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Internal Oxidation–Reduction of *trans*-$Co(en)_2SO_3OH_2^+$

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In a range of perchloric acid media up to 7 *M*, *trans*-$Co(en)_2SO_3OH_2^+$ disproportionates according to the reaction *trans*-$Co(en)_2SO_3OH_2^+ + 3H^+ \rightarrow Co_{aq}^{2+} + HSO_3 + 2enH^+$. The HSO_3 radical yields dithionic acid and it may be scavenged by Fe^{2+} and O_2. The disproportionation reaction is acid catalyzed and protonation of the reactant is complete above 1 *M* $HClO_4$. At 73°, the rate of disproportionation is given by $k_{obsd} = 3.61 \times 10^{-4}$ sec^{-1} with $\Delta H^{\ddagger} = 32.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9 \pm 1$ eu. The value of k_{obsd} varies directly as the activity of water in the perchloric acid medium. The mechanism of the reaction is discussed.

Introduction

Inner-sphere electron-transfer reactions involve the formation of an activated complex in which the oxidant and the reductant become bonded through a bridging ligand and usually evidence for its structure must be inferred from a variety of kinetic and isotopic techniques.[1] In some cases, the redox process yields a bridged intermediate in which the oxidation states are characteristic of the final products. This intermediate, or "successor complex,"[2] then undergoes a slower dissociation to yield the final products. An example[3] is the oxidation of $Co^{II}(EDTA)^{2-}$ by $Fe^{III}(CN)_6^{3-}$ to yield $(EDTA)Co^{III}NCFe^{II}(CN)_5^{5-}$ which subsequently forms the final products $Co^{III}(EDTA)^-$ and $Fe^{II}(CN)_6^{4-}$.

The complex *trans*-$Co(en)_2SO_3OH_2^+$ is a convenient model for a bridged transition state prior to electron transfer between the $Co^{III}(en)_2$ oxidant and the reductant $S^{IV}O_3^{2-}$. It may be termed a "precursor complex." Although the oxidant and reductant are bonded directly, this complex is normally inert with respect to internal oxidation–reduction or disproportionation. The preceding paper[4] showed that *trans*-$Co(en)_2SO_3OH_2^+$ and its conjugate base *trans*-$Co(en)_2SO_3OH$ may undergo rapid substitution reactions around room temperature without any evidence for concomitant redox reactions. However at elevated temperatures and in concentrated acid media, protonated *trans*-$Co(en)_2SO_3OH_2^+$ has been found to undergo internal oxidation–reduction yielding Co_{aq}^{2+} and dithionic acid, $H_2S_2O_6$, as ultimate products. We adduce evidence in this paper that the initial products of the disproportionation are cobalt(II) and the sulfite radical ion of formal oxidation state S(V).

In acid media, the sulfite radical ion, SO_3^-, is considered[5] to exist in the protonated form HSO_3 and this will be assumed in this paper. In the absence of radical scavengers, HSO_3 radicals dimerize to form dithionic acid. Thus dithionic acid is formed when sulfurous acid is oxidized by metal oxides,[6] such as β-MnO_2, which are capable of one-electron oxidation. In homogeneous solution, the oxidation of sulfites by aquated metal cations,[7,8] such as Fe_{aq}^{3+} and Cu_{aq}^{2+}, yields dithionates with minor amounts of sulfates. This is accounted for by the reaction scheme[7]

$$Fe_{aq}^{3+} + HSO_3^- \rightleftharpoons Fe(HSO_3)^{2+}$$

$$Fe(HSO_3)^{2+} \longrightarrow Fe^{2+} + HSO_3 \qquad (k_1)$$

$$HSO_3 + Fe_{aq}^{2+} \longrightarrow Fe_{aq}^{3+} + HSO_3^- \qquad (k_2)$$

$$HSO_3 + Fe_{aq}^{3+} + H_2O \longrightarrow Fe_{aq}^{2+} + SO_4^{2-} + 3H^+ \qquad (k_3)$$

$$HSO_3 + HSO_3 \longrightarrow H_2S_2O_6 \qquad (k_4)$$

In perchlorate media, Karrakar[8] found that $k_2/k_3 = 22$. The oxidation of Fe^{2+} can be used to estimate the HSO_3 radical, provided chemical yields are corrected for the side reaction with the product Fe_{aq}^{3+}.

