3)_2^-$	452, 295, 264	200, 20 890, 19 950	26
	295, 264	20 950, 20 000	12

redox decomposition of $R(CN)SO_3$, referred to above, starts to interfere and the absorbance at 278 nm slowly decreases (Figure 3).

These and other subsequent reactions are summarized in Scheme I. A detailed study[16] revealed that acidification of $R(CN)SO_3$ to pH <3 slowly produces $R(H_2O)SO_3^+$, whereas strong acidification (pH <<1) in the presence of free CN^- results in the formation of $R(CN)OH_2^{2+}$ (see Experimental Section). The $R(H_2O)SO_3^+$ species is in equilibrium with the $R(OH)SO_3$ species, for which the pK_a value is 9.5.[12] The dotted lines in Scheme I postulate possible alternative reaction routes; however, no evidence is at present available to support these. The subsequent reactions following the formation of $R(CN)OSO_2$ (as outlined in Scheme I) are such that they can effectively be neglected when moderate pH and total sulfite concentration conditions are selected for the kinetic measurements of the different reaction steps leading to the formation of $R(CN)SO_3$. It follows from the spectral data in Table I that a good agreement exists between the data obtained in this study and those for similar or related complexes reported in the literature. This situation further assists the handling of the fairly complex system outlined in Scheme I.

SO_2 Uptake and Elimination. If we dissolve $Na_2S_2O_5$, Na_2SO_3, and SO_2(g) in aqueous solution the following equilibria set in:

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \quad K_1 \tag{1}$$

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

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O \quad K_3 \tag{3}$$

SO_2 gas dissolves readily in water to give a mixture called "sulfurous acid", which consists mainly of dissolved and loosely hydrated molecular sulfur dioxide. Sulfurous acid shows two characteristic acid dissociations for which pK_1 = 1.9 and pK_2 = 6.3 at 25 °C and ionic strength 1.0 M.[10,31] K_1 is, furthermore, somewhat temperature dependent, and an average value of $\Delta H_1 = -4.3$ kcal mol^{-1} was estimated from literature data.[10] K_2, on the other hand, is independent of temperature over the range involved in this investigation. The value of K_3, viz. 0.07 or 0.088 M^{-1},[22,23] is such that $S_2O_5^{2-}$ exists in solution as ≥99% HSO_3^- at $[Na_2S_2O_5] \leq 0.05$ M. It is also important to note that the hydration of SO_2 and dehydration of HSO_3^- are very fast (1×10^8 s^{-1} and 2.5×10^9 M^{-1} s^{-1} at 25 °C, respectively), such that equilibria 1 and 2 are maintained rapidly.

Table II. Rate Data for the Formation and Acidification of $R(CN)OSO_2$[a]

		k_{obsd},[b] s^{-1}	
pH	10^2[total S], M	formation[c]	acidification[d]
6.42	0.15	1.46 ± 0.03	
6.39	0.37	1.84 ± 0.02	
6.31	0.75	2.55 ± 0.03	
6.26	1.5	3.38 ± 0.04	
6.22	2.2	4.66 ± 0.02	
6.18	3.7	7.80 ± 0.07	
5.99	5.6	12.0 ± 0.1	
6.00	7.5	14.5 ± 0.1	
7.02	2.4	0.76 ± 0.02	
6.83	2.4	1.03 ± 0.30	
6.40	2.4	2.54 ± 0.42	
6.09	3.0	6.25 ± 0.15	
5.85	3.0	9.36 ± 0.15	
5.42	3.0	18.5 ± 0.2	
5.14	3.0	33.1 ± 0.9	
4.97	3.0	38.6 ± 1.4	
4.59	3.0	75.8 ± 5.1	
4.70	4.8	60.2 ± 2.2	
4.32	7.5	118 ± 6	
4.16	4.0	144 ± 16	
3.95	4.0	176 ± 22	
3.78	4.0	166 ± 26	
5.95	3.0		5.38 ± 0.23
5.84	3.0		9.06 ± 0.39
5.72	3.0		8.70 ± 0.25
5.62	3.0		12.2 ± 1.1
5.23	3.0		28.4 ± 0.5
4.79	3.0		52.4 ± 2.6
4.60	3.0		73.0 ± 1.0
4.52	3.0		120 ± 2
4.51	3.0		73.7 ± 1.4
4.14	3.0		172 ± 5
4.12	3.0		187 ± 6
3.78	3.0		290 ± 6

