steric factors commonly influence the rates of reactions. Therefore the faster rate of hydrolysis of *cis*-$[Cr(cyclen)Cl_2]^+$ compared to that of *cis*-$[Cr(isocyclam)Cl_2]^+$ or *cis*-$[Cr(cyclam)Cl_2]^+$ could be due to the fewer number of carbon atoms in cyclen compared with those in cyclam and isocyclam. The smaller coordinated macrocycle should allow a more facile water attack on the chromium(III) than the larger ring systems. However, most of the linear tetradentate ligands have fewer carbon atoms than cyclen. Also, coordinated linear tetradentates have more flexibility in allowing a water molecule into the coordination sphere of the chromium(III) by being better able to move the terminal amine groups than the more inflexible and cumbersome tetradentate macrocycle. Therefore, it would be expected that the cis complexes containing a linear tetradentate ligand should be more reactive than the cis complexes containing cyclen. Since the opposite is true, with the exception of *cis*-*β*-$[Cr(2,2,2\text{-tet})]^+$, a simple steric argument cannot explain the rapid rate of acid hydrolysis of *cis*-$[Cr(cyclen)Cl_2]^+$ compared to that of other *cis*-$[Cr(N_4)Cl_2]^+$ complexes where N_4 is a linear tetradentate ligand.

A more subtle steric factor that may be responsible for the relative rate constants for the chromium(III) complexes listed in Table II is the conformation of the sec-NH protons. The conformation of the sec-NH protons will influence the steric barrier to an incoming water molecule and will affect the bond strain. The conformation of the sec-NH protons has been shown to affect the rate of aquation of many chromium(III) complexes.[10,11] Also the chemical equivalence of the two cis or trans chlorides will depend on the conformation of sec-NH protons. For example, if three of the NH groups are on one side of the N_4Cr plane and the fourth NH group is on the other side of the N_4Cr plane, the two chlorides will not be in the same environment, and as a result, their susceptibility to acid hydrolysis will be different. Therefore, without knowledge of the conformation of the chelate rings in solution for all complexes, the rapid rate of aquation of *cis*-$[Cr(cyclen)Cl_2]^+$ cannot be unambiguously assigned to any one factor.

The differences in the rate constants for the *trans*-$[Cr(N_4)Cl_2]^+$ complexes cannot be attributed to differences in the strain of the nitrogen to chromium bonds. The rates of aquation of *trans*-$[Cr(N_4)Cl_2]^+$ complexes are considerably more sensitive to the nature of the macrocycle around the chromium(III) than are the cis isomers. *trans*-$[Cr(isocyclam)Cl_2]^+$ aquates so fast that stop-flow techniques were necessary to follow the reaction. In contrast, its isomer, *trans*-$[Cr(cyclam)Cl_2]^+$, aquated about 4×10^7 times slower than *trans*-$[Cr(isocyclam)Cl_2]^+$, and *trans*-$[Cr([15]aneN_4)Cl_2]^+$ also aquated very slowly. Although it has been shown that isocyclam is a weaker field ligand than cyclam, the coordinated isocyclam may be less rigidly bonded to chromium(III) than cyclam, and as a result, an incoming water molecule should find easier access to the chromium(III) ion. It is, therefore, unlikely that the large differences in the rate constants observed for the trans Cr(III) complexes containing these ligands are caused only by the small differences in ring strain. Since an associative mechanism is expected, steric hindrance by hydrogen atoms on the trans six-membered rings may be responsible for the inertness of *trans*-$[Cr(cyclam)Cl_2]^+$ and *trans*-$[Cr[15]aneN_4)Cl_2]^+$ ions. The greater flexibility of the trans isocyclam may contribute to a less sterically hindered access by a water molecule than the cyclam.

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Registry No. *cis*-$[Cr(cyclen)Cl_2]^+$, 101009-52-3; *cis*-$[Cr(isocyclam)Cl_2]^+$, 101009-49-8; *cis*-$[Cr(cyclen)(H_2O)Cl]^{2+}$, 101009-50-1; *trans*-$[Cr(isocyclam)Cl_2]^+$, 101009-51-2.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. Formation, Aquation, and Intramolecular Electron-Transfer Reactions of the *trans*-Aquo(sulfito-*O*)bis(ethylenediamine)cobalt(III) Ion[1a]

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The rates of the rapid biphasic reversible uptake of SO_2 by the title complex have been determined by the stopped-flow technique, over the ranges $4.75 < pH < 7.00$, $10 < t < 20$ °C, and $0.01 < [S_T] < 0.1$ M at $I = 1.00$ M ($NaClO_4$). The reaction was found to follow two consecutive second-order steps. The rate parameters at 10 °C for the second-order reactions of SO_2 with *trans*-$Co(en)_2(OH_2)(OH)^{2+}$ and *trans*-$Co(en)_2(OH)_2{}^+$ are, respectively, $k = (7.5 \pm 0.5) \times 10^7$ and $(2.2 \pm 0.3) \times 10^9$ $M^{-1}\ s^{-1}$; $\Delta H^* = 6.4 \pm 2$ and 7.6 ± 3 kcal mol^{-1}, and $\Delta S^* = -11 \pm 1.4$ and -54 ± 30 cal $deg^{-1}\ mol^{-1}$. The reaction of the resulting mono(sulfito) species with SO_2 to form the bis(sulfito) species gave a second-order rate constant with hydrogen ion dependence of the form $k/[SO_2] = a + b/[H^+]$, where $a = (4.6 \pm 0.5) \times 10^6\ s^{-1}\ M^{-1}$ and $b = (5.4 \pm 0.2)\ s^{-1}$ at 10 °C. The products obtained are shown by spectral studies to be the O-bonded bis(sulfito) complex, which in the unstable protonated form $Co(en)_2(OSO_2H)_2{}^+$ eliminates SO_2 in a biphasic reaction in which the pseudo-first-order rate constants are directly proportional to $[H^+]$ in the ranges $2.97 < pH < 5.6$ and $10 < t < 15$ °C at $I = 1.00$ M ($NaClO_4$) with rate constants of $(2.4 \pm 0.4) \times 10^6$ and $(2.89 \pm 0.06) \times 10^3$ $M^{-1}\ s^{-1}$ at 10 °C; $\Delta H^* = 11$ and 14 kcal mol^{-1} and $\Delta S^* = 25$ and 27 cal $deg^{-1}\ mol^{-1}$. The O-bonded bis(sulfito) intermediate undergoes reduction to Co(II) in the ranges $2.14 < pH < 5.5$ and $0.02 < [S_T] < 0.08$ M at $I = 1.0$ M ($NaClO_4$) at 25 °C, with a complicated hydrogen ion dependence. At pH = 5.5 and 25 °C, the pseudo-first-order rate constant for this relatively slow process is $(2.1 \pm 0.1) \times 10^{-3}\ s^{-1}$. At pH >6, the sulfito-*O* intermediate rearranges to its sulfur-bonded analogue.