The initial formation of inner-sphere sulfitometal complexes (*e.g.*, $Fe(HSO_3)^{2+}$) has been proposed[6,7] but their stationary concentration appears to be too low to permit spectroscopic detection. The species *trans*-$Co(en)_2SO_3OH_2^+$ is thus a convenient model for such complexes for the thermal generation of an HSO_3 radical.

Experimental Section

Materials.—*trans*-$Co(en)_2SO_3OH_2ClO_4$ was prepared by Baldwin's method.[9] *Anal.* Calcd for *trans*-$Co(en)_2SO_3OH_2ClO_4$: C, 13.4; N, 15.6; S, 8.9; H, 4.4; Cl, 10.0. Found: C, 13.2; N, 15.5; S, 8.7; H, 4.3; Cl, 10.5. The *trans* configuration of this complex was confirmed by pmr measurements at 60 MHz using a 0.4 *M* solution of the complex in 80% sulfuric acid as a solvent at 0°. Under these conditions both the $-CH_2$ and the $-NH_2$ protons were detectable. Only two peaks of integrated area 1.0:1.0 were observed at +1.7 ppm ($-CH_2$) and +3.2 ppm ($-NH_2$) relative to acetaldehyde as an internal reference standard. No conformational splitting of the $-CH_2$ peak was observed. This spectrum is clear evidence for the *trans* configuration, in agreement with the ir evidence of Hughes and McWhinnie[10] but at variance with the earlier assignment of Baldwin.[9] The *cis* isomer would have yielded three proton peaks due to $-NH_2$ in the intensity ratio 1:1:2 and probably two peaks for the $-CH_2$ groups. The infrared spectrum of the *trans* preparation agreed with that reported previously by Baldwin.

Stoichiometric Measurements.—The yield of thionate radicals was estimated with Fe^{2+} scavenger which does not itself

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reduce $Co(en)_2SO_3OH_2^+$. A solution of $Co(en)_2SO_3OH_2^+$ (0.010 *M*) and Fe^{2+} (0.10 *M*) in 2.36 *M* $HClO_4$ was heated at 98° for 30 min. On cooling, a 5-ml sample of the reacted solution was mixed with 5 ml of 2 *M* NH_4SCN and the mixture was diluted to 100 ml. The Fe^{3+} was determined as $FeNCS^{2+}$ at 480 nm using $\epsilon(FeNCS^{2+})$ 4310 M^{-1} cm^{-1}.

Dithionic acid was identified qualitatively using $Co(en)_2{}^{35}SO_3OH_2^+$. The yield of dithionic acid was determined from the SO_2 evolved from the hydrolysis

$$H_2S_2O_6 + H_2O \longrightarrow H_2SO_4 + (H_2SO_3) \longrightarrow H_2O + SO_2$$

A solution of *trans*-$Co(en)_2SO_3OH_2^+$ (1.0×10^{-3} *M*) in 2.36 *M* $HClO_4$ was bubbled with a nitrogen gas stream for 45 min at room temperature. The gas stream was led through two bubbler units containing 4.0×10^{-3} *M* $K_2Cr_2O_7$ in 2 *M* H_2SO_4. The temperature of the reaction mixture was then raised to 98° and the liberated SO_2 trapped in the two bubblers. Only 2% of the SO_2 passed into the second bubbler. The reduction of the $K_2Cr_2O_7$ concentration by SO_2 was determined at 435 nm using $\epsilon(Cr_2O_7{}^{2-})$ 470 M^{-1} cm^{-1}.

