

Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 2. Formation and Aquation of Aquo(sulfito-O)(2,2',2''-triaminotriethylamine)cobalt(III) Ion^{1,2}

A. A. EL-AWADY*³ and G. M. HARRIS*

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The rates of the rapid reversible uptake of SO₂ by diaquo(2,2',2''-triaminotriethylamine)cobalt(III) complex ions have been determined by the stopped-flow technique over the ranges 3.5 < pH < 6.6, 10 < t < 25 °C, and 0.006 < [total sulfite] < 0.07 M at I = 1.00 M (NaClO₄). The rate parameters at 10 °C for the second-order reactions of SO₂ with Co(tren)(H₂O)₂³⁺, Co(tren)(OH)(OH₂)²⁺, and Co(tren)(OH)₂⁺ are respectively as follows: $k = (5.0 \pm 0.3) \times 10^5$, $(3.3 \pm 0.1) \times 10^7$, and $(7.6 \pm 1.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $\Delta H^\ddagger = 36 \pm 1$, 4.5 ± 0.1 , and $11.5 \pm 0.3 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = 94 \pm 3$, -8.0 ± 0.3 , and $23 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The product obtained is shown by spectral studies to be an O-bonded monodentate sulfito complex, which, in the unstable protonated form Co(tren)(OH₂)(OSO₂H)²⁺, eliminates SO₂ with rate parameters at 10 °C of $k = (1.4 \pm 0.1) \times 10^3 \text{ s}^{-1}$, $\Delta H^\ddagger = 11.1 \pm 0.8 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -4.6 \pm 0.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$. Comparisons are made between the results of this study and those of similar previous studies involving CO₂, SO₂, SO₃²⁻, HSeO₃⁻, HMoO₄⁻, and HWO₄⁻, leading to a number of worthwhile mechanistic conclusions.

Introduction

In the preceding paper in this series,² we have reported a kinetic study of the very fast direct addition of aqueous SO₂ to the species Co(NH₃)₅OH²⁺ to yield an unstable O-bonded monosulfito complex ion. This type of reaction affords a close mechanistic parallel to the now fully documented phenomenon of reversible CO₂ uptake by a large number of octahedral hydroxometal complexes.⁴ In such rapid reactions, all of which occur with half-times of seconds or less, it can be unequivocally concluded that they take place without the metal-oxygen bond fission which is characteristic of conventional hydroxo or aquo ligand replacement. A number of other recent studies have pointed up the similarly high reactivity of several additional group 6 moieties toward cobalt(III)-aquo complex ions, including the SO₃²⁻ ion,⁵⁻⁸ the HSeO₃⁻ ion,⁹ the HMoO₄⁻ ion,¹⁰ and the HWO₄⁻ ion.¹¹ All of these require the stopped-flow technique for rate measurement and therefore necessitate the postulation of a "direct addition" mechanism of the type already mentioned. We now report the results of our second study of SO₂ uptake and elimination, this time by the sterically robust complex ion diaquo(2,2',2''-triaminotriethylamine)cobalt(III), Co(tren)(H₂O)₂³⁺. In the higher acidity range (pH ≤ 6.6), the SO₂ uptake behavior of this system is quite similar to that of its pentaammine analogue, including complete reversibility of the process at the high-acid end of the range (pH < 3). A new feature appears, however, in that there is evidence for rapid SO₂ addition, not only as expected to the two deprotonated species Co(tren)(OH₂)-

Table I. Acid Dissociation Constants for Co(tren)(OH₂)₂³⁺ and SO₂(aq) (I = 1.0 M (NaClO₄))

temp, °C	pK ₁ ^a	pK ₂ ^a	pK ₃ ^b	pK ₄ ^b
6.0	1.69	6.30	6.07 ± 0.05	8.30 ± 0.05
10.0	1.74	6.30	6.01 ± 0.06	8.31 ± 0.04
14.0	1.79	6.30	5.96 ± 0.03	8.22 ± 0.04
18.0	1.84	6.30	5.89 ± 0.05	8.27 ± 0.06
22.0	1.87	6.30	5.85 ± 0.04	8.24 ± 0.04
25.0	1.90	6.30	5.80 ± 0.04	8.23 ± 0.03

^a Determined as outlined previously.^{2,16,17} ^b Previously reported values for pK₃ and pK₄ at 20 °C are 5.42 and 7.8, respectively, at I = 0.1 M (NaClO₄)¹³ and 5.35 and 7.95, respectively, at I = 0.5 M (NaClO₄).¹⁴

(OH)²⁺ and Co(tren)(OH)₂⁺, but also to the diaquo ion itself, Co(tren)(OH₂)₂³⁺. Furthermore, as will be fully discussed in a subsequent paper,¹² while the expected slow reduction of cobalt(III) by the O-bonded sulfito ligand is observed in the lower pH range, above pH 7 the final process is not redox but substitution for the second aquo ligand by SO₃²⁻ to yield a very stable bis(sulfito) end product.

Experimental Section

Materials. [Co(tren)(CO₃)](ClO₄) was prepared from commercially available 2,2',2''-triaminotriethylamine tris(hydrochloride) (Strem Chemicals) or the free base (The Ames Laboratories, Inc., Milford, Conn.) by following previously described procedures.^{13,14}

[Co(tren)(OH₂)₂](ClO₄)₃ was prepared from the carbonate salt as described elsewhere.¹⁴ The purity of the compound was checked by elemental analysis¹⁵ and by the comparison of the UV-vis spectrum (Cary 118C spectrophotometer) with that reported earlier^{13,14} (see Table II). All chemicals were of reagent grade, and the laboratory-distilled water was further purified by passage through a mixed-bed anion-cation exchange resin column. Solid sodium metabisulfite, Na₂S₂O₅, was used as the source of sulfite; this salt is very stable in storage but hydrates very rapidly and completely upon dissolution in water to yield sulfite.²