Introduction

The fast reversible uptake of SO_2 by octahedral hydroxo–metal complexes is well documented in the literautre[2–5] and occurs without metal–oxygen bond fission, as confirmed by oxygen-17 NMR measurements of the SO_2 uptake and elimination reactions

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(1) (a) A preliminary report of this work was presented at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983. See Abstract INOR 292. (b) Present address: Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia. (c) State University of New York at Buffalo.

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of hydroxopentaamine–cobalt(III) ion.[6] This behavior contrasts with that of conventional hydroxo or aquo ligand replacements, which are usually quite slow,[7] as compared to the stopped-flow time scale of the SO_2 uptake reactions. The obvious conclusion is that the latter systems involve a "direct addition" mechanism initiated by bond formation between sulfur and the oxygen of the hydroxo ligand of the complex.

The published work so far includes a study of only two diaquo complex ions, the diaquo ((2,2′,2″-triaminotriethyl)amine)cobalt(III) species[3a] and the analogous ion to that of the present study, *cis*-diaquobis(ethylenediamine)cobalt(III).[8] The latter has been found to react in a fashion very similar to the "tren" analogue just mentioned, as might be expected due to their structural similarities. However, considerable differences in the nature of the reactions would be expected to be found with a complex with the two aquo groups in the "trans" configuration, and the determination of these differences has been the purpose of the present study. The major contrast is the one which might have been predicted—both aquo ligands are involved with the formation of a *trans*-bis(disulfito) complex by consecutive second-order reactions, which differ not only in the magnitude of the rate constants but in the apparent mechanism of the reactions. The acid-catalyzed elimination of SO_2 from the O-bonded bis(sulfito) intermediate is also a biphasic process, again with differing rate constants. In mildly acidic solutions, however, internal redox of this species to produce cobalt(II) is the only observable reaction.

Experimental Section

Materials. Except where indicated, reagent grade chemicals were used without further purification. The laboratory-distilled water was purified by passage through a mixed-bed anion–cation exchange resin column. Solid sodium metabisulfite $Na_2S_2O_5$ (Baker Analyzed) was used as the source of sulfite; this salt is very stable in storage but hydrates very rapidly upon dissolution in water to yield sulfite.[2]

Preparation and Characterization of Compounds. *trans*-Aquohydroxobis(ethylenediamine)cobalt(III) perchlorate $[Co(en)_2(OH_2)(OH)](ClO_4)_2$ was prepared from the corresponding dichlorochloride[9] by a slight modification of published procedures.[10–12] In a typical preparation 2.24 g (7.85 mmol) of *trans*-$[Co(en)_2Cl_2]Cl$ were dissolved in 5 mL of H_2O and cooled in an ice bath for 30 min with stirring. A 3.33-g (14.35-mmol) sample of Ag_2O was then added a little at a time with stirring while the mixture was kept in the ice bath (15 min). The cold mixture was then filtered and the filtrate treated with 2.9 g of $NaClO_4$ and again placed in the ice bath while stirring was continued. A cooled concentrated (70%) solution of $HClO_4$ was added dropwise until the pH reached the 3–3.5 range. A maroon solid precipitated. The mixture was cooled for an additional 30 min, filtered, washed with alcohol, and air-dried. The purity of the compound was checked by spectral analysis (dissolving in 0.1 M cold aqueous perchloric acid and reproducing published spectra of the *trans*-diaquo analogue), and by elemental anlysis.[13,14] Anal. Calcd for $[Co(en)_2(OH_2)(OH)](ClO_4)_2$: Co, 14.27; C, 11.63; H, 4.64; N, 13.56; Found: Co, 14.30; C, 11.60; H, 4.71; N, 13.54. The UV–visible spectra were measured on a Cary 118 C, Cary 14, or Perkin-Elmer 552 spectrophotometer.

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. The "pH-jump" (equilibrium) method using the automated Durrum Model 110 stopped-flow spectrophotometer assembly was employed to study the SO_2 uptake and elimination processes. The procedure is essentially the same as described earlier.[1–5,15] In the SO_2 uptake experiments, one reservoir syringe of the stopped-flow device was filled with the McIlvaine[16] phosphate–citric acid buffer (at twice as high a concentration as suggested in the paper) in which an appropriate amount of $Na_2S_2O_5$ is dissolved and the second syringe was filled with a solution of the diaquo complex. This latter solution was freshly prepared before each run by dissolving appropriate amounts of the *trans*-aquo hydroxo complex in cold 0.01 M perchloric acid. The ionic strength of both solutions was adjusted to 1 M by adding calculated quantities of a stock solution of sodium perchlorate. At the pHs of the experiments the rate of SO_2 uptake is very much faster than trans to cis isomerization.[17] It is also safe to assume that the bis(sulfito-*O*) product is in the trans form, since immediate addition of excess acid eliminates SO_2 from the complex, yielding the original *trans*-diaquo starting material. 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 410 nm, with some done at 430 and 450 nm, and no variations were indicated in the rate data derived. The obtained oscilloscope traces were indicative of a biphasic reaction. We thus collected relative absorbance (in V) time data from the digitalized transient recorder and obtained the rate constants by the use of a nonlinear least-squares treatment described in the section entitled Treatment of Data.

The SO_2 elimination process was studied more or less as described previously,[1–5] with the "pH-jump" procedure. In this, the O-bonded (bis(sulfito)) species is prepared in situ, by dissolving solid *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$ in a cold (1–5 °C) 1 M $NaClO_4$ solution containing an appropriate amount of $Na_2S_2O_5$ calculated to give a molar ratio of complex to sulfur(IV) of 1:4 and immediately adjusting the pH to 6 in order to stabilize the formed sulfito species. This solution is placed in one syringe of the stopped-flow assembly and reacted with the phosphate–citrate buffer solution of the appropriate pH in the other syringe. The observed reaction was again biphasic. In this case, however, the two steps occur on a vastly different time scale, allowing us to study them separately. The observed pseudo-first-order rate constants were thus obtained from automated least-squares analysis of the digitalized stopped-flow data and are reported as the mean of at least six kinetic runs. Here again most of the data were obtained at a wavelength setting of 410 nm.

