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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 4. Intramolecular Electron-Transfer and Sulfito Ligand Addition Reactions of Aquo(sulfito-*O*)(2,2′,2″-triaminotriethylamine)cobalt(III) Ion[1,2]

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The title complex ion, $[Co(tren)(OH_2)(OSO_2)]^+$, is produced by the rapid reversible uptake of SO_2 by the aquo analogue, $[Co(tren)(OH_2)(OH)]^{2+}$, and subsequently undergoes two types of much slower reaction, depending on the pH of the system. The first of these, taking place within the range $2.9 < pH < 5.4$, is an internal redox process that produces cobalt(II) and sulfate in an exact stoichiometric ratio. The rate of this reaction is nearly independent of total sulfite concentration ($0.04 < [S]_t < 0.16$ M) and $[H^+]$, with a limiting rate constant at the high-pH end of the range of $k_3 = 1.0 \times 10^{-3}$ s^{-1} at 25 °C ($\Delta H^{*} = 24.2 \pm 2.0$ kcal mol^{-1} and $\Delta S^{*} = 8.2 \pm 6.6$ cal deg^{-1} mol^{-1} within the limits $15.7 < t < 34.2$ °C). However, over the range $7.2 < pH < 8.9$, internal redox no longer occurs, the only observable reaction being addition of a second sulfite group to yield a complex ion of stoichiometry $[Co(tren)(SO_3)_2]^-$. This reaction is first order in total sulfite concentration at a given pH and varies with $[H^+]$ such that $k_{obsd}/[S]_t = a[H^+]/([H^+] + b)$. Mechanisms that are consistent with these data involve either SO_3^{2-} addition to the complex $[Co(tren)(OH_2)(OSO_2)]^+$ or HSO_3^- addition to the deprotonated congener $[Co(tren)(OH)(OSO_2)]$ as the rate-determining step. The corresponding rate constants at 25 °C are 0.40 and 2.0 M^{-1} s^{-1}, respectively, with $\Delta H^{*} \sim 12$ kcal mol^{-1} in both cases and $\Delta S^{*} \sim -19$ and -16 cal deg^{-1} mol^{-1}, respectively, within the limits $6.7 < t < 25.0$ °C. Infrared spectral data suggest that the disulfito end product contains one O-bonded and one S-bonded sulfito ligand, and so the complex may be designated $[Co(tren)(OSO_2)(SO_3)]^-$, but this interpretation is not fully consistent with the rate data.

Introduction

The second paper in this series[3] presented the results of our investigation of the formation and aquation kinetics of the title compound, $[Co(tren)(OH_2)(OSO_2)]^+$. An earlier study[4] had indicated that, at least for the pentaammine analogue, the next step is an internal electron-transfer reaction leading to cobalt(II) and sulfate as the final products of the reaction over a fairly wide pH range (3.4–7.7). However, a recent study[5] of the S-bonded *trans*-aquobis(ethylenediamine)(sulfito)cobalt(III)/sulfite system suggests the possibility of additional sulfite uptake in the tetraamine aquosulfite system to form a disulfito final product, at least at the high-pH end of the scale. We have now looked for these eventualities in the case of the tren congener and find evidence for both types of behavior such that internal redox is the major process when pH ≤ 5.4, while formation of a disulfito species is the only observable reaction when pH ≥ 7.2. Kinetic studies have been completed for both of these processes, permitting the postulation of detailed mechanisms for each.

Experimental Section

Materials. All chemicals used 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, $Na_2S_2O_5$, was used as the source of sulfite as in the previous studies.[3,4] $[Co(tren)(CO_3)](ClO_4)$ and $[Co(tren)(OH_2)_2](ClO_4)_3$ were prepared by methods reported in the literature.[3,6,7] The purity of these compounds was checked by elemental analysis[8] and by comparison of the UV–vis spectra (Cary 118 spectrophotometer) to those reported earlier. $[Co(tren)(OH_2)_2]Cl_3$ was prepared in solution from the corresponding perchlorate salt by exchanging the perchlorate for chloride with use of a Bio-Rad AG-1 X-8 (100–200) mesh anion-exchange resin column in the chloride form. $[Co(tren)(OH_2)(OSO_2)](ClO_4)$ was prepared in situ by dissolving appropriate amounts of $Co(tren)(OH_2)_2(ClO_4)_3$ in water at 0–5 °C and adding $Na_2S_2O_5$ to give a molar ratio of complex to sulfur of 1:2 or 1:4. The pH was immediately adjusted to 5.5 and the spectrum recorded. The postulated new compound, $Na[Co(tren)(SO_3)_2]$, was prepared from the carbonato salt. A 1-g sample of $[Co(tren)(CO_3)]ClO_4$ was dissolved in 15 mL of water and 1.5 g of $Na_2S_2O_5$ added. The resulting solution was heated on a steam bath until a yellow crust appeared on the surface. The mixture was then cooled, filtered, washed with alcohol, and air-dried. The resulting yellow solid was recrystallized from the minimum amount of water and evaporated at room temperature until formation of the yellow solid commenced, which was collected as before; yield ~40%. Anal. Calcd for $Na[Co(tren)(SO_3)_2]\cdot 6H_2O$: Co, 11.87; C, 14.52; N, 11.29; H, 6.09; S, 12.92. Found: Co, 12.18; C, 14.63; N, 11.19; H, 5.28; S, 14.34; Cl, 0.27. Chloride is seen to be negligible, so there is practically no unreacted complex as an impurity. However, the low H and high S percentages suggest the possibility of a small amount of sodium sulfite or sulfate impurity, with perhaps fewer water molecules of crystallization.