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Table II. UV-Visible Absorption Spectra of Some S- and O-Bonded Sulfito Co(III) Species

complex ^a	λ_{\max} , nm	ϵ , M ⁻¹ cm ⁻¹	ref
Co(tren)(OH) ₂ ³⁺	503, 355	111, 87	this work
	503, 358	110, 83	13
	503, 358	110, 80	14
Co(tren)(OH) ₂ (OSO ₂) ⁺	510, 325	136, 1825	this work
Co(NH ₃) ₅ (OSO ₂) ⁺	518, 330	~88, ~2100	2
(en) ₂ Co(OS(O)-CH ₂ CH ₂ NH ₂) ₂ ²⁺	512, 326	134, 4100	18
Co(tren)(SO ₃) ₂ ⁻	450, 300	250, ~16 000	
	(sh)		
Co(NH ₃) ₅ SO ₃ ⁺	283, 225	17 500, 4000	this work
	456, 278	148, 18 600	2, 19, 20, 21, 22
(en) ₂ Co(S(O) ₂ -CH ₂ CH ₂ NH ₂) ₂ ²⁺	432, 288	220, 14 200	18
	472	159	20
<i>trans</i> -Co(NH ₃) ₄ (OH) ₂ (SO ₃) ⁺	473, 273	120, 6460	19
	452, 295	200, 20 900	21
<i>cis</i> -Co(NH ₃) ₄ (SO ₃) ₂ ⁻	264	20 000	
	454	210	23
<i>trans</i> -Co(NH ₃) ₄ (SO ₃) ₂ ⁻	~430 (sh), 327	490, 29 500	21
	463, 272	162, 13 800	24
Co(en) ₂ (SO ₃)(NH ₃) ⁺	452, 275	216, 6560	24
Co(en) ₂ (SO ₃)(NCS)	460, 275	240, 7110	24
Co(en) ₂ (OH)(SO ₃) ⁺	460, 280	158, 18 620	24
Co(en) ₂ (H ₂ O)(SO ₃) ⁺	465	162	25

^a en ≡ ethylenediamine.

Determination of Acid Dissociation Constants. The values for the first and second acid dissociation constants K_3 and K_4 for Co(tren)(OH)₂³⁺ were determined at five different temperatures and an ionic strength $I = 1.0$ M (NaClO₄) by titrating a 4×10^{-3} M complex solution with 0.1 M NaOH (see Table I). The pH measurements were made with a Fisher Model 420 pH/ion meter and a Markson combination electrode. The pK values utilized for the acid dissociation constants K_1 and K_2 of "H₂SO₃" (aqueous SO₂) at the various temperatures and an ionic strength of 1.0 M (NaClO₄) are also included in the tabulation.

Spectral Measurements. Preliminary experiments in which buffered Na₂S₂O₅, NaHSO₃, or Na₂SO₃ solutions were added to buffered Co(tren)(OH)₂³⁺ solutions showed an instantaneous color change from pink to orange at pH 4–7. At pH below 5.7 the orange solution slowly fades at room temperature to produce the almost colorless light pink solution characteristic of cobalt(II). At higher pH, however, the orange solution changes to a stable bright yellow solution. These color changes were followed spectrophotometrically in the UV-vis region by means of the Cary 118C spectrophotometer. It was observed that the concentration of the orange solution depended on the amount of sulfite added and the pH of the solution. The maximum concentration of the orange intermediate was found to occur in the range $5.5 \leq \text{pH} \leq 6.2$. The spectrum of the resulting solution was recorded at 10 °C to slow down its redox decomposition (pH < 5.7) or the subsequent formation of the yellow complex (pH > 7). A comparison of the UV-vis absorption spectrum of our orange intermediate with those previously reported for similar S- and O-bonded (sulfito)cobalt(III) species (Table II) shows clearly that the present intermediate conforms to the spectral criteria for the O-bonded arrangement. In addition, the formation of the intermediate is a reversible process. Thus acidification to pH ≤ 3 of its solutions immediately after its formation at pH > 7 results in the quantitative regeneration of the diaquo species. Acidification of analogous S-bonded complexes (e.g., *cis*-Co(en)₂(SO₃)(H₂O)⁺), however, results in small and rather slow spectral changes. These observations are in agreement with those recorded for the SO₂ uptake and elimination reactions of the aquopentaamminecobalt(III) species.² Attempts to isolate our O-bonded intermediate were unsuccessful due to its subsequent reactions leading either to redox decomposition at low pH or to the formation of the stable yellow species at high pH.¹² Recently, however, Adamson and co-workers¹⁸ have isolated what appears to be the first robust Co(III)

Table III. Dependence of SO₂ Uptake Rate Constant on pH and Total Sulfite at 10 °C

pH	S _T , M	k_{obsd} , s ⁻¹	k_t , s ⁻¹
4.0 ± 0.2	0.0136	116 ± 2	69 ± 2
	0.0266	204 ± 4	157 ± 4
	0.0419	316 ± 8	259 ± 8
4.2 ± 0.15	0.0537	404 ± 22	357 ± 22
	0.0094	77 ± 1	47 ± 1
	0.0188	113 ± 4	83 ± 4
4.5 ± 0.01	0.0376	211 ± 5	181 ± 5
	0.0470	265 ± 7	235 ± 7
	0.0657	395 ± 8	365 ± 8
5.0 ± 0.1	0.0096	50 ± 1	35 ± 1
	0.0166	75 ± 2	60 ± 2
	0.0250	107 ± 2	92 ± 2
6.0 ± 0.1	0.0306	137 ± 2	122 ± 2
	0.0444	191 ± 5	176 ± 5
	0.0094	26.0 ± 0.2	21.3 ± 0.2
6.7 ± 0.1	0.0188	47 ± 2	42 ± 2
	0.0376	101 ± 2	96 ± 2
	0.0470	125 ± 1	120 ± 1
6.0 ± 0.1	0.0657	176 ± 3	171 ± 3
	0.0088	4.8 ± 0.2	4.3 ± 0.2
	0.0138	7.4 ± 0.2	6.9 ± 0.2
6.7 ± 0.1	0.0190	11.2 ± 0.1	10.7 ± 0.1
	0.0217	13.2 ± 0.2	12.7 ± 0.2
	0.0283	18.5 ± 0.2	18.0 ± 0.2
6.7 ± 0.1	0.0094	1.03 ± 0.04	0.94 ± 0.04
	0.0188	2.18 ± 0.02	2.09 ± 0.02
	0.0376	5.6 ± 0.1	5.5 ± 0.1
6.7 ± 0.1	0.0470	7.9 ± 0.1	7.8 ± 0.1
	0.0657	12.9 ± 0.2	12.8 ± 0.1