The slow redox reaction of the O-bonded sulfito complex was followed on a Perkin-Elmer 552 spectrophotometer utilizing time-drive chart procedure. In the kinetic experiments, known amounts of solid $Na_2S_2O_5$ were dissolved in McIlvaine phosphate–citric acid buffers 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 and thermostated to the desired temperature. After a lapse of 20–30 min, solid trans-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$ was rapidly transferred to the volumetric flask and dissolved in the solution. A portion of the resulting solution was then transferred to the spectrophotometer cell, which was placed in the thermostated cell compartment. In a number of experiments, spectrum vs. time curves were obtained over the wavelength range 650–350 nm. In most of the runs, however, the experiments were done at the fixed wavelength of 400 nm. 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 3 half-lives.

In all the experiments, SO_2 uptake/elimination, or redox kinetics, the final pH values were measured with a Fisher Model 420 pH/ion meter or a Beckman expandometer and a Markson combination electrode, by using a water-jacketed sample holder thermostated at the desired temperature.

Treatment of Data. The data for the SO_2 uptake reaction was found to be well fitted by the assumption of two consecutive first-order steps of the form

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P \qquad (1)$$

where R, I, and P represent the reacting species, the mono(sulfito) com-

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Table I. Dependence of Observed Rate Constants on pH for SO_2 Uptake by *trans*-$[Co(en)_2(OH_2)_2]^{3+}$[a]

pH	k_{f1}, s^{-1}	k_{f2}, s^{-1}	pH	k_{f1}, s^{-1}	k_{f2}, s^{-1}
		(a) 10 °C			
7.00	10.2 ± 2	1.75 ± 0.08	6.01	147 ± 5	14.6 ± 1.0
6.94	14.6 ± 3	2.23 ± 0.08	5.97	170 ± 6	13.6 ± 2.0
6.84	15.3 ± 2	2.90 ± 0.3	5.90	178 ± 9	13.2 ± 2.0
6.79	18.8 ± 2	3.30 ± 0.3	5.85	224 ± 14	19.3 ± 0.9
6.75	20.0 ± 2	3.9 ± 0.4	5.70	294 ± 20	26.3 ± 2
6.67	27.8 ± 2	5.9 ± 1.0	5.67	365 ± 23	28.4 ± 3
6.60	38.5 ± 2	5.3 ± 0.4	5.66	299 ± 20	34 ± 9
6.58	35.1 ± 5	5.9 ± 0.6	5.52	544 ± 90	36 ± 8
6.43	43.2 ± 4	6.0 ± 1.0	5.45	485 ± 70	39 ± 3
6.35	55.4 ± 6	6.5 ± 1.0	5.33	577 ± 85	42 ± 10
6.32	57.8 ± 3	7.8 ± 0.8	5.23	826 ± 100[b]	51 ± 15
6.25	72.5 ± 4	10.7 ± 1.0	5.18	1107 ± 200[b]	52 ± 11
6.20	118.0 ± 11	11.2 ± 0.7	4.96		205 ± 30
6.06	105 ± 8	13.2 ± 0.8	4.75		210 ± 40
6.05	127 ± 3	13.3 ± 1.0			
		(b) 15 °C			
6.94	9.8 ± 2	1.7 ± 1.0	6.02	127 ± 25	17.0 ± 1.2
6.91	13.6 ± 1.5	2.6 ± 0.5	5.82	300 ± 30	28.1 ± 1.8
6.81	21.4 ± 2.0	3.7 ± 0.5	5.63	510 ± 45	39.3 ± 1.5
6.71	22.4 ± 2.0	3.5 ± 0.6	5.59	511 ± 45	37.2 ± 2
6.60	33.1 ± 2.0	5.1 ± 0.6	5.51	518 ± 43	39 ± 2
6.44	51 ± 3	6.4 ± 2.0	5.31		51 ± 9
6.22	106 ± 7	13.5 ± 1.5	5.15	1430 ± 350[b]	72 ± 3
		(c) 20 °C			
6.94	15.5 ± 2.0	3.6 ± 0.5	6.55	49 ± 5	8.8 ± 1.0
6.85	18.6 ± 3.0	4.2 ± 0.7	6.41	75 ± 6	12.4 ± 2
6.77	28.3 ± 3.5	5.4 ± 0.6	6.19	165 ± 15	23 ± 3
6.68	30.1 ± 3	6.0 ± 1.0	5.99	241 ± 37	29 ± 6

[a] For [complex] = (4–8) × 10^{-4} M, $[S_T]$ = 0.04 M, and I = 1.0 M ($NaClO_4$, citrate–phosphate). [b] These values are questionable.

plex and the bis(sulfito) complex, respectively. The mole fractions of the various species present at time *t* are given by

$$f_R = e^{-k_1 t} \tag{2}$$

$$f_I = \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{3}$$

$$f_P = 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \tag{4}$$

The total relative absorbance of the solution at any time *t* is given by

$$A_t = A_R f_R + A_I f_I + A_P f_P \tag{5}$$

Substituting (2), (3), and (4) into (5) and rearranging, we get

$$A_t - A_P = \left\{A_R + \frac{A_I k_1}{k_2 - k_1} + \frac{A_P k_2}{k_1 - k_2}\right\} e^{-k_1 t} + \left\{\frac{A_I k_1}{k_1 - k_2} - \frac{A_P k_1}{k_1 - k_2}\right\} e^{-k_2 t} \tag{6}$$

Equation 6 reduces to

$$A_t - A_P = Ce^{-k_1 t} + De^{-k_2 t} \tag{7}$$

with *C* and *D* representing the constant preexponential factors. On the assumption that k_1 is larger than k_2, a plot of ln $(A_t - A_P)$ vs. time should give a straight line at long times; a plot of ln $(A_t - A_P - De^{-k_2 t})$ vs. time should give a straight line in the early stages of the reaction. Initial values of k_1 and k_2 were obtained graphically by this method, and these were used to get the final values with an iterative[18] least-squares treatment.