Rate Measurements.—Normally, the rate of disappearance of *trans*-$Co(en)_2SO_3OH_2^+$ was determined at 465 nm, corresponding to the absorption maximum of this complex ion. The reactant solutions were contained in glass vessels maintained at a constant temperature. Aliquot samples were withdrawn at regular time intervals and cooled to room temperature, and absorbance measurements were made with a Shimadzu QR-50 spectrophotometer whose cell compartment was maintained at 20°.

For some reactions, the rate of formation of $Co_{aq}{}^{2+}$ was measured by analysis of the blue $Co(SCN)_4{}^{2-}$ species. Aliquot samples (2 ml) from the reaction mixture were added to a chilled solution of 7 *M* NH_4SCN solution (1 ml), a 50:50 ether–amyl alcohol mixture (5 ml) was added, and the optical absorbance of the blue ether solution was measured at 600 nm.

The rate of hydrolysis of dithionic acid was measured titrimetrically. Sodium dithionate was dissolved in 2.36 *M* $HClO_4$ (500 ml) to form 0.100 *M* dithionic acid and the solution was deoxygenated with a nitrogen stream bubbling through the solution for 45 min at room temperature. The reaction flask was then immersed in a water bath maintained at 82.0°. Aliquot samples (10 ml) were removed at regular intervals and quenched in 0.100 *M* $BaCl_2$ solution (10 ml) at ice temperature. The pH of the solution was raised to 1.0 prior to titration using concentrated NaOH solution. The excess Ba^{2+} was then back-titrated with 0.0842 *M* H_2SO_4 using sodium rhodizonate as an indicator.

Results

Stoichiometry of the Reaction.—The disappearance of 1.00 mol of *trans*-$Co(en)_2SO_3OH_2^+$ was accompanied by the formation of 1.00 ± 0.05 mol of $Co_{aq}{}^{2+}$. Table I shows that in 2.36 *M* $HClO_4$ at 65°, the first-order rate constant for $Co(en)_2SO_3OH_2^+$ consumption was $(0.98 \pm 0.03) \times 10^{-4}$ sec^{-1} while the rate constant for $Co_{aq}{}^{2+}$ formation was $(1.00 \pm .07) \times 10^{-4}$ sec^{-1}. The 1:1 stoichiometry in cobalt was thus maintained throughout the course of the reaction.

Thionate radical formation in acid media was estimated by means of the reaction

$$Fe^{2+} + HSO_3 + H^+ \longrightarrow Fe^{3+} + H_2SO_3 \qquad (1)$$

where 1 mol of HSO_3 should be equivalent to 1 mol of Fe^{3+} and 1 mol of SO_2, evolved from the acid medium. A 1.00-mol sample of *trans*-$Co(en)_2SO_3OH_2^+$ was allowed to react in the presence of 1.00 mol of Fe^{2+} scavenger and yielded, in a nitrogen-purged environment, 0.94 mol of Fe^{3+} and 0.97 mol of H_2SO_3. The product of reaction 1, Fe^{3+}, may also react with HSO_3 to yield $SO_4{}^{2-}$ and Fe^{2+} (see the Introduction). The yields of Fe^{3+} and H_2SO_3 must therefore be corrected by the known ratio $k_2/k_3 = 22$; thus 1.00 mol of *trans*-$Co(en)_2SO_3OH_2^+$ would yield, in the absence of the competing reaction of Fe^{3+}, 0.985 mol of Fe^{3+} and 1.01 mol of H_2SO_3. Of these determinations the Fe^{3+} yield is considered more reliable.