complex containing an O-bonded sulfite ligand [(en)₂Co(OS(O)-CH₂CH₂NH₂)₂]²⁺. The spectral characteristics of this species parallel very closely those observed for our orange intermediate (Table II).

Rate Measurements. All rate measurements were made at an ionic strength of 1.0 M (NaClO₄) over the ranges of temperature, pH, and total sulfite concentration given in the Results. The "equilibrium method"^{22,26} was employed to study the SO₂ uptake process. In this method appropriate amounts of solid [Co(tren)(OH)₂]₂(ClO₄)₃ are dissolved in McIlvaine phosphate-citric acid buffers²⁷ of a given pH value, and the ionic strength is adjusted to 1.0 M with NaClO₄. Similarly known amounts of solid Na₂S₂O₅ are dissolved in the same buffer system with the same ionic strength adjustment. The resulting solutions are thermostated and introduced separately into the thermostated storage syringes of an automated Durrum Model 110 stopped-flow assembly, and the runs are made in the usual fashion. The reactions were studied under pseudo-first-order conditions in which the sulfite concentration is at least 10 times that of the Co(III) complex. Most of the experiments were performed at a wavelength setting of 430 nm, with some done at 410 and 480 nm, and no variations were indicated in the rate data derived. The SO₂ elimination process was followed by a "pH-jump" procedure. In this, the O-bonded (sulfito) species is prepared in situ by dissolving appropriate amounts of solid Co(tren)(OH)₂(ClO₄)₃ in 1 M NaClO₄ at 0–5 °C, adding Na₂S₂O₅ to give a molar ratio of complex to sulfur(IV) of 1:2, and immediately adjusting the pH to 5.5 in order to stabilize the rapidly formed sulfite species. This solution is placed in one syringe of the stopped-flow assembly and reacted with phosphate-citrate buffer solution of the appropriate pH in the other syringe. All observed pseudo-first-order rate constants were obtained from automated least-squares analysis of the digitalized stopped-flow data and are

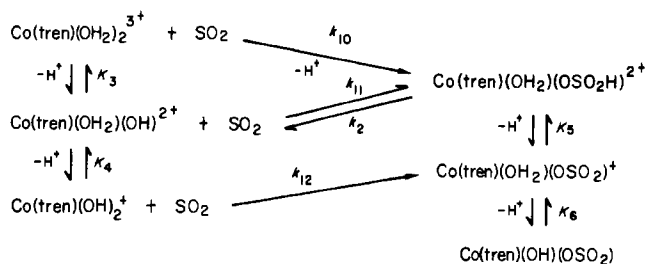
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Table IV. Dependence of SO₂ Uptake Rate Constant on pH and Temperature at S_T = 0.038 M