$[Co(tren)(SO_3)_2]Na\cdot NaClO_4\cdot H_2O$. In an attempt to isolate the same compound obtained in the kinetic experiments, we decided to do the preparation under the conditions of these experiments. In this preparation 2 g of $[Co(tren)(OH_2)_2](ClO_4)_3$ was dissolved in 10 mL of H_2O. In a separate beaker 1.5 g of $Na_2S_2O_5$ was dissolved in 10 mL of water and the pH adjusted to 8.0 with 5.0 M NaOH. The two solutions were then mixed, and the pH was adjusted once more to 8.0. The resulting solution was left standing in the beaker overnight to enable slow evaporation. A yellow powder was isolated, filtered, washed with alcohol, and air-dried. The solid was recrystallized from a minimum amount of water, separated by slow evaporation at room temperature, and isolated as before. The resulting yellow powder gave no test for ionic sulfite with $BaCl_2$ solution. A white solid was obtained, however, when a concentrated solution of the complex was treated with KCl solution, indicating the presence of perchlorate. Attempts to remove the perchlorate by recrystallization were unsuccessful. The yield was ~25%. Anal. Calcd for $CoC_6N_4H_{18}O_6S_2Na\cdot NaClO_4\cdot H_2O$: Co, 11.16; C, 13.64; N, 10.60; H, 3.80; S, 12.12; Na, 8.70; Cl, 6.70. Found:[8] Co, 11.11; C, 13.58; N, 10.23; H, 4.27; S, 12.14; Na, 8.47; Cl, 5.20. Attempts to prepare the Ba salt always resulted in the coprecipitation of $BaSO_4$ and/or $BaSO_3$ with the yellow complex.

To avoid the coprecipitation of $NaClO_4$ as occurred in the above preparation, we decided to start with $[Co(tren)(OH_2)_2]Cl_3$. This complex was prepared in solution as described earlier, and the above procedure for the preparation of the sulfito complex was followed.

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(1) A preliminary report of this work was presented at the 179th National Meeting of the American Chemical Society, Houston, TX, March 1980. See Abstract No. INOR 134.

(2) Preceding paper in this series: Dash, A. C.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 3160.

(3) El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 1660.

(4) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880.

(5) Farrell, S. M.; Murray, R. S. *J. Chem. Soc., Dalton Trans.* **1977**, 322.

(6) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1975**, *97*, 1733.

(7) Scheidegger, H. A. Doctoral Thesis, Eidgenössichen Technischen Hochschule, Zurich, 1966.

(8) Galbraith Laboratories, Inc., Knoxville, TN 37921.

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The resulting yellow compound always coprecipitated with NaCl. Attempts to remove NaCl by several recrystallizations were unsuccessful. The resulting yellow compound gave, however, a UV–vis spectrum identical with that of the other preparations. In addition, the IR spectra recorded by use of a Beckman AccuLab 4 or Perkin-Elmer 621 IR spectrometer were identical, with the exception of the perchlorate peaks, which were present in the preparation using the perchlorate salt as the starting material.

Rate Measurements. All rate measurements were made at an ionic strength of 1.0 M ($NaClO_4$) over the ranges of temperature, pH, and total sulfite concentration given in the Results and Discussion. In the kinetic experiment known amounts of solid $Na_2S_2O_5$ were dissolved in McIlvaine phosphate–citric acid buffers[9] or borate–boric acid buffers[10] of a given pH value, and the ionic strength was adjusted to give $I = 1.0$ M with $NaClO_4$. These solutions were prepared in a volumetric flask in which sufficient space was left for the complex. In a separate flask a concentrated solution of $[Co(tren)(OH_2)_2](ClO_4)_3$ was also prepared. The two solutions were then thermostated to the desired temperature. After a lapse of 20–30 min, 1–2 mL of $[Co(tren)(OH_2)_2](ClO_4)_3$ was transferred rapidly to the buffered sulfite volumetric flask. The resulting solution was rapidly adjusted to the mark and transferred to the spectrophotometer cell, which was placed in the thermostated-cell compartment of the Cary UV-visible spectrophotometer. In a number of experiments, spectrum vs. time curves were obtained over the wavelength range 600–330 nm. In most of the runs, however, the experiments were done at a fixed wavelength. The redox reaction was studied at 520, 480, and 430 nm, while the sulfite substitution reaction was studied at 450 nm. The pH measurements were made with a Fisher Model 420 pH/ion meter and a Markson combination electrode, by using a water-jacketed sample holder thermostated at the desired temperature. The observed pseudo-first-order rate constants were calculated from ln $(A_t - A_\infty)$ vs. t data (A_t and A_∞ are the absorbances of the solution at times t and infinity, respectively) by using a least-squares program. The plots were in general linear for at least 4 half-lives.

Results and Discussion

Redox Decomposition of $[Co(tren)(OH_2)(OSO_2)]^+$. Preliminary experiments in which buffered $Na_2S_2O_5$ solutions were added to buffered $[Co(tren)(OH_2)_2]^{3+}$ solutions showed the instantaneous color change from pink to orange characteristic of SO_2 uptake as discussed in detail in our previous paper.[3] At pHs below 5.7 the orange solution slowly fades at room temperature to produce a very light pink solution, but at higher pHs the orange solution takes on a permanent bright yellow color. These color changes were followed spectrophotometrically in the UV–visible region, and spectral analysis of the light pink solutions obtained at pHs lower than 5.4 suggested nearly complete conversion of the cobalt(III) complex to cobalt(II). This spectral analysis identified cobalt(II) by either the tetrachloro[11] or the tetrakis(thiocyanato)cobalt(II)[12] method, standardized by use of $CoCl_2 \cdot 6H_2O$ (AR). The fate of the sulfur-containing reaction product was determined by the addition of barium chloride solution, which resulted in the formation of a white precipitate, insoluble in dilute hydrochloric acid. The $BaSO_4$ precipitate thus formed was filtered, washed with dilute HCl, dried, and weighed. The molar ratio of sulfate to cobalt in the system was found to be exactly 0.5, indicating that sulfate is the sole oxidation product in the reaction. The stoichiometry of this reaction thus appears to be

$$2[Co(tren)(OH_2)(OSO_2)]^+ + 11H_2O \rightarrow 2Co(H_2O)_6^{2+} + 2tren + HSO_4^- + HSO_3^-$$