Results and Discussion

The addition of buffered solutions of $Na_2S_2O_5$ to an aqueous solution of *trans*-$[Co(en)_2(OH_2)_2]^{3+}$ causes an immediate color change from light pink to greenish yellow, at pH 3–6. This is presumed on the basis of our previous studies[1-5] and its spectral characteristics[19] to be evidence for the formation of the O-bonded sulfito intermediate. Maximum buildup of the intermediate occurs at pH ~6. Acidification of the greenish yellow solution to pH 1–2 results in rapid regeneration of the *trans*-diaquo complex. Attempts to isolate the O-bonded sulfito complex in the solid state were unsuccessful. At pH < 6 the greenish yellow solution slowly changes to an almost colorless solution characteristic of cobalt(II). This fact was confirmed by tests for cobalt(II) in the form of $Co(NCS)_4^{2-}$.[20] At pH >6 the greenish yellow solution changes to bright yellow, the spectral features[21] of which are similar to those of the known S-bonded sulfito complexes. In addition, tests for Co(II) on the bright yellow solutions left at room temperature for several days were negative.

Table II. Dependence of SO_2 Uptake Rate Constants on pH and Total Sulfite at 10 °C

pH	$[S_T]$, M	k_{f1}, s^{-1}	k_{f2}, s^{-1}
6.30 ± 0.05	0.01	20 ± 2	1.9 ± 0.4
	0.02	39 ± 2	3.9 ± 0.3
	0.03	54 ± 4	6.6 ± 0.5
	0.04	56 ± 6	6.5 ± 1.0
	0.04	58 ± 3	7.8 ± 0.8
	0.06	95 ± 7	11.0 ± 0.6
5.80 ± 0.1	0.01	37.5 ± 1.0	7.2 ± 0.1
	0.02	78 ± 3	11.7 ± 0.1
	0.03	109 ± 9	14.3 ± 0.2
	0.03	127 ± 13	13.3 ± 1.0
	0.04	171 ± 5	21.1 ± 0.3
	0.04	178 ± 9	19.2 ± 2
	0.04	224 ± 14	19.3 ± 0.9
	0.06	265 ± 23	28.4 ± 3
	0.10	498 ± 90	44 ± 2

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(19) The characteristic peak for the O-bonded sulfito species is at 345 nm with an extinction coefficient of 2300, which is comparable to λ_{max} at 310 nm (ϵ = 2100)[2] for $[Co(NH_3)_5OSO_2]^+$, 330 nm (ϵ = 1928)[3] for α,β-*S*-$[Co(tetren)(OSO_2)]^+$, 325 nm (ϵ = 1825)[3a] for $[Co(tren)(OH_2)(OSO_2)]^+$, and 310 nm ($\epsilon$ = 1500)[8] for *cis*-$[Co(en)_2OH_2(OSO_2)]$.

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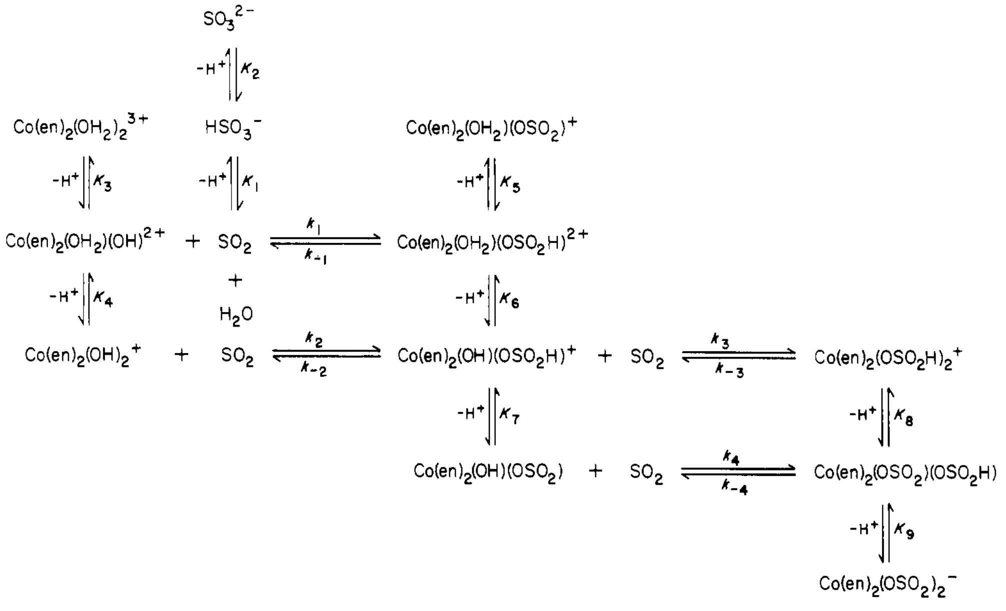
(21) At pH values above 6 the solution changes from greenish yellow to bright yellow. The spectrum of the bright yellow solution at pH 9 gave the following absorption maxima and the corresponding molar absorptivity (M^{-1} cm^{-1}): vis. 578 (ϵ = 45.5), 404 (ϵ = 2164), 325 (ϵ = 11096), 263 nm (ϵ = 5932) compared to O-bonded sulfito species with a characteristic peak at 345 nm (ϵ = 2300).

Scheme I. Mechanism for the SO_2 Uptake and Elimination Process of *trans*-$Co(en)_2(OH_2)_2^{3+}$



The SO_2 uptake kinetics study was performed in the ranges $4.75 < pH < 7.00$ and $10 < t < 20$ °C and with 0.04 M total sulfite. These data are summarized in Table I. In addition, the SO_2 uptake process was further studied at 10 °C as a function of total sulfite concentrations $[S_T]$ $(0.01 < [S_T] < 0.1)$ at the pH values 6.3 ± 0.05 and 5.8 ± 0.1. These data appear in Table II, and an essentially linear dependence of the observed rate constants k_{f1} and k_{f2} is noted at each pH. The data given in Tables I and II illustrate the steep decline in k_{f1} and k_{f2} as the pH is increased. Since both steps in the biphasic reaction are proportional to $[S_T]$, it is clear that each reaction is a SO_2 uptake. This behavior is unlike that observed for cis-$[Co(en)_2(OH_2)_2]^{3+}$ [8] or $[Co(tren)(OH_2)_2]^{3+}$ [3a,22] in which only one step is observed and only the monosulfito species is obtained in the fast first step. Scheme I gives a mechanism in which a monosulfito species is formed by the reaction of the hydroxo aquo or the dihydroxo complexes with SO_2, followed by further SO_2 uptake of the resulting hydroxosulfito-*O* complex. The first step is similar to schemes proposed in our previous studies.[1-5]

The rate law for the formation and decomposition of the O-bonded mono(sulfito) complexes corresponding to Scheme I takes the form

$$\frac{d\ \ln\ [\text{aquo complex}]_T}{dt} = k_{f1(obsd)} = \{k_1\alpha_1[SO_2] + k_2\alpha_2[SO_2] + k_{-1}\beta_1 + k_{-2}\beta_2\} \quad (8)$$

where α_1 and α_2 are the fractions of the aquo hydroxo and dihydroxo species, respectively. These fractions may be calculated from the relations

$$\alpha_1 = K_3[H^+]/([H^+]^2 + K_3[H^+] + K_3K_4) \quad (9)$$

$$\alpha_2 = K_3K_4/([H^+]^2 + K_3[H^+] + K_3K_4) \quad (10)$$

and the known values[23] of K_3 and K_4 and the observed pH values.