temp, °C	pH	k _{obsd} , s ⁻¹	k _f , s ⁻¹	pH	k _{obsd} , s ⁻¹	k _f , s ⁻¹	pH	k _{obsd} , s ⁻¹	k _f , s ⁻¹	
10.0	3.50	474 ± 26	325 ± 26	4.49	152 ± 2	137 ± 2	5.85	32 ± 1	31 ± 1	
	3.50	481 ± 28	332 ± 28	4.54	172 ± 4	158 ± 4	5.85	29.6 ± 0.4	29 ± 0.4	
	3.65	425 ± 16	320 ± 16	4.57	146 ± 3	133 ± 3	5.90	25.2 ± 0.6	24.6 ± 0.6	
	3.76	357 ± 6	275 ± 6	4.68	134 ± 3	124 ± 3	5.91	28.3 ± 0.6	28 ± 0.6	
	3.81	271 ± 5	198 ± 5	4.91	119 ± 3	113 ± 3	5.92	27.9 ± 0.3	27.3 ± 0.3	
	3.83	286 ± 10	216 ± 10	4.97	101 ± 5	96 ± 5	5.92	28.0 ± 0.3	27.4 ± 0.3	
	3.85	257 ± 6	191 ± 6	4.99	101 ± 2	96 ± 2	5.96	26.7 ± 0.3	26.2 ± 0.3	
	3.86	276 ± 13	211 ± 13	5.01	96 ± 1	91 ± 1	5.99	21.8 ± 0.4	21.3 ± 0.4	
	3.90	261 ± 4	202 ± 4	5.12	73 ± 3	69 ± 3	6.06	18.8 ± 0.3	18.4 ± 0.3	
	3.98	262 ± 10	213 ± 10	5.23	77 ± 1	74 ± 1	6.06	20.6 ± 0.7	20.2 ± 0.3	
	3.98	270 ± 10	221 ± 10	5.33	64 ± 2	62 ± 2	6.10	19.3 ± 0.4	19 ± 0.4	
	4.10	229 ± 10	192 ± 10	5.33	64 ± 2	62 ± 2	6.17	18.2 ± 0.3	18.0 ± 0.3	
	4.15	224 ± 4	191 ± 4	5.35	63 ± 3	61 ± 3	6.28	12.0 ± 0.3	11.8 ± 0.3	
	4.19	209 ± 6	179 ± 6	5.45	64 ± 1	62 ± 1	6.34	10.3 ± 0.2	10.1 ± 0.2	
	4.20	211 ± 5	181 ± 5	5.50	51 ± 0.5	49 ± 1	6.37	12.5 ± 0.7	12.3 ± 0.7	
	4.29	182 ± 4	158 ± 4	5.66	43 ± 1	42 ± 1	6.53	6.4 ± 0.2	6.3 ± 0.2	
	4.32	179 ± 4	157 ± 4	5.78	30.7 ± 0.3	30 ± 0.5	6.57	6.2 ± 0.3	6.1 ± 0.3	
	4.46	154 ± 4	138 ± 4	5.85	27.5 ± 0.6	27 ± 0.6	6.58	6.7 ± 0.1	6.6 ± 0.1	
	14.0	3.98	456 ± 30	386 ± 30	4.49	248 ± 3	226 ± 3	5.37	88 ± 2	86 ± 2
		4.07	408 ± 23	352 ± 13	4.83	185 ± 2	175 ± 2	5.85	43 ± 1	42 ± 1
4.12		385 ± 19	335 ± 19	5.02	148 ± 2	142 ± 2	5.91	42 ± 1	41 ± 1	
4.18		365 ± 18	321 ± 18	5.05	130 ± 3	124 ± 3	6.10	29 ± 1	28 ± 1	
4.29		301 ± 12	267 ± 12	5.24	102 ± 1	98 ± 1	6.17	22.3 ± 1	22 ± 1	
4.37		272 ± 7	244 ± 7	5.34	91 ± 1	88 ± 1	6.37	15.7 ± 1	15 ± 1	
6.58							6.58	10.0 ± 0.4	10 ± 0.4	
18.0	4.49	400 ± 22	374 ± 22	5.22	124 ± 3	119 ± 3	5.91	53 ± 1	52 ± 1	
	4.63	352 ± 19	333 ± 19	5.36	124 ± 1	120 ± 1	6.10	33 ± 1	32 ± 1	
	4.84	286 ± 10	274 ± 10	5.38	117 ± 2	114 ± 2	6.17	30 ± 1	29 ± 1	
	4.87	220 ± 15	209 ± 15	5.57	82 ± 1	80 ± 1	6.37	22 ± 1	22 ± 1	
	5.02	205 ± 3	197 ± 3	5.79	58 ± 2	57 ± 2	6.58	13 ± 0.3	13 ± 0.3	
	5.19	155 ± 4	150 ± 4	5.85	61 ± 3	60 ± 3				
	6.37						6.37	30 ± 1	29 ± 1	
22.0	5.85	81 ± 2	79 ± 2	6.10	41 ± 2	40 ± 2	6.58	19 ± 1	19 ± 1	
	5.91	80 ± 2	78 ± 2	6.17	37 ± 2	37 ± 2				
25.0	5.85	99 ± 2	97 ± 2	6.10	54 ± 2	53 ± 2	6.37	36 ± 1	35 ± 2	
	5.91	90 ± 2	88 ± 2	6.17	50 ± 2	49 ± 2	6.58	22 ± 1	22 ± 1	

Scheme I



reported as the mean of at least six kinetic runs.

Results and Discussion

The SO₂ uptake process was first studied at 10 °C as a function of total sulfite concentration S_T at various pH values between 4 and 6.7. These data appear in Table III, and an essentially linear dependence of k_{obsd} on S_T is noted at each pH. Our second set of data was obtained at a fixed S_T value of 0.038 M, within the acidity range 3.5 < pH < 6.6 and at a number of temperatures in the range 10–25 °C. These data, given in Table IV, illustrate the steep decline in k_{obsd} as the pH is increased. It is clear that the SO₂ uptake behavior of this complex is very similar to that of the pentaamine analogue, so we devised a reaction mechanism analogous to that proposed for the pentaamine² (see Scheme I) but including some new features proven necessary in our subsequent detailed analysis of the present data. As will be shown below, these modifications require that allowances be made for SO₂ reactions with the diaquo and dihydroxo species, as well as with *cis*-Co(tren)(H₂O)(OH)²⁺, the most prevalent species over a considerable part of the pH range of the experiments.

According to Scheme I, the observed pseudo-first-order rate constants should be the sum of a forward rate constant k_f for

SO₂ uptake and a backward rate constant k_b for SO₂ elimination from the protonated sulfite product such that

$$k_{\text{obsd}} = k_f + k_b \quad (1)$$

It is readily derived from the proposed mechanism that

$$k_f = \left(\frac{k_{10}[\text{H}^+]}{K_3} + k_{11} + \frac{k_{12}K_4}{[\text{H}^+]} \right) \left(\frac{K_3[\text{H}^+]}{[\text{H}^+]^2 + K_3[\text{H}^+] + K_3K_4} \right) [\text{SO}_2] \quad (2)$$

and

$$k_b = k_2[\text{H}^+]^2 / ([\text{H}^+]^2 + K_5[\text{H}^+] + K_5K_6) \quad (3)$$

Also, the SO₂ concentration may be calculated at each pH from the equation

$$[\text{SO}_2] = [\text{H}^+]^2 S_T / ([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2) \quad (4)$$

At low [H⁺] (pH > 5.5), there is an almost negligible contribution from the reverse process, so that the expression for k_{obsd} (eq 1) reduced to that for k_f (eq 2). As will be obvious later, the term involving k₁₀ is much smaller than those involving k₁₁ and k₁₂ in this pH range, so the observed rate constant is given by

$$k_{\text{obsd}} = k_f = \left(k_{11} + \frac{k_{12}K_4}{[\text{H}^+]} \right) \left(\frac{K_3[\text{H}^+]}{[\text{H}^+]^2 + K_3[\text{H}^+] + K_3K_4} \right) [\text{SO}_2] \quad (5)$$