[a] Conditions: Temperature 25 °C; [Co(III)] = $(1-4) \times 10^{-3}$ M; wavelength 312 nm; ionic strength 0.5 M. [b] Mean value of at least six kinetic runs. [c] $R(CN)OH_2^{2+} + SO_2/HSO_3^-$. [d] $R(CN)OSO_2 + H^+$.

Kinetic data for the formation of $R(CN)OSO_2$ were obtained by reacting the $R(CN)OH_2^{2+}$ complex with freshly prepared and buffered sulfite solutions, whereas for the acidification reaction fresh mixtures of $R(CN)OH_2^{2+}$ and sulfite (which rapidly produce $R(CN)OSO_2$) were acidified with an appropriate buffer solution. In contrast to the earlier investigated systems,[10,11] the present case is such that the forward and reverse reactions cannot be separated

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Table III. Temperature Dependence of k_{obsd} for the Formation and Acidification of R(CN)OSO$_2$[a]

temp, °C	formation[b] pH	formation[b] k_{obsd},[d] s^{-1}	acidification[c] pH	acidification[c] k_{obsd},[d] s^{-1}	$10^{-8}k_5$,[e] M^{-1} s^{-1}	$10^{-6}k_{-5}$,[e] M^{-1} s^{-1}	K_5[f]
10	6.19	1.81 ± 0.10	4.18	39.5 ± 3.1	0.578	0.558	103
15	6.16	2.86 ± 0.15	4.14	71.0 ± 4.9	0.767	0.925	83
20	6.21	4.64 ± 0.10	4.32	78.7 ± 1.8	1.18	1.49	79
25	6.16	5.50 ± 0.32	4.14	172 ± 5	1.04	2.27	46
30	6.17	10.9 ± 0.6	4.38	164 ± 6	2.03	3.58	57
35	6.16	16.5 ± 0.4	4.22	323 ± 28	2.78	4.98	56
$\Delta H^\ddagger$, kJ mol^{-1}					41 ± 6	61 ± 1	−20 ± 6[g]
$\Delta S^\ddagger$, J K^{-1} mol^{-1}					50 ± 20	83 ± 4	−32 ± 21[g]

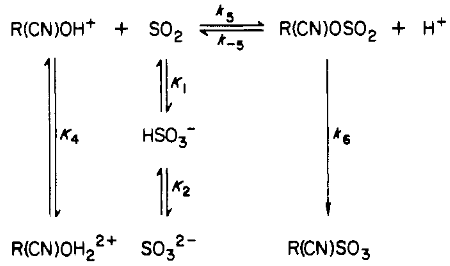
[a] Conditions: [Co(III)] = 1.5×10^{-3} M; [total S] = 3×10^{-2} M; ionic strength 0.5 M; wavelength 312 nm. [b] $R(CN)OH_2^{2+} + SO_2/HSO_3^-$. [c] $R(CN)OSO_2 + H^+$. [d] Mean value of at least six kinetic runs. [e] Calculated by using eq 4 and the following values for $K_2 \times 10^2$: 1.82 (10 °C), 1.62 (15 °C), 1.41 (20 °C), 1.26 (25 °C), 1.11 (30 °C), 1.00 (35 °C).[10] [f] $K_5 = k_5/k_{-5}$. [g] Thermodynamic parameters $\Delta H°$ and $\Delta S°$.