Table III. Rate Constants and Activation Parameters for k_{f1} (Mono(sulfito) Formation)

temp, °C	$10^{-7}k_1$,[a] $M^{-1}\ s^{-1}$	$10^{-9}k_2$,[a,b] $M^{-1}\ s^{-1}$	$10^{-3}k'_2$,[c] $M^{-1}\ s^{-1}$
10.0	7.5 ± 0.5	2.2 ± 0.3	1.4 ± 0.3
15.0	9.3 ± 0.6	1.4 ± 0.2	1.1 ± 0.2
20.0	11.5 ± 0.9	1.4 ± 0.3	1.3 ± 0.3

$\Delta H^\ddagger = 6.4 \pm 2$ kcal mol^{-1}; $\Delta S^\ddagger = -11.0 \pm 1.4$ cal $K^{-1}\ mol^{-1}$

[a] The corresponding values for the *cis*-$Co(en)_2(OH_2)_2^{3+}$ analogue are $5.9 \times 10^7\ M^{-1}\ s^{-1}$ for k_1 and $10.0 \times 10^9\ M^{-1}\ s^{-1}$ for k_2 at 10 °C. [b] SO_2 reaction. [c] HSO_3^- reaction.

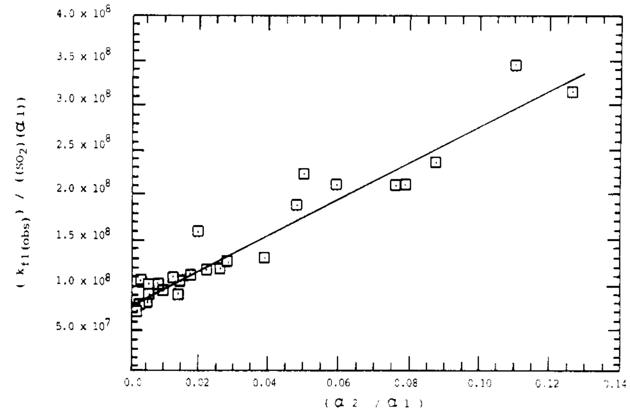


Figure 1. Plot of $k_{f1}(obsd)/\alpha_1[SO_2]$ vs. α_2/α_1 for the first step in the SO_2 uptake by *trans*-$(Co(en)_2(OH_2)_2)^{3+}$ at 10 °C.

Similarly β_1 and β_2 are the fractions of the aquo bisulfito and aquo sulfito species, respectively, at a given pH and temperature. These fractions are given by the relations

$$\beta_1 = [H^+]^2/([H^+]^2 + (K_5 + K_6)[H^+] + K_6K_7) \quad (11)$$

$$\beta_2 = K_6[H^+]/([H^+]^2 + (K_5 + K_6)[H^+] + K_6K_7) \quad (12)$$

In addition, the SO_2 concentrations may be calculated[24] at each pH from ($[S_T]$ = total free sulfite in solution)

$$[SO_2] = [H^+]^2[S_T]/([H^+]^2 + K_1[H^+]^2 + K_1K_2) \quad (13)$$

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[22] The tren analogue $Co(tren)(OH_2)_2^{3+}$ gives a monosulfito species,[3a] $k = 3.9 \times 10^7\ M^{-1}\ s^{-1}$, which subsequently undergoes two types of much slower reactions, depending on the pH of the solution. In the range $2.9 < pH < 5.4$, an internal redox process to Co(II) is observed. 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, $k = 0.18\ M^{-1}\ s^{-1}$ (see El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 4251). The corresponding rate constants for *trans*-$Co(en)_2(OH_2)_2^{3+}$ are respectively $9.3 \times 10^7\ M^{-1}\ s^{-1}$ and $5.1 \times 10^6\ M^{-1}\ s^{-1}$.

[23] The values of K_3 and K_4 are reported[12] to be 3.55×10^{-5} M and 1.15×10^{-8} M at 25 °C and $I = 1.0$ M. These values are used without adjustment for changed electrolyte or temperature, since such adjustments are known to be relatively small and do not affect the conclusions drawn from our data.

[24] The values of K_1 are interpolated from the previously published data.[3] They are 1.82×10^{-2}, 1.57×10^{-2}, 1.38×10^{-2}, and 1.26×10^{-2} M at 10, 15, 20, and 25 °C, respectively. K_2 is temperature-independent within the present range of temperature,[3a] where it has a value of 5.01×10^{-7} M.

Scheme II. Alternate Mechanism for the SO_2 Uptake and Elimination Process of *trans*-$Co(en)_2(OH_2)_2^{3+}$

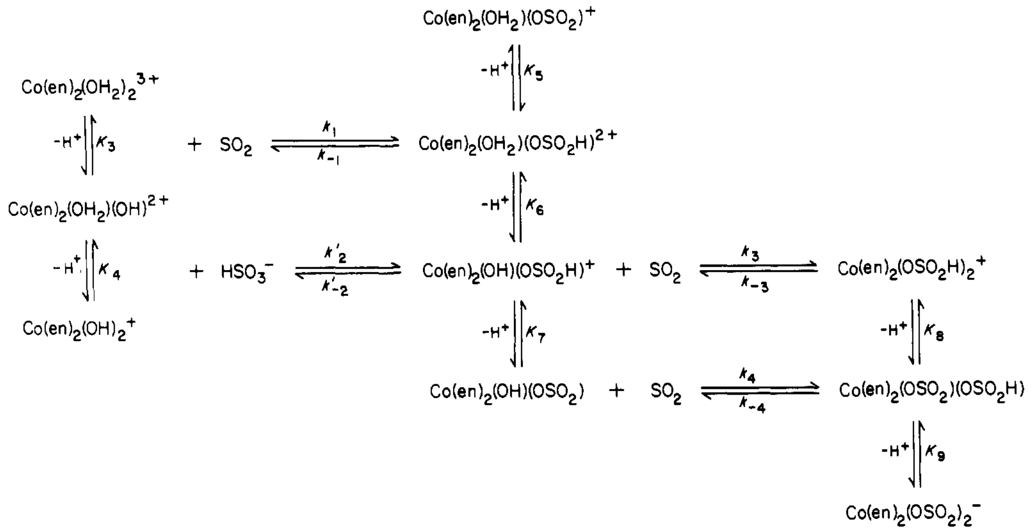

Table IV. Rate Constants and Activation Parameters for k_{f2} (Bis(sulfito) Formation)