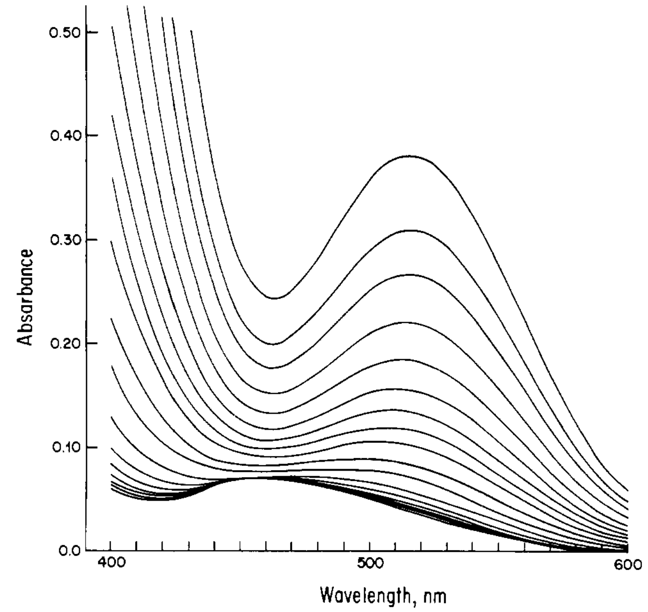

Figure 1. Spectral changes during redox decomposition of $[Co(tren)(OH_2)(OSO_2)]^+$ at 25 °C; $[Co]_t = 3.0 \times 10^{-3}$ M, $[S]_t = 0.08$ M, and pH = 3.78. Curves from top to bottom are at the following times after mixing: 90, 300, 450, 650, 850, 1050, 1250, 1450, 1650, 2000, 2350, 2900, 3450, 4000, 4550, and 5100 s and 30 h.

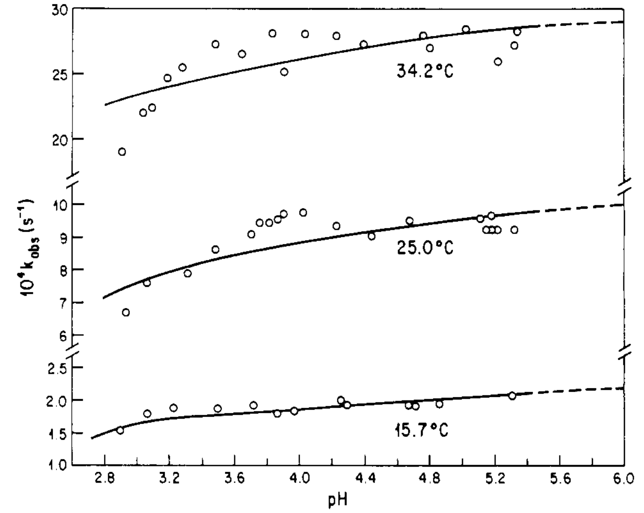

Figure 2. Plots of k_{obsd} for internal redox process vs. pH at $[S]_t = 0.08$ M and at the temperatures specified. Solid lines are values of k_{obsd} calculated according to the rate law (eq 1).

Moreover, it was noted in separate experiments that addition of tren or tren·3HCl to $Co(OH_2)_6^{2+}$ solutions in the pH range of the redox study did not affect the spectrum of the hexaaquo species, confirming the proposed release of the tetraamine from the cobalt(II) center as given in the stoichiometric equation above. However, studies at higher pH values (>7.4) do show spectral changes indicative of cobalt(II) chelation.[13,14]

The kinetics of the redox decomposition was studied over the pH range $2.9 < \text{pH} < 5.4$ and total sulfite concentration range $0.04 < [S]_t < 0.16$ M and at 15.7, 25.0, and 34.2 °C. Figure 1 shows the spectral changes during a typical run in the redox study. The final spectrum indicates that a large fraction of the cobalt(III) complex has been converted to $Co(H_2O)^{2+}$, since the absorbance is quite small over the whole visible-wavelength range. However, the residual absorbance

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(9) Elving, P. J.; Makowitz, J. M.; Rosenthal, I. *Anal. Chem.* **1956**, *28*, 1179.

(10) Perrin, D. D.; Dempsey, B. "Buffers for pH and Metal Ion Control"; Chapman and Hall: London, 1974; Wiley: New York, 1974.

(11) Thacker, M. A.; Scott, K. L.; Simpson, M. E.; Murray, R. S.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1974**, 647.

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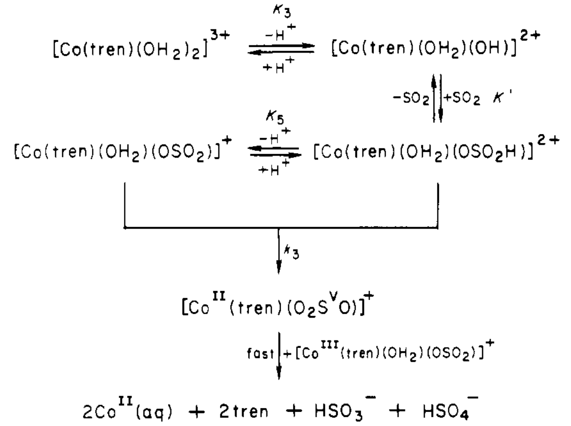
(13) Paoletti, P.; Ciampolini, M.; Sacconi, L. *J. Chem. Soc.* **1963**, 3589.

(14) Bogdansky, F. M.; Ph.D. Thesis, Department of Chemistry, State University of New York, Buffalo, NY, 1971; p 78.

Scheme I. Mechanism for the Reduction of Aquo(sulfito-*O*)(2,2′,2″-triaminotriethylamine)cobalt(III) Ion



at 450 nm (see Figure 1) is the result of the parallel nonredox sulfite addition reaction to be discussed in detail below. This reaction is the only observable process at pH >7.2, but its importance falls off rapidly at lower pH values. For the purposes of the present analysis of the kinetics of the low-pH system, the sulfite addition reaction may be neglected since it makes a relatively small contribution to the overall spectral changes that provide the data for the redox study.