TABLE I

RATE CONSTANTS FOR THE INTERNAL REDOX REACTION OF *trans*-$Co(en)_2SO_3OH_2^{+\,a}$

Temp, °C	$[HClO_4]$, *M*	10^4k_{obsd}, sec^{-1}	$10^4k_{obsd}/a_{H_2O}$, sec^{-1}
73.0	0.0236	0.73	0.73
73.0	0.0377	1.30	1.30
73.0	0.095	2.50	2.50
73.0	0.185	3.45	3.45
73.0	0.48	3.63	3.69
73.0	0.95	3.70	3.50
73.0	2.36	3.22	3.70
73.0	4.72	2.27	3.50
73.0	7.08	1.42	4.63
65.0	2.36	0.98[b]	1.12
76.8	2.36	3.22	3.80
82.0	2.36	10.2	11.7
73.0	2.36	3.17[c]	3.63
73.0	2.36	3.30[d]	3.78

[a] In all cases, $[Co(en)_2SO_3OH_2^+] = 0.003$ *M*. [b] When measured by rate of formation of $Co_{aq}{}^{2+}$, $10^4k_{obsd} = 1.00 \pm 0.07$ sec^{-1}. [c] Solution contained 0.003 *M* $Fe_{aq}{}^{2+}$. [d] Solution contained 0.003 *M* $Cu_{aq}{}^{2+}$.

A further small source of uncertainty in estimating the stoichiometric yield of HSO_3 is the scavenging effect of traces of oxygen still retained in the nitrogen-purged reaction media. When 1.00 mol of *trans*-$Co(en)_2SO_3OH_2^+$ reacted in the presence of 1.00 mol of Fe^{2+} scavenger in an air-saturated medium, the yield of Fe^{3+} fell to 0.64 mol. This indicates that oxygen (10^{-3} *M*) can compete with Fe^{2+} (10^{-2} *M*) in scavenging the HSO_3 radical. In the absence of Fe^{2+} scavenger and in the presence of oxygen, no SO_2 was detectable and the HSO_3 radical was converted to sulfate. In the absence of both Fe^{2+} and oxygen, 1.00 mol of *trans*-$Co(en)_2SO_3OH_2^+$ yields exclusively dithionic acid, $H_2S_2O_6$.

The overall stoichiometry of the primary reaction can then be written

$$trans\text{-}Co(en)_2SO_3OH_2^+ + 3H^+ \longrightarrow Co_{aq}{}^{2+} + HSO_3 + 2enH^+ + H_2O \qquad (2)$$

The subsequent reactions of the HSO_3 radical can then be represented as either

$$HSO_3 + HSO_3 \longrightarrow H_2S_2O_6 \text{ (absence of scavengers)}$$

or

$$HSO_3 + O_2 + H_2O \longrightarrow H_2SO_4 + HO_2 \text{ (presence of oxygen)}$$

or

$$HSO_3 + Fe^{2+} + H^+ \longrightarrow Fe^{3+} + H_2SO_3 \text{ (presence of } Fe^{2+}\text{)}$$

In perchloric acid concentrations exceeding 7 *M*, there was evidence for a concurrent hydrolysis reaction but this reaction was not investigated further.

Absence of Alternative Redox Reactions.—It was possible that the stoichiometry observed could arise from an initial hydrolysis of the sulfito ligand to yield sulfurous acid which then rapidly reduced the diaquo product

$$\textit{trans}\text{-}\mathrm{Co(en)_2SO_3OH_2^+ + 2H^+ \xrightarrow{slow} Co(en)_2(OH_2)_2^{3+} + H_2SO_3}$$

$$\mathrm{Co(en)_2(OH_2)_2^{3+} + H_2SO_3 \xrightarrow{fast} Co^{2+} + HSO_3 + 2enH^+}$$