This equation can be cast in either of two forms which enable evaluations of k₁₁ and k₁₂K₄. In the first of these, we have

$$k' = \frac{k_{\text{obsd}}([\text{H}^+]^2 + K_3[\text{H}^+] + K_3K_4)}{K_3[\text{H}^+][\text{SO}_2]} = k_{11} + k_{12}K_4/[\text{H}^+] \quad (6)$$

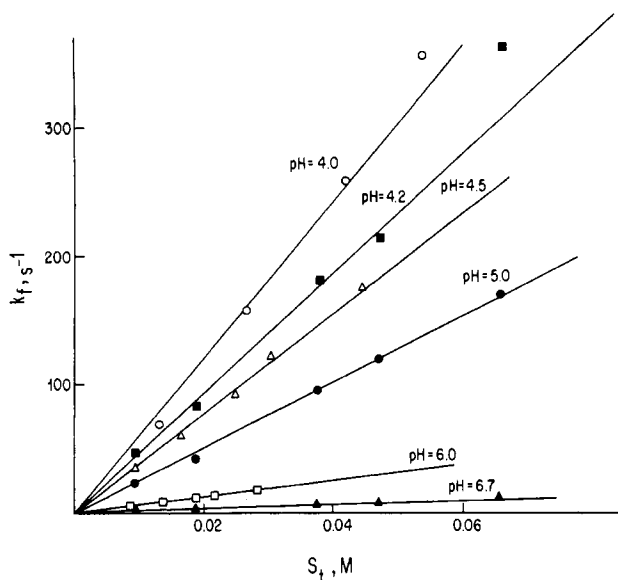
Table VII. Rate Constants and Activation Parameters for the SO₂ Elimination Reaction

temp, °C	10 ⁻⁵ k' ₂ , M ⁻¹ s ⁻¹	10 ⁴ K ₅ , ^a M	10 ⁷ k ₂ = k' ₂ K ₅ , s ⁻¹
6.0	3.0 ± 0.1	3.4	1.2
10.0	4.7 ± 0.2	2.7	1.3
14.0	6.6 ± 0.2	2.1	1.4
18.0	8.0 ± 0.3	1.6	1.3

$$\Delta H^\ddagger = 11.1 \pm 0.8 \text{ kcal mol}^{-1}$$

$$\Delta S^\ddagger = 7.0 \pm 0.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

^a Estimated as explained in footnote 28a.

**Figure 2.** Variation of SO₂ uptake rate constant, k_f , with total sulfite concentration at several fixed acidities at 10 °C.

existing data.^{28a} While there is little doubt that $K_5K_6 \ll [H^+]$,^{28b} the requirement that K_5 substantially exceed $[H^+]$ over the whole range of the experiments is not fulfilled. However, K_5 is probably large enough to approximate to the linear variation expressed by (8). The estimated values of K_5 for the various temperatures have therefore been used to determine the "true" second-order rate constants k_2 which are included in Table VII. It is seen that k_2 appears to be essentially independent of temperature in the range studied. However, this is a result of procedure for estimating the change in K_5 with temperature and should not therefore be given much weight. The figures quoted in Table IX relate in fact to the composite rate constant k'_2 .

The determination of the rate parameters for the reaction of the diaquo species with molecular SO₂ was accomplished

(28) (a) The pK for proton dissociation from the O-bonded selenito ligand in the species *cis*-Co(en)₂(OH₂)(OSeO₂H)²⁺ is given^{28a} as 4.35 at 25 °C. However, aqueous selenic acid is a little weaker than aqueous SO₂ (the pKs for the two species are 2.36 and 1.90 at 25 °C, respectively). One should therefore expect a value for pK₅ in our system of a little less than 4 at 25 °C. We have consequently adopted a value for this of 3.9 at 25 °C. Then, assuming K_5 has the same temperature variation as K_1 for aqueous SO₂ (Table I), one derives the values given in Table VII for K_5 at the various experimental temperatures. (b) The value of the pK corresponding to pK₆ for the sulfur-bonded species *trans*-Co(en)₂(OH₂)(SO₃)⁺ is known⁶ to be 9.45 at 25 °C. While the parallel to our system is not by any means clear-cut, an order of magnitude estimate for K_5K_6 can reasonably be set at $<10^{-12}$, thus considerably smaller than any of the $[H^+]^2$ values of the applicable data.

(29) Dasgupta, T. P.; Harris, G. M., in preparation.

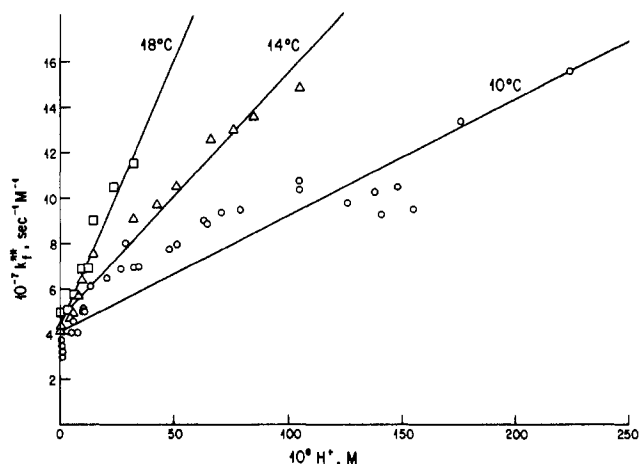
(30) Dash, A. C.; El-Awady, A. A.; Harris, G. M., in press.

(31) DeJovine, J. M.; Wan, W. K.; Harris, G. M., in preparation.

(32) Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* **1978**, *17*, 3123.

(33) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965.