The values of the observed pseudo-first-order rate constants, k_{obsd}, obtained at the various total sulfite concentrations, acidities, and temperatures employed, are presented in Table I. An inclusive display of these data (Figure 2) shows that k_{obsd} increases slightly as the pH increases but appears to approach a maximum constant value at each temperature. A mechanism consistent with the observed rate data is given in Scheme I, where the SO_2 uptake/elimination processes may be treated as an equilibrium since these reactions are so much faster[3] than the redox process. The assumption is made that the latter involves both the protonated and deprotonated forms of the aquo sulfito ion with identical rate constants, since it seems unlikely that the presence of the remote proton should have much effect on whatever the rate-determining step is for the electron transfer. The appropriate rate law is readily shown to be of the form[15]

$$k_{obsd} = \frac{k_3\{K_3K_5K'[SO_2] + K_3K'[SO_2][H^+]\}}{K_3K_5K'[SO_2] + K_3K'[SO_2][H^+] + K_3[H^+] + [H^+]^2} \quad (1)$$

The magnitude of K_3 at various temperatures has been previously measured,[2] from which the appropriate values at 15.7, 25.0, and 34.2 °C are deduced to be 1.17×10^{-6}, 1.58×10^{-6}, and 2.00×10^{-6} M, respectively. Also, the constant K' is seen to be given by the ratio of the rate constants for SO_2 uptake and elimination, i.e., $K' = k_{11}/k_2$. k_2 is not known by direct experiment, but $k'_2 = k_2/K_5$ is,[3] so $K'K_5 = k_{11}/k'_2$, for which values at the three temperatures specified are readily deduced to be 56.3, 38.8, and 27.7, respectively. Finally, K_5 itself can be satisfactorily estimated as previously explained,[3] which leads to the values 1.55, 1.26, and 1.00×10^{-4} M, respectively. The above analysis has been tested by extrapolating the k_{obsd} values to an apparent limiting value at pH 6, where $k_{obsd} \sim k_3$ and has the values 2.2×10^{-4}, 10.0×10^{-4}, and 29.0×10^{-4} s^{-1}, respectively, at the three specified temperatures (see Figure 2).[16] Smoothed-out values of k_{obsd} can then be calculated, and these are plotted as curves in Figure 2. It is obvious that a reasonably good fit is obtained in spite of the experimental scatter, adequately confirming the rate-determining concepts of Scheme I.

Table I. Dependence of k_{obsd} on pH, Temperature, and Total Sulfite[a] for the Reduction of $[Co(tren)(OH_2)(OSO_2)]^+$

pH	$10^4 k_{obsd}$, s^{-1}	pH	$10^4 k_{obsd}$, s^{-1}	pH	$10^4 k_{obsd}$, s^{-1}
			15.7 °C		
2.91	1.51 ± 0.01	3.86	1.80 ± 0.04	4.72	1.90 ± 0.04
3.06	1.60 ± 0.02	3.92	1.84 ± 0.04	4.85	1.95 ± 0.04
3.22	1.73 ± 0.03	4.23	2.00 ± 0.04	5.32	2.05 ± 0.03
3.51	1.74 ± 0.04	4.27	1.92 ± 0.04	5.36	2.05 ± 0.03
3.73	1.91 ± 0.04	4.66	1.92 ± 0.05		
			25.0 °C		
2.94	6.72 ± 0.11	3.89	9.71 ± 0.09	5.16[c]	9.20 ± 0.08
3.06	7.61 ± 0.05	4.04	9.76 ± 0.07	5.18	9.30 ± 0.13
3.32	7.95 ± 0.16	4.26	9.32 ± 0.07	5.18	9.25 ± 0.08
3.47	8.65 ± 0.15	4.44	9.06 ± 0.28	5.18[e]	9.70 ± 0.14
3.69	9.09 ± 0.20	4.68	9.54 ± 0.14	5.21	9.11 ± 0.22
3.78	9.42 ± 0.13	5.11[d]	9.60 ± 0.15	5.22[b]	9.11 ± 0.05
3.82	9.42 ± 0.13			5.32[e]	9.15 ± 0.16
3.87	9.58 ± 0.13				
			34.2 °C		
2.94	19.1 ± 0.2	3.65	26.5 ± 0.1	4.75	28.0 ± 0.2
3.04	22.0 ± 0.5	3.83	28.1 ± 0.1	4.80	27.0 ± 0.6
3.09	22.4 ± 0.1	3.89	25.1 ± 0.1	5.02	28.4 ± 0.3
3.18	24.7 ± 0.2	4.02	28.0 ± 0.2	5.22	26.0 ± 0.3
3.28	25.5 ± 0.1	4.22	27.9 ± 0.2	5.33	27.3 ± 0.4
3.48	27.3 ± 0.1	4.39	27.3 ± 0.5	5.36	28.3 ± 0.4

[a] Unless noted otherwise all experiments were done at $[S]_t$ = 0.08 M. [b] $[S]_t$ = 0.04 M. [c] $[S]_t$ = 0.06 M. [d] $[S]_t$ = 0.12 M. [e] $[S]_t$ = 0.16 M.

What actually happens in the remainder of the redox process is difficult to visualize. In earlier work with the pentaammineaquo complex,[4] the formation of SO_3^- radical ion was proposed as the rate-determining step, but no positive evidence could be adduced for its existence. A recent parallel study[2,17] utilizing the straight-chain pentadentate ligand tetraethylenepentamine (tetren) in place of five separate NH_3 groups shows that there is no facile redox process in this system at all, the only observable reactions being

$$[Co(tetren)OH_2]^{3+} \underset{-SO_2}{\overset{+SO_2}{\rightleftharpoons}} [Co(tetren)OSO_2]^+ \rightarrow [Co(tetren)SO_3]^+$$

However, the findings of other recent studies involving *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$ complex ions[18,19] parallel the present study, with only redox observable when pH <6 and only a second sulfite addition observable for pH >7. A possible explanation of these facts is that sulfite chelation is part of the redox process, which could occur for the pentaammine species by cis NH_3 elimination, for the tren or *cis*-(en)$_2$ species by cis aquo elimination, and for the *trans*-(en)$_2$ by trans aquo elimination accompanied by rearrangement. The latter pro-

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(15) In our earlier paper[4] the term describing the redox of $[Co(NH_3)_5SO_3H]^{2+}$ was omitted in the derivation of the analogue to our eq 1. However, this did not affect the calculation of the k_3 values very much since most of the data was obtained at pH >5, where $k_{obsd} \sim k_3$. This pH range was largely inaccessible for redox study in the present system due to the replacement of the redox reaction by sulfite addition at high pH.