$$\mathrm{2HSO_3 \xrightarrow{slow} H_2S_2O_6}$$

This possible reaction scheme was eliminated by the following check experiments. A perchloric acid solution (2.36 *M*), containing *cis*-$\mathrm{Co(en)_2(OH_2)_2^{3+}}$ (0.020 *M*) and $\mathrm{Na_2SO_3}$ (0.100 *M*), was heated at 75° in a sealed vessel for 3 hr. No $\mathrm{Co^{2+}}$ was detected above a concentration 10^{-4} *M*. The half-time for the internal redox reaction of $\mathrm{Co(en)_2SO_3OH_2^+}$ was 36 min under the same conditions. After 3 hr, 0.0194 *M* $\mathrm{Co^{2+}}$ should have been produced by the alternative reaction scheme. An analogous experiment with *trans*-$\mathrm{Co(en)_2(OH_2)_2^{3+}}$ and excess $\mathrm{Na_2SO_3}$ in 2.36 *M* $\mathrm{HClO_4}$ again yielded no detectable $\mathrm{Co^{2+}}$ in the time taken to establish the *cis* → *trans* equilibrium (10 min) and thereafter for a time corresponding to 4 half-times of the internal redox reaction. It was concluded that the alternative hydrolysis–redox reaction scheme could be excluded.

The formation of dithionic acid has been represented as arising from dimerization of $\mathrm{HSO_3}$ radicals. An alternative reaction mechanism could be

$$\textit{trans}\text{-}\mathrm{Co(en)_2SO_3OH_2^+ + H^+ \xrightarrow{slow} Co^{2+} + HSO_3}\text{, etc.}$$

$$\mathrm{HSO_3} + \textit{trans}\text{-}\mathrm{Co(en)_2SO_3OH_2^+ \xrightarrow{fast} Co^{2+} + H_2S_2O_6}$$

Since $\mathrm{Fe^{2+}}$ is an efficient scavenger for $\mathrm{HSO_3}$ radicals, then the presence of $\mathrm{Fe^{2+}}$ should eliminate the reaction of the $\mathrm{HSO_3}$ radical with the sulfito complex. The rate constant for disappearance of $\mathrm{Co(en)_2SO_3OH_2^+}$ should then be halved in the presence of $\mathrm{Fe^{2+}}$, if this reaction scheme operated. Table I shows that, within experimental error, the observed rate constant is unaltered by the addition of $\mathrm{Fe^{2+}}$. The alternative reaction scheme based on secondary $\mathrm{HSO_3}$ radical attack on the *trans*-$\mathrm{Co(en)_2SO_3OH_2^+}$ substrate can therefore be excluded. This observation also establishes that $\mathrm{Fe^{2+}}$ can be used as a radical scavenger without reducing $\mathrm{Co(en)_2SO_3OH_2^+}$. Table I also shows that the rate constant is unaffected by the addition of $\mathrm{Cu^{2+}}$ which is another radical scavenger for $\mathrm{HSO_3}$.

Rate of the Internal Redox Reaction.—First-order rate constants for the internal redox reaction(II) were determined under a variety of conditions summarized in Table I. At 73° in perchloric acid concentrations ranging from 0.0236 to 0.95 *M*, the reaction exhibits acid catalysis. Values of k_{obsd} increase with increasing acid concentration to an essentially constant value, corresponding to complete protonation of the reactant sulfito complex

$$\mathrm{Co(en)_2OH_2SO_3H_{\mathit{n}-1}{}^{\mathit{n}+} + H_{aq}{}^+ \rightleftharpoons Co(en)_2OH_2SO_3H_{\mathit{n}}{}^{(\mathit{n}+1)+}} \qquad (K_{\mathrm{a}})$$

where the degree of protonation, *n*, cannot be specified from the kinetic data.

The *trans*-$\mathrm{Co(en)_2SO_3OH_2^+}$ ion was subject to base titration but no evidence was obtained for protonation of the sulfito ligand above pH 1. The acidity constant of the aquo ligand[4] is 9.45 at 25°. It is assumed therefore that above pH 1 the species *trans*-$\mathrm{Co(en)_2SO_3OH_2^+}$ is not protonated and that $n = 1$ in the equation. The rate data are consistent with an acidity constant for *trans*-$\mathrm{Co(en)_2OH_2SO_3H^{2+}}$ of $K_{\mathrm{a}} = 0.065$. There is no evidence that the nonprotonated *trans*-$\mathrm{Co(en)_2OH_2SO_3^+}$ undergoes the internal redox reaction at temperatures below 82°.