(34) Harris, G. M.; Hyde, K. E. *Inorg. Chem.* **1978**, *17*, 1892.

**Figure 3.** Variation of quantity $k^{**} = k_f(K_3 + [H^+])/K_3[SO_2]$ with $[H^+]$ at several fixed temperatures.

as now described. At high $[H^+]$ (pH < 5.5), the fraction in the dihydroxo form is negligible, and we can thus neglect its contribution to the forward rate constant, the equation for which thus takes the form (see (2))

$$k_f = \left(\frac{k_{10}[H^+]}{K_3} + k_{11} \right) \left(\frac{K_3}{K_3 + [H^+]} \right) [SO_2] \quad (9)$$

Equation 9 can be rearranged to give

$$k_f \left(\frac{K_3 + [H^+]}{K_3[SO_2]} \right) = \frac{k_{10}}{K_3} [H^+] + k_{11} \quad (10)$$

Plots of the left-hand side of (10) (symbolized as k^{**}), calculated by use of the k_f values in Tables III and IV and the other known parameters vs. $[H^+]$ at the various temperatures yield straight lines of intercept k_{11} and slope k_{10}/K_3 (see Figure 3). Least-squares analysis of the plots yields the following values of k_{10} and k_{11} : $10^{-5}k_{10} = 5.0 \pm 0.3$, 12 ± 1 , and $30 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$ at 10.0, 14.0, and 18.0 °C, respectively, and $10^{-7}k_{11} = 4.1 \pm 0.2$, 4.7 ± 0.3 , and $4.2 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ at the same temperatures. The latter values are somewhat deviant from the more dependable values of Table V, but they do attest to the internal consistency of the treatment. The activation parameters for k_{10} are $\Delta H^\ddagger = 36 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 94 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$. These are very far removed from the corresponding values relating to k_{11} and k_{12} (Table V). However, they perhaps should not be taken too seriously without further confirmation, since the derivation of both k_{10} and k_{11} from (10) requires the use of k_f values for which the subtracted k_b corrections are very substantial (see data of Tables III and IV for pH < 5.5).

One final confirmation of the efficacy of our analysis of the rate data is provided by considering only the k_f values in the intermediate pH range ($5.5 < \text{pH} < 6.2$). Under these conditions the SO₂ uptake reactions of both the diaquo and dihydroxo species make a relatively small contribution, and (2) reduces to

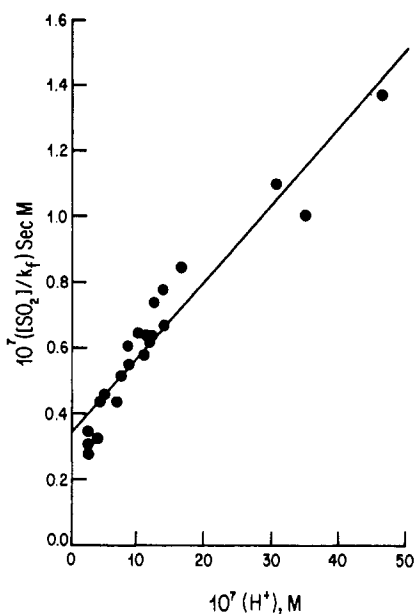
$$k_f = k_{11} \left(\frac{K_3}{[H^+] + K_3} \right) [SO_2] \quad (11)$$

A plot of $[SO_2]/k_f$ vs. $[H^+]$ should be linear with a slope of $1/k_{11}K_3$ and an intercept of $1/k_{11}$. Such a plot for data at 10 °C is shown in Figure 4, and the derived values are $k_{11} = (3.0 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $\text{p}K_3 = 5.8 \pm 0.1$. It is seen that both these values are in reasonable agreement with the results quoted in Tables V and I, respectively.

Table VIII. Rate Constants for the Reaction of Various Aquoamminecobalt(III) Complex Ions with Some Group 6 Oxides and Oxyanions in Aqueous Solution at 25 °C^a

complex ion	reactant	k , M ⁻¹ s ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal deg ⁻¹ mol ⁻¹	ref
Co(tren)(OH) ₂ ³⁺	SO ₂	9 × 10 ⁶	36 ± 1	94 ± 3	this work
Co(tren)(OH)(OH ₂) ²⁺	SO ₂	5.3 × 10 ⁷	4.5 ± 0.1	-8.0 ± 0.3	this work
Co(tren)(OH) ₂ ⁺	SO ₂	2.4 × 10 ⁹	11.5 ± 0.3	23 ± 3	this work
<i>cis</i> -Co(en) ₂ (OH)(OH ₂) ²⁺	SO ₂	1.0 × 10 ⁸	6.0 ± 0.1	-1.6 ± 0.2	29
Co(NH ₃) ₅ OH ²⁺	SO ₂	4.7 × 10 ⁸	9.8 ± 0.3	14.0 ± 0.4	2
Co(tetren)OH ²⁺	SO ₂	3.3 × 10 ⁸	-0.5 ± 1.0	-21 ± 3.5	30
<i>trans</i> -Co(en) ₂ (SO ₃)(OH ₂) ⁺	SO ₃ ²⁻	600 ^b			7
Co(NH ₃) ₅ OH ₂ ³⁺	HSeO ₃ ⁻	147	13.5 ± 0.5	-9.0 ± 1.0	9b
Co(NH ₃) ₅ OH ²⁺	HSeO ₃ ⁻	8			9c
Rh(NH ₃) ₅ OH ²⁺	HSeO ₃ ⁻	20			9c
<i>cis</i> -Co(en) ₂ (OH ₂) ₂ ³⁺	HSeO ₃ ⁻	281 ^b	13.0 ± 0.5	-9.6 ± 1.0	9b
<i>cis</i> -Co(en) ₂ (OH)(OH ₂) ²⁺	HSeO ₃ ⁻	4			9c
<i>trans</i> -Co(en) ₂ (OH ₂) ₂ ³⁺	HSeO ₃ ⁻	787 ^b	11.5 ± 0.6	-12.6 ± 1.4	9b
<i>cis</i> -Co(tn) ₂ (OH ₂) ₂ ³⁺	HSeO ₃ ⁻	291 ^b	12.9 ± 0.3	-9.9 ± 0.9	9b
<i>trans</i> -Co(tn) ₂ (OH ₂) ₂ ³⁺	HSeO ₃ ⁻	1032 ^b	12.1 ± 0.8	-10.1 ± 1.1	9b
Co(NH ₃) ₅ OH ₂ ³⁺	HMoO ₄ ⁻	3.2 × 10 ⁵			10
Co(NH ₃) ₅ OH ²⁺	HMoO ₄ ⁻	6.6 × 10 ⁴			10
<i>cis</i> -Co(en) ₂ (OH ₂) ₂ ³⁺	HWO ₄ ⁻	3.2 × 10 ⁷			11
<i>cis</i> -Co(en) ₂ (OH)(OH ₂) ²⁺	HWO ₄ ⁻	1.0 × 10 ⁷			11
Co(tren)(OH)(OH ₂) ²⁺	CO ₂	44	14.7 ± 0.1	-1.9 ± 0.2	14
Co(NH ₃) ₅ OH ²⁺	CO ₂	220	15.3 ± 0.9	3.6 ± 3.0	26
<i>cis</i> -Co(en) ₂ (OH)(OH ₂) ²⁺	CO ₂	280	14.8 ± 0.2	2.0 ± 0.8	31