(16) The corresponding ΔH^* and ΔS^* values are 24.2 ± 2.0 kcal mol^{-1} and 8.2 ± 6.6 cal deg^{-1} mol^{-1}. These are to be compared with the results obtained for the $[Co(NH_3)_5OSO_2]^+$ system[4]—viz., $\Delta H^* = 26.9 \pm 1.2$ kcal mol^{-1}, $\Delta S^* = 23.1 \pm 4.2$ cal deg^{-1} mol^{-1}, and $k_3 = 1.4 \times 10^{-2}$ s^{-1} at 25 °C. The greater than 10-fold increase in k_3 for the pentaammine complex is seen to be a result of the very much larger ΔS^* value for the latter species.

(17) The S-bonded final product exhibits no tendency toward internal redox whatsoever, only showing evidence for very slow hydrolysis even at 90 °C in 0.5 M acid.

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

(19) El-Awady, A. A.; Harris, G. M., unpublished data.

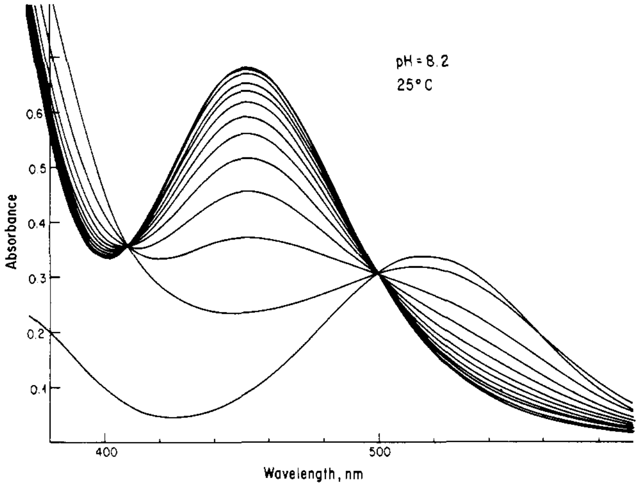

Figure 3. Spectral changes during the sulfite addition reaction of $[Co(tren)(OH_2)(OSO_2)]^+$ at 25 °C; $[Co]_t = 2.7 \times 10^{-3}$ M, $[S]_t = 0.06$ M, and pH = 8.2. Curves from bottom to top at $\lambda = 450$ nm: first, aquo complex before addition of sulfite; then, 60, 220, 360, 500, 650, 800, 1000, 1250, 1500, 2000, and 3500 s and 20 h after sulfite addition.

posal is somewhat similar to that concerning the redox of the S-bonded species *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$, for which it is suggested that conversion to the cis analogue is rate determining.[11] However, whether sulfite chelation to form a doubly O-bonded species is a probable step in our systems remains to be confirmed. A preparation of the chelated sulfito complex ion $[Co(en)_2O_2SO]^+$ has been reported,[20] although further confirmation of this synthesis has not as yet appeared in the literature. The only similar synthesis is that recently reported[21] for the species $[Co(AA)_2O_2SO]^+$ where AA ≡ 2,2′-bipyridine or 1,10-phenanthroline. None of these compounds have been shown to undergo facile internal redox in the lower pH range, which in any case the authors do not claim to have investigated.

Further work is obviously needed to clarify this situation, but in the meantime we will adopt the concept of a partially stabilized but still highly reactive chelated sulfito intermediate in which ligand-to-metal internal electron transfer has already occurred (see Scheme I). The final step in the redox process has to involve a second cobalt(III) complex ion, which over most of our experimental pH range will be a second aquo-sulfito complex ion because of the completeness of the equilibrium described by K'. The final products of this fast second-order process will then be in accordance with the observed stoichiometry.

Sulfite Uptake by $[Co(tren)(OH_2)(OSO_2)]^+$. As mentioned earlier, the O-bonded sulfito product of the rapid SO_2 uptake by the diaquo(triaminotriethylamine)cobalt(III) complex undergoes either of two relatively slow subsequent reactions—the redox process just discussed (the dominant process for pH <5.4) and a color change from the orange-red sulfito species to a bright yellow final product (the sole process for pH >7.2). The spectra recorded in Figure 3 indicate the progress of this latter reaction, which is essentially complete within 1 h under typical pH and temperature conditions. Tests performed on the final solutions in such experiments showed no trace of cobalt(II) product, and elemental analyses of separately prepared samples of the yellow product (see Experimental Section) proved its composition to be $Na[Co(tren)(SO_3)_2]$. The persistence of the two isosbestic points at 410 and 498 nm after the initial 60-s interval[22] shows that the