temp, °C	$10^{-6}a$,[a] s^{-1} M^{-1}	b,[b] s^{-1}
10.00	4.6 ± 0.5	5.4 ± 0.2
15.00	5.1 ± 0.8	4.7 ± 0.2
20.00	11.2 ± 1.3	5.2 ± 0.3

$\Delta H^\ddagger = 14 \pm 6$ kcal mol^{-1}; $\Delta S^\ddagger = 10 \pm 3.5$ kcal K^{-1} mol^{-1}

[a] $a = k_3K_5/(K_5 + K_6)$. [b] $b = K_4K_5K_6/(K_5 + K_6)$.

At low $[H^+]$, where the contribution by the reverse SO_2 elimination process is negligible (pH >5.0), eq 8 reduces to

$$k_{f1}(\text{obsd}) = (k_1\alpha_1 + k_2\alpha_2)[SO_2] \tag{14}$$

i.e.

$$k_{f1}(\text{obsd})/\alpha_2[SO_2] = k_1\frac{\alpha_1}{\alpha_2} + k_2 \tag{15}$$

or

$$k_{f1}(\text{obsd})/\alpha_1[SO_2] = k_1 + k_2\frac{\alpha_2}{\alpha_1} \tag{16}$$

The values of k_1 and k_2 were obtained by linear regression analyses of the experimental data using eq 15 and 16 and are summarized in Table III. A graphical representation of such an analysis of the data at 10.0 °C is represented in Figure 1. In addition, Table III gives the activation parameters for k_{f1}.

Two conclusions are derived from the previous analyses. First, it was observed that the plots were linear over the entire range of pH studied, an indication of the negligible contribution of the back-reaction to the SO_2 uptake experiments under the conditions studied. Secondly, the value of k_2, 2.2×10^9 M^{-1} s^{-1}, is approaching the diffusion-controlled limit, as was found to be the case for the SO_2 uptake by the tren[3a] and the *cis*-ethylenediamine congeners.[8] This latter condition could be rectified by the assumption of a mechanism (Scheme II) involving simultaneous addition of HSO_3^- and SO_2 to *trans*-$[Co(en)_2(OH_2)(OH)]^{2+}$. In this k_{f1} takes the form

$$k_{f1} = k_1\alpha_1(SO_2) + k'_2\alpha_1(HSO_3^-) \tag{17}$$

$$k_{f1} = \left(k_1 + \frac{k'_2K_1}{[H^+]}\right)\alpha_1[SO_2] \tag{18}$$

or

$$k_{f1}/\alpha_1[SO_2] = k_1 + k'_2K_1/[H^+] \tag{19}$$

The values of k_1 and k'_2 are obtained from a linear least-squares fit of the data to eq 19 and the known values of K_1 (the acid dissociation constant of sulfurous acid). The values of k_1 obtained from this treatment are essentially the same as those given in the previous treatment (Scheme I), and the values of k'_2 are given in Table III. In addition, one also notes that the second-order rate[25] constants k_2 and k'_2 are related to each other by the relationship

$$k'_2 = k_2\frac{K_4}{K_1} \tag{20}$$

The pseudo-first-order rate constant k_{f2} (see data in Table I) was found to be well fitted by an equation of the form

$$k_{f2}/[SO_2] = a + b/[H^+] \tag{21}$$

Application of Scheme I or II gives a rate law dependence of the form

$$k_{f2}/[SO_2] = \frac{k_3K_6[H^+] + k_4K_6K_7}{[H^+]^2 + (K_5 + K_6)[H^+] + K_6K_7} \tag{22}$$

Assuming that $[H^+]^2 \sim K_6K_7 \ll (K_5 + K_6)[H^+]$, eq 22 reduces to

$$k_{f2}/[SO_2] = \frac{k_3K_6}{K_5 + K_6} + \frac{k_4K_6K_7}{(K_5 + K_6)[H^+]} \tag{23}$$

The parameters a and b in eq 21 are thus

$$a = \frac{k_3K_6}{K_5 + K_6} \qquad b = \frac{k_4K_6K_7}{K_5 + K_6} \tag{24}$$

The values of a and b and the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are given in Table IV.

The SO_2 elimination kinetics study was performed in the range $2.97 < pH < 5.6$ and at 10 and 15 °C at $I = 1.00$ M ($NaClO_4$). The reaction was found to be biphasic, and the values of the two rate constants were sufficiently different to allow their independent determination. The experimentally determined values of these rate constants are given as a function of pH and temperature in Table V. One notes that the values of k_{r1} and k_{r2} are much larger than the isomerization rates of $[Co(en)_2(OH_2)(OH)]^{2+}$.[17] Plots of pseudo-first-order rate constants k_{r1} and k_{r2} vs. hydrogen concentration gave good straight lines with essentially zero in-

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(25) The fact that the rate constant k_2 (2.2×10^9 M^{-1} s^{-1}) is approaching the diffusion-controlled limit gives higher credibility to Scheme II, in which simultaneous addition of HSO_3^- and SO_2 to *trans*-$[Co(en)_2(OH_2)(OH)]^{2+}$ is proposed. Similar routes have been proposed for the formation of a (sulfito)pentaammineplatinum(IV) complex.[5]