Above 2 *M* $\mathrm{HClO_4}$, values of k_{obsd} *fall* with increasing acid concentration. This reduction is associated with the known[11] reduction in water activity as the perchloric acid concentration is increased. Table I shows that the values of $(k_{\mathrm{obsd}}/a_{\mathrm{H_2O}})$ remain constant, within experimental error, from 1 to 6 *M* $\mathrm{HClO_4}$. Hence the rate law may be expressed in the form

$$-d[\mathrm{Co(en)_2SO_3OH_2^+}]/dt = k'[\mathrm{Co(en)_2SO_3HOH_2^{2+}}]a_{\mathrm{H_2O}}$$

At 73°, $k' = (3.61 \pm 0.11) \times 10^{-4}\ \mathrm{sec^{-1}}$. The value of k_{obsd}, as determined by the rate of disappearance of $\mathrm{Co(en)_2SO_3OH_2^+}$, rises above 6 *M* $\mathrm{HClO_4}$ because of the onset of a parallel reaction of solvolysis of the sulfito ligand yielding a product whose uv–visible spectrum is identical with that of *cis*-$\mathrm{Co(en)_2(OH_2)_2^{3+}}$. As the water activity is further reduced in the region of 10 *M* $\mathrm{HClO_4}$, this hydrolysis reaction becomes the predominant reaction. However the kinetics of this solvolytic reaction were not examined because of the uncertain character of the solvent medium.

The activation parameters for the internal redox reaction were determined in a medium of 2.36 *M* $\mathrm{HClO_4}$ wherein protonation of the sulfito complex is complete. Over the range 65–82°, $\Delta H^{\ddagger} = 32.8 \pm 0.5$ kcal mol^{-1} and at 73°, $\Delta S^{\ddagger} = 9 \pm 1$ cal deg^{-1} mol^{-1}.

Rate of Disproportionation of Dithionic Acid.—Experiments were conducted to check that the rate of disproportionation of dithionic acid, a product of the internal redox reaction, was slower than the rate of the main reaction. At 82°, the reaction $\mathrm{H_2S_2O_6 + H_2O \rightarrow H_2SO_3 + H_2SO_4}$ exhibits a first-order rate constant $k = 1.7 \times 10^{-4}\ \mathrm{sec^{-1}}$ in 2.36 *M* $\mathrm{HClO_4}$. This rate constant is one-sixth of the value for the internal redox reaction. It was also confirmed that the oxidation of $\mathrm{Fe^{2+}}$ in the presence of dithionic acid was negligible at 82°. This demonstrated that the disproportionation of dithionic acid did not generate significant concentrations of oxidizing radicals. The slow disproportionation of dithionic acid could not therefore complicate the stoichiometric evidence for thermal generation of $\mathrm{HSO_3}$ radicals from *trans*-$\mathrm{Co(en)_2SO_3OH_2^+}$.

Discussion

The one-electron reduction of spin-paired ($\mathrm{t_{2g}}^6$) cobalt(III) complexes may be considered to involve electron transfer from the reductant to the d_{z^2} orbital of cobalt. For an inner-sphere reduction, the ligand

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[11] J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4966 (1961).

bridging the reductant to the cobalt(III) oxidant lies along the z axis. In order that $\Delta H^{\ddagger}$ be reduced to an accessible value, the energy of the d_{z^2} orbital must be reduced by removing both this bridging ligand and the ligand *trans* to it along the z axis. The kinetic behavior of *trans*-$Co(en)_2SO_3OH_2^+$ seems to be consistent with this general mechanism.

In *trans*-$Co(en)_2SO_3OH_2^+$, the aquo ligand is unusually labile and $\Delta H^{\ddagger}$ for dissociative release of this ligand has the unusually low value[4] of 15.9 kcal mol^{-1}. The motion of the aquo ligand away from the cobalt(III) center in the internal redox reaction would not therefore constitute a large energy barrier. By contrast, the sulfito ligand with a large ligand field appears to be bonded strongly to the cobalt(III) center and the energy barrier for removal of this reducing ligand should be substantial. The value of $\Delta H^{\ddagger} = 32.8$ kcal mol^{-1} for the overall internal redox reaction is consistent with this. Furthermore the value $\Delta S^{\ddagger} = 9$ eu is consistent with a transition state in which the $-SO_3$ and $-OH_2$ ligands are substantially dissociated from the cobalt(III) center.