^a tetren ≡ tetraethylenepentamine; tn ≡ trimethylenediamine. ^b Limiting second-order rate constants estimated by use of ion-pairing data discussed in the respective references—i.e., $k_2(\text{lim}) = (k_1(\text{lim}))K_{\text{IP}}$ (no similar ion-pairing effects found for SO₂ or CO₂ reactions).

**Figure 4.** Variation of quantity $[SO_2]/k_f$ with $[H^+]$ at 10 °C.

A number of fruitful comparisons may now be made concerning the relative reactivities of cobalt(III)-aquo complex ions toward SO₂ as well as SO₃²⁻ and several other group 6 oxyanions. Similar comparisons are also possible with respect to the acid-catalyzed decomposition rates of some of the product complexes. The available data on these two types of reactions are summarized in Tables VIII and IX, all expressed as rate constants extrapolated³⁵ where necessary to 25 °C. Some examples of carbonate data are also included for use in the discussion to follow. Considering first the formation reactions of Table VIII, the most obvious feature is the division

Table IX. Rate Constants for the Aqueation Reactions of Various Protonated Sulfito and Selenito Complex Ions in Aqueous Solutions at 25 °C

complex	k , s ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal deg ⁻¹ mol ⁻¹	ref
Co(tren)(OH ₂)-(OSO ₂ H) ²⁺	3.8 × 10 ³	11.1 ± 0.8	7.0 ± 0.4	this work
<i>cis</i> -Co(en) ₂ (OH ₂)-(OSO ₂ H) ²⁺	6.0 × 10 ³ ^a			29
Co(NH ₃) ₅ (OSO ₂ H) ²⁺	1.0 × 10 ³ ^a			2
Co(tetren)(OSO ₂ H) ²⁺	1.1 × 10 ³	7.2 ± 2.5	-20.4 ± 8.7	30
Co(NH ₃) ₅ (OSeO ₂ H) ²⁺	0.28	12.3 ± 0.8	-19.5 ± 2.7	9b
<i>cis</i> -Co(en) ₂ (OH ₂)-(OSeO ₂ H) ²⁺	0.18	12.4 ± 0.8	-15.3 ± 2.0	9b
<i>trans</i> -Co(en) ₂ (OH ₂)-(OSeO ₂ H) ²⁺	1.1	11.7 ± 0.6	-20.5 ± 2.8	9b
<i>cis</i> -Co(tn) ₂ (OH ₂)-(OSeO ₂ H) ²⁺	0.20	12.6 ± 0.7	-19.4 ± 2.8	9b
<i>trans</i> -Co(tn) ₂ (OH ₂)-(OSeO ₂ H) ²⁺	0.32	12.9 ± 0.7	-18.8 ± 2.6	9b
Co(tren)(OH ₂)-(OCO ₂ H) ²⁺	1.19	14.3 ± 0.4	-10.2 ± 1.2	32
Co(NH ₃) ₅ OCO ₂ H ²⁺	1.10	16.8 ± 0.2	-2 ± 1	33
<i>cis</i> -Co(en) ₂ (OH ₂)-(OCO ₂ H) ²⁺	0.45			34

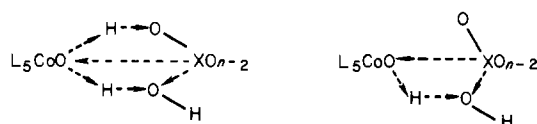
^a Extrapolated from data at 10 °C by using the same ΔH^\ddagger value and the same acid dissociation constant for the OSO₂H ligand as for the "tetren" and "tren" analogues for the (NH₃)₅ and (en)₂ species, respectively.

of the second-order rate constant values into two main groupings. Thus, the values for SO₂, HMoO₄⁻ and HWO₄⁻ fall within the range of approximately 10⁵-10⁹ M⁻¹ s⁻¹, while for SO₃²⁻ and HSeO₃⁻, the range is about 10-10³ M⁻¹ s⁻¹, which also is seen to bracket the values for comparable CO₂ uptake reactions. It is clear that the major factor determining these rate groupings is the increase in ΔH^\ddagger and decrease in ΔS^\ddagger for the slower group, indicative of less facile processes from the standpoint of both energy input into and ease of achieving the appropriate geometry for the transition state. In all examples given, the mechanisms suggested by the authors involve direct addition of the entering group 6 center to the oxygen of the Co-OH or Co-OH₂ moiety. This requires,