Table II. Dependence of k_{obsd} on pH, Temperature, and Total Sulfite for Substitution Reaction of $[Co(tren)(OH_2)(OSO_2)]^+$

pH	$[S]_t$, M	$10^3 k_s$, s^{-1}	$k_s/[S]_t$, s^{-1} M^{-1}
		6.7 °C	
7.20	0.04	1.46 ± 0.06	0.0366 ± 0.002
7.34	0.04	1.31 ± 0.05	0.0328 ± 0.001
7.53	0.04	1.24 ± 0.04	0.0310 ± 0.001
7.78	0.04	0.878 ± 0.01	0.0220 ± 0.0003
7.91	0.04	0.432 ± 0.009	0.0108 ± 0.0002
7.95	0.08	0.850 ± 0.007	0.0106 ± 0.0001
8.10	0.04	0.350 ± 0.006	0.00875 ± 0.0001
8.23	0.04	0.234 ± 0.003	0.00585 ± 0.00008
8.28	0.04	0.184 ± 0.001	0.0046 ± 0.00002
		15.0 °C	
7.35	0.04	4.04 ± 0.09	0.101 ± 0.002
7.36	0.04	3.93 ± 0.07	0.098 ± 0.002
7.41	0.04	3.66 ± 0.09	0.092 ± 0.002
7.45	0.04	3.44 ± 0.07	0.086 ± 0.002
7.50	0.12	10.40 ± 0.08	0.086 ± 0.002
7.54	0.04	3.37 ± 0.08	0.084 ± 0.002
7.63	0.04	1.79 ± 0.04	0.045 ± 0.001
7.81	0.04	1.40 ± 0.03	0.035 ± 0.001
7.98	0.04	0.86 ± 0.02	0.021 ± 0.0005
8.02	0.04	0.85 ± 0.02	0.021 ± 0.0005
8.05	0.08	1.80 ± 0.03	0.225 ± 0.0004
8.18	0.04	0.53 ± 0.01	0.013 ± 0.0002
8.31	0.04	0.435 ± 0.005	0.011 ± 0.0001
8.41	0.04	0.31 ± 0.05	0.0077 ± 0.001
8.49	0.04	0.22 ± 0.02	0.0055 ± 0.0005
		25.0 °C	
7.15	0.04	8.05 ± 0.02	0.2013 ± 0.0005
7.31	0.04	7.05 ± 0.01	0.1763 ± 0.0002
7.33	0.04	6.23 ± 0.01	0.1558 ± 0.0002
7.37	0.04	6.34 ± 0.08	0.1558 ± 0.002
7.52	0.04	5.81 ± 0.05	0.145 ± 0.001
7.53	0.04	5.40 ± 0.08	0.135 ± 0.002
7.56	0.06	7.62 ± 0.01	0.1270 ± 0.0002
7.58	0.04	4.72 ± 0.04	0.118 ± 0.001
7.61	0.02	2.57 ± 0.01	0.1285 ± 0.0005
7.63	0.04	5.01 ± 0.04	0.125 ± 0.001
7.81	0.04	2.66 ± 0.02	0.0665 ± 0.0005
7.81	0.06	5.03 ± 0.03	0.0838 ± 0.0005
7.86	0.04	2.91 ± 0.09	0.0728 ± 0.002
7.89	0.04	2.93 ± 0.04	0.0733 ± 0.001
8.00	0.04	1.89 ± 0.03	0.0473 ± 0.0008
8.01	0.08	4.65 ± 0.07	0.0581 ± 0.0009
8.04	0.04	1.39 ± 0.02	0.0348 ± 0.0005
8.06	0.08	3.30 ± 0.02	0.0413 ± 0.0002
8.21	0.06	2.12 ± 0.04	0.0353 ± 0.0007
8.26	0.08	1.35 ± 0.02	0.0169 ± 0.0003
8.45	0.04	0.58 ± 0.05	0.0145 ± 0.0002
8.65	0.04	0.41 ± 0.05	0.0103 ± 0.001
8.87	0.04	0.211 ± 0.002	0.0053 ± 0.00005

stoichiometry of the observed reaction must be replacment of the remaining aquo group of the O-bonded sulfito complex by a second sulfito ligand.

The rate of the sulfite addition reaction was studied over the pH range 7.15–8.9 and total sulfite concentration range 0.02–0.12 M at 6.7, 15.0, and 25.0 °C. Table II gives the values of k_s for various values of the pH, total sulfite concentration, and temperature. The data show that k_s is directly proportional to total sulfite concentration at fixed pH and temperature. Plots of $k_s/[S]_t$ vs. $[H^+]$ at each temperature give curves which appear to satisfy the relationship $k_s/[S]_t = a[H^+]/([H^+] + b)$. Inverse plots of the type $[S]_t/k_s$ vs. $1/[H^+]$ show satisfactory linearity (see Figure 4) with experimentally indeterminate intercepts (i.e., $1/a \leq 10$) and slopes such that a/b has the values quoted in Table III. Of the six possible

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(20) Baldwin, M. E. *J. Chem. Soc.* **1961**, 3123.

(21) Schiavon, G.; Marchetti, F.; Paradisi, C. *Inorg. Chim. Acta* **1979**, *33*, L101.

(22) Note that the original spectral change (complete in less than 1 min) represents the formation of $[Co(tren)(OH_2)(OSO_2)]^+$ immediately after mixing $[Co(tren)(OH_2)_2]^{3+}$ with sulfite under the specified conditions of Figure 3.

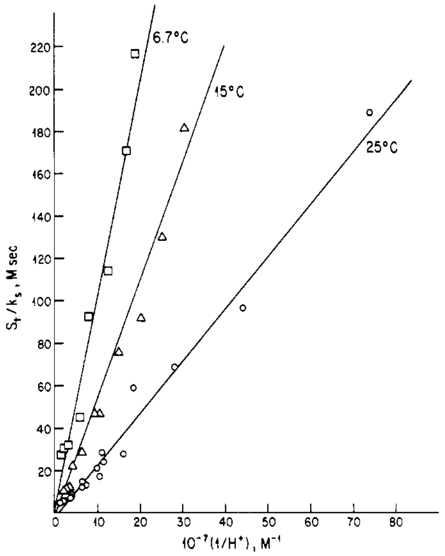


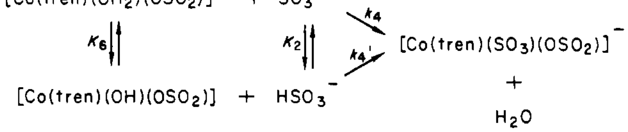
Figure 4. Plots of $[S]_t/k_s$ (k_s = observed rate constant for sulfite addition) vs. $[H^+]^{-1}$ at the temperature specified.