Acid catalysis of the internal oxidation–reduction of *trans*-$Co(en)_2SO_3OH_2^+$ is also consistent with the partial dissociation of the $-SO_3$ ligand in the transition state. Protonation of an oxygen atom of the S-bonded sulfito ligand would be expected to labilize the sulfito ligand and reduce $\Delta H^{\ddagger}$. The value of the corresponding acidity constant for $Co(en)_2OH_2SO_3H^+$, $pK_a = 1.2$, suggests that the electron density on the peripheral oxygen atoms of the S-bonded sulfito ligand is very similar to that in H_2SO_3 ($pK_a = 1.8$) even though the sulfito ligand is bonded through sulfur. When orthophosphate is bonded to cobalt(III) through oxygen,[12] there is a substantial enhancement (of about 2.5 pK_a units) of the basicity of the phosphato ligand as compared to the free orthophosphate.

The observed rate constant for disproportionation exhibits a first-order dependence on the activity of water in the perchloric acid media. Since the reactant and the transition state have the same overall formal charge, it is possible that the ratio of their activity coefficients does not change significantly in the perchloric acid media employed. It is possible then, but not established, that the observed first-order dependence on water activity implies that the stoichiometric composition of the transition state includes one additional water molecule. One water molecule could be involved in the hydration of the emerging HSO_3 radical. Another possibility is that a water molecule bonds partially to the cobalt(III) center as the sulfito ligand moves away from this center. The loss of crystal-field stabilization energy on departure of the strong ligand field would be offset by bond formation to the incoming water and $\Delta H^{\ddagger}$ would be held at a moderate value. This function of water would be analogous to SN2 attack in aquation reactions of cobalt(III) complexes. However these suggestions can only be tentative due to the assumption made with respect to the activity coefficient ratio for reactant and transition state.

The presence of an aquo ligand *trans* to a bridging ligand appears to be associated with abnormally high redox rates. In the case of Fe_{aq}^{2+} reduction[13] of *cis* and *trans* isomers of $Co(en)_2AX$, in which ligand X is assumed to bridge with Fe(II), there is a reasonable correlation between the rates of reduction and the position of ligand A in the spectrochemical series. However a *trans*-OH_2 ligand to X is associated with anomalously high rates of reduction. Likewise *trans*-$Co(en)_2SO_3OH_2^+$ is the only sulfito complex of cobalt(III) which has been reported to undergo disproportionation. Species like *trans*-$Co(NH_3)_4ASO_3^+$,[14] $Co(CN)_5SO_3^{4-}$,[15] and *trans*-$Co(en)_2(SO_3)_2^{-4}$ all undergo conventional aquation and substitution reactions. In sulfito complexes of iron(III), there is also some evidence that sulfitoaquo complexes are prone to disproportionation. Danilczuk and Swinarski[16] found that the species $Fe(SO_3)_3^{3-}$ was quite stable in the presence of excess free sulfite ion. The $Fe(SO_3)_3^{3-}$ complex could contain no aquo ligands if the sulfito ligands were bidentate. However $FeSO_3^+$ and $Fe(SO_3)_2^-$, both of which must contain aquo ligands and which are probably *trans* to the sulfito ligands, establish the equilibrium: $Fe^{III}(SO_3)_n^{3-2n} \rightleftarrows Fe_{aq}^{2+} + (n/2)S_2O_6^{2-}$. As in the *trans*-$Co(en)_2SO_3OH_2^+$ complex, the production of dithionate, *via* HSO_3 radicals, seems to require aquo ligands *trans* to the reducing sulfito ligand.

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