Table IV. Summary of Available Rate and Activation Parameters for the Formation and Acid-Catalyzed Decomposition of O-Bonded Sulfito Complexes of Co(III) at 25 °C

complex ion	$10^{-8}k_5$, M^{-1} s^{-1}	$10^{-6}k_{-5}$, M^{-1} s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	ref
trans-$Co(NH_3)_4(CN)OH^+$	1.04 ± 0.07		41 ± 6	50 ± 20	this work
$Co(NH_3)_5OH^{2+}$	4.7 ± 0.3		41 ± 1	59 ± 2	10
($\alpha\beta S$)-Co(tetren)OH^{2+}	3.3 ± 0.3		−2 ± 4	−88 ± 15	14
$Co(tren)(OH_2)_2^{3+}$	0.09 ± 0.01		150 ± 4	393 ± 12	32
$Co(tren)(OH_2)OH^{2+}$	0.53 ± 0.04		19 ± 1	−33 ± 1	32
$Co(tren)(OH)_2^+$	24 ± 3		48 ± 1	96 ± 13	32
cis-$Co(en)_2(OH_2)OH^{2+}$	1.05 ± 0.05		25 ± 1	−7 ± 1	33
trans-$Co(NH_3)_4(CN)OSO_2$		2.5 ± 0.3	61 ± 1	83 ± 4	this work
$Co(NH_3)_5OSO_2^+$		2.2 ± 0.4[a]			10
($\alpha\beta S$)-Co(tetren)OSO$_2^+$		~4 ± 1[b]	56 ± 20	71 ± 80	14
$Co(tren)(OH_2)OSO_2^+$		1.5 ± 0.2	46 ± 3	29 ± 2	32

[a] Value at 10 °C. [b] Extrapolated from literature data.

Scheme II



completely and the system always goes to equilibrium. The measured rate constants, summarized in Table II, are therefore composite values for both reactions. The drastic increase in k_{obsd} with decreasing pH is in line with our earlier observations for related systems,[10,11] suggesting that a similar mechanism is operative in the present system. The suggested mechanism, outlined in Scheme II, is similar to that suggested for the formation and decomposition of other O-bonded sulfito complexes,[10–14] as well as for the R(CN)OCO$_2$ species.[21] The R(CN)OH$^+$ species is the only one capable of taking up SO$_2$ to produce the R(CN)OSO$_2$ species. In Scheme II all the K's are defined as acid-dissociation constants, and for simplicity, the hydrogen ions participating in the equilibria are omitted. Under the present conditions pK_4 = 7.55 as reported elsewhere.[21]

The rate law for the formation and acidification of R(CN)OSO$_2$ based on Scheme II is given by[10]

$$k_{obsd} = k_5[SO_2]f_{R(CN)OH} + k_{-5}[H^+]$$
$$= k_5\left\{\frac{[H^+]^2[\text{total S}]}{[H^+]^2 + K_1[H^+] + K_1K_2}\right\}\left\{\frac{K_4}{K_4 + [H^+]}\right\} + k_{-5}[H^+] \quad (4)$$

where $f_{R(CN)OH}$ is the fraction of the total Co(III) species present in the hydroxo form. It follows from eq 4 that a plot of $k_{obsd}/[H^+]$ vs. $[SO_2]f_{R(CN)OH}/[H^+]$ should be linear with slope k_5 and intercept k_{-5}. The data in Table II are plotted in this fashion in Figure 4. Within the experimental scatter usually observed for such measurements,[10,34] the data fit eq 4 with $k_5 = (1.04 \pm 0.07) \times 10^8$ M^{-1} s^{-1} and $k_{-5} = (2.5 \pm 0.3) \times 10^6$ M^{-1} s^{-1} at 25 °C. Very encouraging is the fact that the acidification data points coincide so well with the formation data (see Figure 4), indicating that eq 4 does describe both reaction steps.