Table III. Rate Parameters for Sulfite Addition Reaction of $[Co(tren)(OH_2)(OSO_2)]^+$

temp, °C	$10^{-6}a/b$, M^{-2} s^{-1}	k_4,[a] M^{-1} s^{-1}	k'_4,[b] M^{-1} s^{-1}
6.7	0.95 ± 0.07	0.10	0.50
15.0	1.82 ± 0.07	0.18	0.91
25.0	4.0 ± 0.1	0.40	2.0
$\Delta H^{\ddagger}$, kcal mol^{-1}	12.4 ± 0.3	12	12
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	13.4 ± 0.3	−19	−16

[a] Calculated by assuming $K_6 \sim 10^{-7}$ M over this temperature range, as already discussed.[23] [b] Calculated by utilizing the value of K_2 recorded previously (5×10^{-7} M) for this temperature range.[3]

rate-determining reactions (these alternatives are the reactions of either $[Co(tren)(OH_2)(OSO_2)]^+$ or its deprotonated analogue with SO_2, HSO_3^-, or SO_3^{2-}) only two are consistent with the observed $[H^+]$ dependence. These two are the kinetically indistinguishable processes described by k_4 and k'_4 in eq 2.



(2)

The corresponding rate expressions are[23] given by eq 3 and 4. It is seen that the parameter a/b can be identified with

$$k_s/[S]_t = \frac{k_4[H^+]}{[H^+] + K_6} \tag{3}$$

$$k_s/[S]_t = \left(k'_4\frac{K_6}{K_2}\right)\frac{[H^+]}{[H^+] + K_6} \tag{4}$$

Table IV. UV-Visible Absorption Spectra

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
$[Co(tren)(OH_2)(OSO_2)]^+$	510, 325	136, 1825	2
$[Co(en)_2(OH_2)(SO_3)]^+$	470, 280	180, 16 000	20[a,b]
$[Co(tren)(SO_3)(OSO_2)]^-$	450, 300 sh, 283, 225	250, ~16 000, 17 500, 4000	this work
cis-$[Co(NH_3)_4(SO_3)_2]^-$	452, 295, 264	200, 20 900, 20 000	24
$[Co(en)_2(O_2SO)]^+$	440, 325 sh, 270	170, ~3000, 15 000	20[a]

[a] Approximate values only, estimated from published spectrum. [b] Not specified whether cis or trans, but probably trans due to unusual strength of the "trans effect" of sulfito ligand in S-bonded complexes.[25]

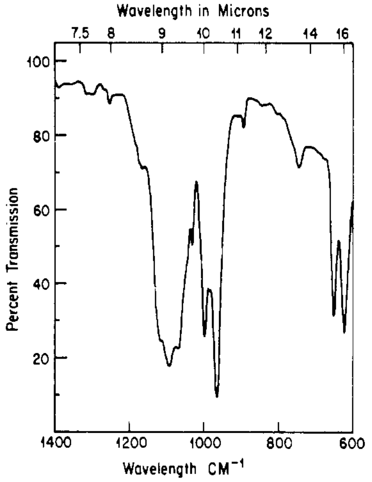


Figure 5. Infrared spectrum of the disulfito final product, Na[Co(tren)$(SO_3)(OSO_2)$].

either k_4/K_6 or k'_4/K_2, leading to the figures for k_4 and k'_4 recorded in Table III. As stated above, the inverse plots of Figure 4 require that $1/a$ ($=1/k_4$ or K_2/k'_4K_6) not exceed 10 M s, and this requirement is satisfactorily fulfilled by both interpretations.

The synthesis and elemental analysis of our disulfito final product has already been discussed (see Experimental Section). Further evidence relative to its makeup is provided by the fact that it readily passes through a cation exchange column and by the characteristics of its UV-visible and infrared spectra. The main features of the former are recorded in Table IV and are seen not to differ greatly from the only previously reported disulfito species for which UV-vis data are available,[24] *cis*-$[Co(NH_3)_4(SO_3)_2]$, which is supposedly S-bonded for both SO_3^{2-} groups. However, the IR spectra lead to a different conclusion. The bands observed (Figure 5) for our complex are given in Table V along with those of several other comparable sulfito complex ions. It is seen that our species has all the bands expected for mono and bis S-bonded nonchelated sulfito ligands (a-e in Table V) but has also several other bands, some of which appear to correspond to the sulfito chelates (f-h in the table) in which the sulfito groups are supposedly doubly O bonded. This would suggest that our final product (as already assumed in the formulation of eq 2) should be designated $[Co(tren)(OSO_2)(SO_3)]^-$, with the S-bonded SO_3^{2-} entering in the process described by k_4 or k'_4. However, this conclusion is difficult to rationalize with the rate data, since the direct formation of an S-bonded species requires complete substitution of sulfite for aquo or hydroxo ligand. Normally, such reactions are much slower that the disulfito formation reaction. For example, the rates of OH or OH_2 replacement in a typical diaquotetraaminecobalt(III) complex as determined in conventional water-exchange studies[26] are

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(23) Equations 3 and 4 are derived on the basis of the assumption that $K_6 \sim 10^{-7}$ M. This assumption follows from the facts that for the similar selenito species[27] *cis*-$[Co(en)_2(OH_2)(OSeO_2)]^+$, p*K* = 8.3 at 25 °C and that there should be a reasonable parallelism between the acidities of the complexes and of HSO_3^- and $HSeO_3^-$ (the p*K* values for the latter are 6.3 at 25 °C and 8.0[27] at 20 °C, respectively). The other criteria applicable when pH > 7 are that $[SO_3^{2-}] \sim [S]_t$ and $[HSO_3^-] \sim [H^+][S]_t/K_2$.

(24) Scott, K. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1486.

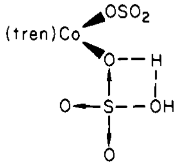
(25) Halpern, J.; Palmer, R. A.; Blakely, L. M. *J. Am. Chem. Soc.* **1966**, *88*, 2877.