(35) The temperature dependence parameters for the first rate constant of Table VIII (k_{10} in the text of this paper) are subject to considerable error, so the extrapolation may not give a valid comparison with the succeeding entry (k_{11} in the text). The actual experimental values at 18 °C are 3.0 × 10⁶ and 4.2 × 10⁷ M⁻¹ s⁻¹, respectively, a difference ratio of 14 rather than the much smaller ratio of 6 from the table.

in the case of SO_2 uptake by Co-OH or Co-OH_2 , the concerted release of one or two protons, respectively, to yield the stable sulfite product.³⁶ Uptake of the anionic species similarly consists of nucleophilic attack by the cobalt(III) moiety on the group 6 center.⁹⁻¹¹ Here, however, concerted release of a water molecule must occur, utilizing an oxygen atom from the entering oxyanion, which can only be fast if oxygen release by the oxyanion occurs readily.¹¹ One notes that this process occurs much more readily for HMoO_4^- and HWO_4^- than for SO_3^{2-} or HSeO_3^- . A possible measure of the relative rates of oxygen atom release from these anions in the uptake reaction is provided by data on oxygen exchange between the various anions and solvent water. For HMoO_4^- and HWO_4^- , this exchange is known¹¹ to be complete in less than 20 s at 25 °C, while SO_3^{2-} and HSeO_3^- are also stated³⁷ to exchange rapidly and completely with water. However, these latter measurements were made in boiling water, but a recent study³⁸ of water exchange with selenite reports an exchange half-time of about 1 h at 0 °C for either SeO_3^{2-} or HSeO_3^- . No temperature dependence data are given, but a fair conjecture (assuming $\Delta H^\ddagger = 25 \text{ kcal mol}^{-1}$) suggests a half-time value of the order of about 1 min at 25 °C, not too different from the molybdate or tungstate figures.

An interesting contrast between the simpler SO_2 addition and the oxyanion additions is that the latter occur somewhat more readily with the Co-OH_2 grouping than with Co-OH , the reverse of our finding in the present work.³⁹ The two forms of the transition state for the HXO_n^- anions may be visualized as⁹



Apparently, the presence of the additional proton in the first

(36) This mechanism is completely analogous to that for CO_2 uptake, which however is a much slower process (see the final entries in Table VIII). This deceleration must result from a combination of the several factors which would tend to hinder CO_2 addition as compared to SO_2 , such as its smaller size, its rigidly linear geometry, the carbon atom's lack of readily available "lone pair" electrons or d orbitals, and perhaps the lower degree of solvation of CO_2 (as indicated by its much lower solubility in water).

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(38) Okumura, A.; Okazaki, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1084.

(39) Evidence for a reaction of this type was not observed in the pentaammine study.² However, in the latter system, the SO_2 uptake reaction becomes too fast for stopped-flow measurement at the low pH values required to obtain the appropriate data. In the case of CO_2 uptake, the carbonate complex product is completely unstable at pH values low enough to ensure the presence of an appreciable fraction of the aquo complex in the totally protonated form.

of these somewhat labilizes the system and accelerates the various bond adjustments required to release the water molecule. However, in SO_2 uptake, it is to be expected that the double proton release in the Co-OH_2 system should be somewhat more difficult to accomplish than the single release with the Co-OH analogue. One notes in contrast that the interaction of SO_4^{2-} appears to be a straightforward dissociative anation which occurs at the slow rate (half-time of many hours at room temperature) characteristic of Co-OH_2 bond fission.⁴⁰ This contrast is clearly the result of the extreme inertness of the SO_4^{2-} entity in aqueous solution, for which oxygen exchange with the solvent has a half-time at 100 °C of several hours even in strongly acidic solution⁴¹ and is much slower otherwise.

Turning now to the elimination rate data of Table IX, we again note the large contrast in rate constants for the sulfite and selenite species. However, here the mechanisms proposed provide a straightforward explanation. For the various protonated sulfite species, the decomposition is accomplished by molecular SO_2 elimination, and there should be no substantial rate constant variations within the group, as is seen to be true (all are within a factor of 6 of one another). The selenite complexes, by contrast, decompose much more slowly (factors between 10^3 and 10^4) though they differ among themselves by a factor again of only about 6. The problem with the selenite release process is probably related to the necessity of including a water molecule in the transition state, explaining in part the large negative ΔS^\ddagger values observed for all these reactions.⁴² Again, however, sulfate complexes do not conform to the pattern, since their aquation appears to involve conventional Co-O bond fission, so that typically the aquation rate constant is many orders of magnitude lower than for any of the SO_3^{2-} or SeO_3^{2-} complexes mentioned above.⁴⁰

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Registry No. $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{3+}$, 41884-78-0; $\text{Co}(\text{tren})(\text{OH})(\text{OH}_2)^{2+}$, 29086-25-7; $\text{Co}(\text{tren})(\text{OH})_2^+$, 55328-50-2; SO_2 , 7446-09-5; $\text{Co}(\text{tren})(\text{OH}_2)(\text{OSO}_2\text{H})^{2+}$, 77029-31-3; $\text{Co}(\text{tren})(\text{OH}_2)(\text{OSO}_2)^+$, 77029-32-4; $\text{Co}(\text{tren})(\text{SO}_3)_2^-$, 77029-33-5.

(40) Haim, A. *Inorg. Chem.* **1970**, *9*, 426.

(41) Radmer, R. *Inorg. Chem.* **1972**, *11*, 1162.

(42) Again it is noted that the rate of the CO_2 reaction is much smaller than that of the SO_2 analogue, although it is much like that of HSeO_3^- . In the formation of the transition state for the elimination reaction, factors of the type invoked³⁶ for the uptake reaction must again come into play.