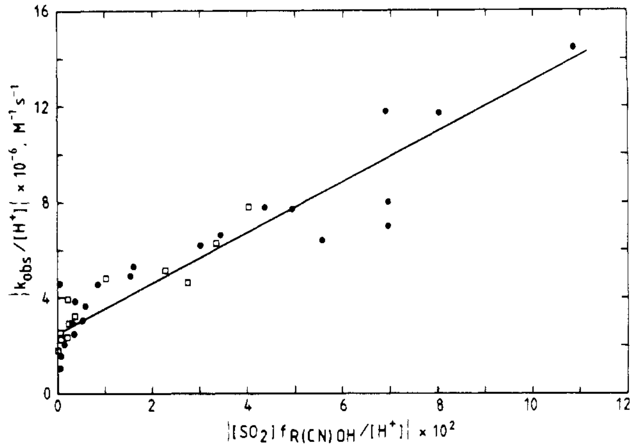


Figure 4. Plot of $k_{obsd}/[H^+]$ vs. $[SO_2]f_{R(CN)OH}/[H^+]$ for the data in Table II: (●) formation rate data; (□) acidification rate data.

The temperature dependence of k_5 and k_{-5} was studied under conditions where mainly the formation reaction or the reverse acidification reaction contributes toward the measured k_{obsd}. However, as mentioned above, these two reactions cannot be completely separated and must both be considered in the analysis of the kinetic data. Equation 4 was used to calculate k_5 and k_{-5} at each temperature, and the results at 25 °C from this two-point analysis are in close agreement with the data obtained from the more extended study at this temperature (Table II). This good correlation is due to the fact that the pH for the formation and acidification measurements was selected far enough apart such that only two points on a plot as in Figure 4 can predict fairly

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Table V. Rate Data for the Linkage Isomerization Reactions[a] *trans*-$Co(NH_3)_4(CN)OSO_2 \xrightarrow{k_6}$ *trans*-$Co(NH_3)_4(CN)SO_3$

10^3[total S], M	pH	$10^4 k_{obsd}$, s^{-1}	$10^3 k_6$,[b] s^{-1}
0.60	6.95	5.66	1.67
	6.77	6.31	1.52
	6.38	7.90	1.41
	6.08	11.8	1.86
	5.91	11.8	1.77
	5.78	13.9	2.03
	5.61	15.3	2.19
	5.60	17.0	2.43
	5.35	13.4	1.87
	5.16	11.2	1.55
	4.83	8.34	1.14
	4.75	10.1	1.39
	4.40	6.79	0.93
0.30	6.02	9.42	1.97
0.47	6.04	8.60	1.47
0.80	6.00	10.2	1.43
1.0	6.12	8.82	1.20
1.4	6.08	8.20	1.02
2.0	6.09	7.93	0.93
			1.6 ± 0.4 (mean)

[a] Conditions: temperature 40 °C; [Co(III)] = 6 × 10^{-4} M; ionic strength 0.5 M; wavelength 278 nm. [b] Calculated with the aid of eq 6, with $K_5 = 43$ as extrapolated from the thermodynamic parameters in Table III.

accurate values for k_5 and k_{-5}. These data were used to calculate the activation parameters and the values of K_5 along with its thermodynamic parameters. A comparison with similar data for closely related Co(III) complexes is given in Table IV.

It follows that the activation parameters for SO_2 uptake by $R(CN)OH^+$ are very close to those for $Co(NH_3)_5OH^{2+}$. In general, all SO_2-uptake reactions by Co(III) hydroxo complexes exhibit low activation enthalpies, which accounts for the rather high order of magnitude of the k_5 values. This is in agreement with the rapid hydration reaction of SO_2, viz. 1 × 10^8 s^{-1} at 25 °C,[35] where the water molecule is replaced by the Co–OH moiety in the present systems. k_5 is throughout the series of complexes ca. 10^6 times larger than the corresponding value for CO_2 uptake reactions.[34] Furthermore, the activation parameters for SO_2-uptake reactions show a good isokinetic correlation.[13] The few data points for the reverse SO_2 elimination reactions also coincide with this correlation, indicating that a common mechanism is operative; i.e., uptake and elimination of SO_2 involves the formation and breakage of the same bond. A similar result was reported for an extended series of CO_2-uptake and -elimination reactions.[34,36] The rate constants for SO_2 elimination in Table IV are of similar magnitude and are considerably larger than for CO_2 elimination.[34] Finally, it can be concluded that the strong trans-labilizing effect usually observed for coordinated cyanide has no marked influence on the SO_2-uptake and -elimination rate constants. This is probably due to the fact that these processes involve the formation and breakage of a secondary ligand bond, respectively. Much larger effects are expected to be observed when the formation or breakage of primary metal–ligand bonds are involved.