Table V. Infrared Vibration Frequencies (cm^{-1}) of Bands due to Sulfito Groups in O- and S-Bonded Sulfito Complexes

a[a]	b	c	d	e	f	g	h	i
1095 s	1068 s	1117 s	1145	1160	1119 s	1140	1146	1165 m
1018 w	1020 w	1062 s	1090	1090	1093 s	1120	1123	1115 sh
943 vs	939 vs	972 vs	990	985	1036 vs	1105	1065	1090 vs
625 s	630 s	625 s	620	620	989 vs	1010	1023	1065 s
					649 m	980	985	1028 m
					625 s	640	640	995 vs
						620	620	965 vs
								647 vs
								623 vs

[a] Key: (a) *cis*-$[Co(en)_2(SO_3)_2]Na$, ref 20; (b) *trans*-$[Co(en)_2(SO_3)_2]Na$, ref 20; (c) $[Co(en)_2(SO_3)(OH)]$, ref 20; (d) *cis*-$[Co(phen)_2(CN)(SO_3)]$, ref 21; (e) *cis*-$[Co(bpy)_2(CN)(SO_3)]$, ref 21; (f) $[Co(en)_2(SO_3)]Cl$ (bidentate), ref 20; (g) *cis*-$[Co(phen)_2(SO_3)]Cl$ (bidentate), ref 21; (h) *cis*-$[Co(bpy)_2(SO_3)]Cl$ (bidentate), ref 21; (i) $Na[Co(tren)(SO_3)(OSO_2)]$, this work.

of the order of magnitude of 10^{-5} M^{-1} s^{-1} at a maximum. As we discussed in some detail previously,[3] rapid replacement of OH or OH_2 by an oxyanion is best explained by the postulation of a mechanism in which cobalt–oxygen bond fission does not occur. As was proposed in the case of the reactions of $HSeO_3^-$ with various aquo species,[27] one can visualize for the present system a transition state of type **1**. This provides a reaction path that is not limited by the rate of Co–O bond fission. However, the reaction product from this must be $[Co(tren)(OSO_2)_2]^+$, which, as stated above, seems to be inconsistent with the infrared data. An immediate rapid rearrangement of one of the OSO_2 ligands could be postulated to obtain the suggested product $[Co(tren)(SO_3)(OSO_2)]^-$, but this appears to be unlikely in view of the previously demonstrated[2] rather slow isomerization of $[Co(tetren)OSO_2]^+$ to $[Co(tetren)SO_3]^+$.



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So far in the above discussion nothing has been said concerning rate data in the range 5.4 < pH < 7.2. In this region, our spectral data became too complicated to interpret with any degree of confidence, due to the simultaneous occurrence of both the redox and sulfite addition reactions. It is clearly evident from the spectral data above pH 7, however (see Figure 3), that the redox contribution is essentially nonexistent. This is understandable if it is accepted that the uncharged deprotonated species $[Co(tren)(OH)(OSO_2)]$ described by K_6 does not readily undergo the electron transfer–chelation reaction described by k_3 because of its resistance to displacement of the relatively firmly bonded hydroxo ligand. This monohydroxo complex is not involved in Scheme I, since, with $K_6 \sim 10^{-7}$, its concentration is negligible in the low-pH range. However, the fraction in this form reaches 0.5 at pH 7 and rises steeply at higher pHs. Since the apparent maximum magnitude of $k_{obsd}(\text{redox}) = k_3$ is already considerably smaller at pH 6 than is $k_{obsd}(\text{add}) = k_s$ at pH 7, no measurable contribution from the former process is to be expected in the high-pH range. Conversely, the contribution of k_s to the overall reaction falls off steadily in the lower pH range and can be estimated[28] from Figure 1 to contribute only about 3% at the pH of that experiment (3.78). In runs made at pH ~5, considerably larger residual peaks at 450 nm were evident in the final spectra. However, the redox rate data obtained by following the decrease in absorbance at 520 nm yielded very satisfactory first-order plots, and the values of k_{obsd} so obtained show no apparent dependence on $[S]_t$ (see data at 25 °C in Table I). This clearly demonstrates that the parallel sulfite addition reaction is not interfering with the evaluation of the redox rate constants, at least up to the limit of pH ~5.4.

Acknowledgment. The authors are grateful to the John D. and Francis H. Larkin Foundation of the State University of New York at Buffalo for financial support and to Western Illinois University for a leave of absence to A.A.E.

Registry No. $[Co(tren)(OH_2)(OSO_2)]^+$, 77029-32-4; $Na[Co(tren)(SO_3)_2]$, 79135-42-5; $[Co(tren)(CO_3)]ClO_4$, 41593-06-0; $Na_2S_2O_5$, 7681-57-4; $[Co(tren)(OH_2)_2](ClO_4)_3$, 75363-51-8; $[Co(tren)(OH_2)_2]Cl_3$, 79135-12-9; $Co(tren)(OH)(OSO_2)$, 79135-13-0; SO_3^{2-}, 14265-45-3.

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(26) Kruse and Taube give data which are consistent with a value of ~10^{-3} s^{-1} for the pseudo-first-order water-exchange rate constant for *cis*-$[Co(en)_2(OH_2)(OH)]^{2+}$ at 25 °C (Kruse, W.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280). The corresponding second-order constant should thus be about 1.8×10^{-5} M^{-1} s^{-1}. The other *cis*-diaquo congeners of the species specified have much smaller water-exchange rates.

(27) Fowless, A. D.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 1271, 1276, 1282.

(28) The initial absorbance of the O-bonded sulfito complex at 510 nm is ~0.38, so that its concentration at $t = 0$ is ~3×10^{-3} M ($\epsilon = 156$ M^{-1} cm^{-1} at this wavelength for this complex—see ref 3, Table II). The residual absorbance at 450 nm at $t = \infty$ is ~0.03 unit above the apparent base line, so the concentration of the disulfito product is ~1×10^{-4} M ($\epsilon = 250$ M^{-1} s^{-1} at this wavelength for this complex—see Table IV of this paper).