Scheme III

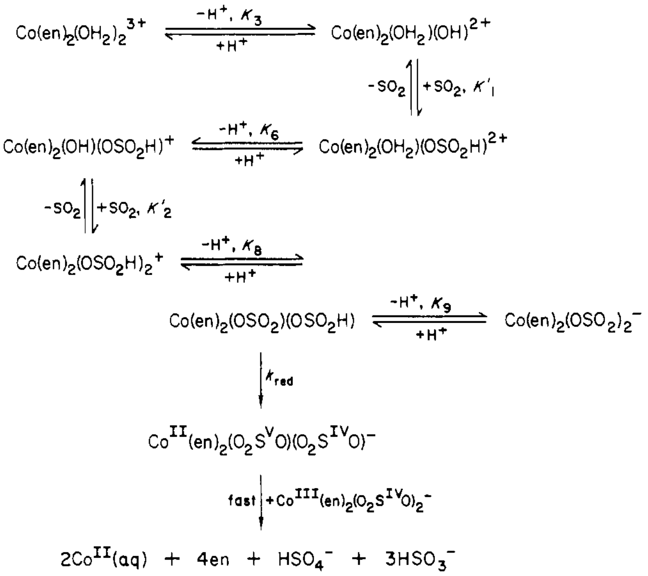


Table V. pH Dependence of the Rate Constants for the Elimination of SO_2 from *trans*-$[Co(en)_2(OSO_2H)_2]$[a]

pH	k_{r1}, s^{-1}	k_{r2}, s^{-1}
	(a) 10 °C	
5.39	10.4 ± 0.3	0.042 ± 0.001
5.25	19.2 ± 1	0.014 ± 0.002
5.07	22.5 ± 0.5	0.0507 ± 0.0002
4.82	42 ± 2	0.065 ± 0.001
4.65	82.8 ± 0.6	0.103 ± 0.004
4.37	113 ± 3	0.165 ± 0.001
4.20	190 ± 1	0.266 ± 0.015
3.87	317 ± 16	0.522 ± 0.02
3.45		1.19 ± 0.05
2.97		3.11 ± 0.04
	(b) 15 °C	
5.64	10 ± 2	0.051 ± 0.002
5.48	13 ± 1	0.0716 ± 0.0005
5.27	23.1 ± 0.9	0.0879 ± 0.004
5.05	44 ± 2	0.0968 ± 0.0005
4.84	61 ± 4	0.1371 ± 0.0006
4.66	106 ± 7	0.168 ± 0.004
4.40	189 ± 8	0.317 ± 0.007
4.25	237 ± 8	0.382 ± 0.005
4.09	404 ± 51	0.60 ± 0.002

[a] For [complex] = 1 mM, $[S_T]$ = 4 mM, and I = 1.0 M ($NaClO_4$, citrate–phosphate).

tercepts. This indicates that the back-reaction rates (SO_2 uptake phase of the overall rate) gave negligible contributions to the observed rate constants for the elimination process. From Schemes I or II, the following relationships are easily obtained:

$$k_{r1} = \frac{k_{-3}[H^+]^2 + k_{-4}K_8[H^+]}{[H^+]^2 + K_8[H^+] + K_8K_9} \tag{25}$$

If $[H^+]^2 \sim K_8K_9 \ll K_8[H^+]$, one obtains

$$k_{r1} = \frac{k_{-3}[H^+]}{K_8} + k_{-4} \tag{26}$$

Similarly for k_{r2} one gets

$$k_{r2} = \frac{k_{-1}[H^+]^2 + k_{-2}K_6[H^+]}{[H^+]^2 + (K_5 + K_6)[H^+] + K_6K_7} \tag{27}$$

Table VI. Rate Data and Activation Parameters for the SO_2 Elimination Reactions

temp, °C	$10^{-6}k'_{-3}$,[a] M^{-1} s^{-1}	$10^{-3}k'_{-2}$,[b] M^{-1} s^{-1}
10.00	2.37 ± 0.14	2.89 ± 0.06
15.00	4.79 ± 0.17	6.68 ± 0.23

[a] $\Delta H^‡$ = 11.2 kcal mol^{-1}; $\Delta S^‡$ = 24.8 kcal K^{-1} mol^{-1}. [b] $\Delta H^‡$ = 13.6 kcal mol^{-1}; $\Delta S^‡$ = 26.5 cal K^{-1} mol^{-1}.

Table VII. Dependence of Observed Rate Constants on pH and $[S_T]$ for the Redox Decomposition of Bis(sulfito-*O*)cobalt(III) Ion at 25 °C[a]

pH	$[S_T]$, M	10^3k_{red}, s^{-1}	pH	$[S_T]$, M	10^3k_{red}, s^{-1}
2.14	0.04	2.51 ± 0.13	4.54	0.04	4.22 ± 0.05
2.64	0.04	3.51 ± 0.03	4.63	0.04	4.47 ± 0.07
2.69	0.04	4.80 ± 0.03	5.19	0.04	2.60 ± 0.02
2.82	0.04	4.82 ± 0.10	5.20	0.04	2.65 ± 0.02
3.50	0.04	6.62 ± 0.10	5.50	0.04	2.08 ± 0.12
3.51	0.04	5.38 ± 0.10	5.02	0.02	3.55 ± 0.03
3.74	0.04	5.60 ± 0.15	5.32	0.06	1.95 ± 0.01
4.46	0.04	4.42 ± 0.07	5.43	0.08	1.30 ± 0.01

[a] For [complex] = 1–4 mM and I = 1.0 M ($NaClO_4$, citrate–phosphate).

and if $[H^+]^2 \sim K_6K_7 \ll (k_5 + K_6)[H^+]$, we get

$$k_{r2} = \frac{k_{-1}[H^+]}{K_5 + K_6} + \frac{k_{-2}K_6}{K_5 + K_6} \tag{28}$$

Equations 26 and 27 reproduce the experimentally observed relationships and show that k_{r1} and k_{r2} are straight-line functions of the hydrogen ion concentration. Fitting the data to equations 26 and 28 by linear least-squares methods gave the data in Table VI, in which

$$k'_{-3} = \frac{k_{-3}}{K_8} \qquad k'_{-2} = \frac{k_{-1}}{K_5 + K_6} \tag{29}$$