Linkage Isomerization Reaction. This reaction, represented by k_6 in Scheme II, is much slower than those described in the previous section. The formation of the $R(CN)OSO_2$ species can therefore be considered as a rapid preequilibration for the subsequent step, and the value of K_5 at 25 °C is 42 ± 8. The linkage isomerization was followed by preparing the $R(CN)OSO_2$ species in solution and measuring the subsequent absorbance increase at 278 nm. The rate constant for this reaction was measured as a function of pH and [total S], for which the results are summarized in Table V. A curve-fitting procedure was adopted to estimate k_{obsd} over the first 30–40 min of the isomerization reaction in order to minimize the influence of the subsequent substitution reactions referred to before.

At a constant [total S], k_{obsd} increases with increasing pH to reach a maximum value at pH ~5.5, after which k_{obsd} decreases with a further increase in pH. This bell-shaped dependence of k_{obsd} on pH can be ascribed to the influence of the preequilibrium since it is strongly pH dependent. The isomerization mechanism can be summarized as in eq 5, and the corresponding rate expression is given in (6). With the aid of this equation, k_6 can be estimated as a function of pH and [total S], and the results are included in Table V. It follows that k_6 is fairly constant over the investigated pH range. Deviations are bound to occur at lower pH due to the interference of the acidification reaction, which makes it difficult to follow the isomerization reaction under such conditions. k_{obsd} and k_6 remain fairly constant over the range of [total S] selected, and deviations due to subsequent substitution processes (see Scheme I) show up at higher [total S] values. All in all, the data in Table V underline the validity of the suggested intramolecular isomerization reaction.

$$\begin{tikzcd}
R(CN)OH^+ + SO_2 \arrow[r, shift left, "K_5"] & R(CN)OSO_2 + H^+ \arrow[l, shift left] \arrow[d, "k_6"] \\
& R(CN)SO_3
\end{tikzcd} \qquad (5)$$

$$\begin{aligned} k_{obsd} &= k_6 f_{R(CN)OSO_2} \\ &= k_6 K_5[SO_2]/([H^+] + K_5[SO_2]) \end{aligned} \qquad (6)$$

The average value of k_6, viz. (1.6 ± 0.4) × 10^{-3} s^{-1} at 40 °C, is of the same order of magnitude as the corresponding rate constant for ($\alpha\beta S$)-Co(tetren)OSO_2^+, viz. (7.8 ± 0.5) × 10^{-4} s^{-1} at 38.7 °C.[14] More mechanistic information on the intimate nature of the linkage isomerization process is obtainable from the temperature and pressure dependence of k_6. Unfortunately, the pH sensitivity of k_{obsd} and the occurrence of subsequent substitution reactions complicated the performance of such measurements. A similar difficulty was encountered with the corresponding tetren system, where competing geometrical isomerization reactions complicate the system.[15]

We wish to make a final comment concerning the redox sensitivity of O-bonded sulfito complexes of Co(III). The introduction of a cyano group trans to the sulfito ligand suppresses the intramolecular redox reaction observed for the pentaammine complex.[10] This observation supports our earlier suggestion[10] that labilization of the trans ammonia ligand in $Co(NH_3)_5OSO_2^+$ occurs prior to intramolecular electron transfer. Alternatively, introduction of a cyano group may influence the redox potential of the Co(III) center and therefore the electron-transfer process. The fact that cyanide can affect the redox stability of O-bonded sulfito complexes to such an extent is of fundamental importance to metal-ion-catalyzed oxidation reactions of SO_2. It has been suggested[6] that rapid SO_2 uptake followed by ligand to metal electron transfer may be important steps in such processes.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. *trans*-$Co(NH_3)_4(CN)OH^+$, 71391-78-1; *trans*-$Co(NH_3)_4(CN)OSO_2$, 97995-46-5; *trans*-$Co(NH_3)_4(CN)SO_3$, 81938-94-5.

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