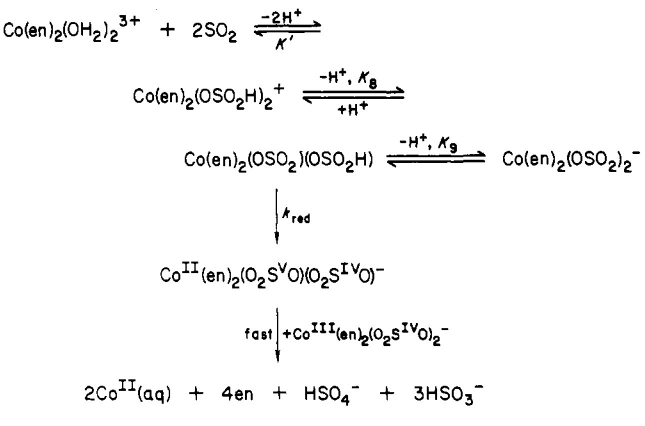
The redox decomposition of *trans*-$[Co(en)_2(OSO_2H)_2]^+$ was investigated in the ranges 2.14 < pH < 5.5 and 0.02 < $[S_T]$ < 0.08 M, at I = 1.0 M ($NaClO_4$) and 25 °C. Preliminary experiments of this relatively slow process showed that at pH lower than 6 the greenish yellow solution of the (sulfito-*O*)cobalt(III) complex very slowly fades in color to a nearly colorless solution, indicative of the complete conversion of the cobalt(III) to cobalt(II). This color change was followed spectrophotometrically and proved the complete conversion to cobalt(II), which was identified in solution by the tetrakis(thiocyanato)cobaltate(II) method.[20] The experimentally determined values for the pseudo-first-order rate constant "k_{red}" for the redox decomposition of the bis(sulfito-*O*) complex are given in Table VII. The variation of the rate constant of the reaction with pH takes the form of a bell-shaped curve. This kind of variation is frequently observed for dibasic acid systems where only the monoprotonated species is reactive. One can achieve such a situation in the present system by the assumption of a mechanism as given in Scheme III or in its slightly simplified form (Scheme IV). This mechanism is very much similar to that proposed in our study of the redox decomposition of the tren analogoue.[3a] The observed rate constant derived from Scheme IV takes the form

$$k_{red}(\text{obsd}) = \frac{k_{red}K_8[H^+]}{K'K_8K_9[SO_2]^2 + K'K_8[H^+][SO_2]^2 + K'[H^+]^2[SO_2]^2 + [H^+]^4} \tag{30}$$

which reduces to

$$k_{red}(\text{obsd}) = \frac{k_{red}K_8[H^+]}{K_8K_9 + K_8[H^+] + [H^+]^2} \tag{31}$$

Scheme IV



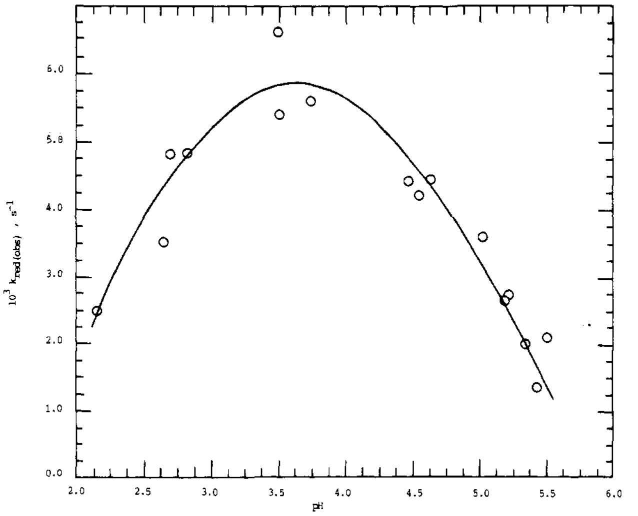


Figure 2. Variation of the observed rate constant k_{red}(obsd) for the reduction of bis(sulfito-*O*)cobalt(III) with pH at 25 °C (data of Table VII).

if $[H^+]^4$ is neglected. This situation is achieved if it is assumed that when the metabisulfite is added to the trans-diaquo and -aquo hydroxo equilibrium mixture, the cobalt(III) species are completely converted to the disulfito complex $Co(en)_2(OSO_2H)_2$. This latter complex then takes the three equilibrium forms given in Scheme IV, in which the monoprotonated species is the one that undergoes reduction to cobalt(II).

Rearrangement of eq 31 gives

$$\frac{[H^+]}{k_{red}(obsd)} = \frac{K_9}{k_{red}} + \frac{[H^+]}{k_{red}} + \frac{[H^+]^2}{k_{red}K_8} \qquad (32)$$

A least-squares fit of the experimental data to the form of eq 32 gave $k_{red} = (6.5 \pm 0.3) \times 10^{-3}$ s^{-1}, $K_8 = (4.4 \pm 0.6) \times 10^{-3}$ M, and $K_9 = (1.2 \pm 0.4) \times 10^{-5}$ M. These parameters gave a very satisfactory fit of all the experimental data as shown in Figure 2. The *K* values are in the range to be expected, since studies of an analogous cobalt(III) system[26] suggested a similar order of magnitude for K_8, while one would expect K_9 to be at least 1 order of magnitude smaller than K_8, due to the considerably decreased positive charge on the monoprotonated bis(sulfito) species relative to the diprotonated one.

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Registry No. *trans*-$[Co(en)_2(OH_2)(OH)]^{2+}$, 24458-51-3; *trans*-$[Co(en)_2(OH)_2]^+$, 21772-94-1; *trans*-$[Co(en)_2(OSO_2H)_2]^+$, 100021-53-2; *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$, 14099-22-0; SO_2, 7446-09-5.

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The Basis of Aryl Substituent Effects on Charge-Transfer Absorption Intensities

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Mulliken's theory for donor–acceptor interactions is used to rationalize the effects of aryl substituents on the intensities of the metal-to-ligand charge-transfer absorptions that are characteristic of Cu(I) complexes with phenanthroline ligands. Depending on the positions of the aryl substituents, the absorption intensity is enhanced or diminished with respect to the unsubstituted complex. The analysis verifies that the transition dipole length is approximately given by the separation between the charge centroids of the donor and acceptor orbitals. In the absence of steric complications, this means that the aryl substituent effects can be traced to readily envisioned resonance interactions. When conjugation with the π system of the substituents extends the acceptor orbital out away from the metal center, the transition dipole length is increased and the intensity is enhanced. Conversely, a decreased transition dipole length results when the substituent spreads the acceptor orbital in a direction opposite to that of the optically induced charge transfer.

Introduction

Although relatively few studies have focused on the origins of absorption intensities, the absorption spectra of complexes of organic ligands with transition-metal ions often show distinct connections between intensity and ligand structure. An understanding of the basis of these effects would aid in the design of more effective ligands for colorimetric analysis as well as in the adjustment of the photochemical and photophysical properties of the complexes themselves. For example, ligand modifications that improve the light-gathering characteristics of a complex enhance its potential for energy-conversion applications.

The charge-transfer (CT) absorption intensities of 1,10-phenanthroline (phen) complexes of copper(I) and iron(II) reveal the dramatic influence that perturbations in ligand structure can

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