

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
THE UNIVERSITY OF ADELAIDE, ADELAIDE, SOUTH AUSTRALIA 5001Internal Oxidation-Reduction of *trans*-Co(en)₂SO₃OH₂⁺

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In a range of perchloric acid media up to 7 *M*, *trans*-Co(en)₂SO₃OH₂⁺ disproportionates according to the reaction *trans*-Co(en)₂SO₃OH₂⁺ + 3H⁺ → Co_{aq}²⁺ + HSO₃ + 2enH⁺. The HSO₃ radical yields dithionic acid and it may be scavenged by Fe²⁺ and O₂. The disproportionation reaction is acid catalyzed and protonation of the reactant is complete above 1 *M* HClO₄. At 73°, the rate of disproportionation is given by $k_{\text{obsd}} = 3.61 \times 10^{-4} \text{ sec}^{-1}$ with $\Delta H^\ddagger = 32.8 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 9 \pm 1 \text{ eu}$. The value of k_{obsd} varies directly as the activity of water in the perchloric acid medium. The mechanism of the reaction is discussed.

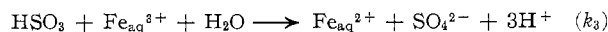
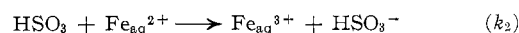
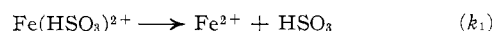
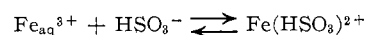
Introduction

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 example³ is the oxidation of Co^{II}(EDTA)²⁻ by Fe^{III}(CN)₆³⁻ to yield (EDTA)Co^{III}NCFe^{II}(CN)₅⁵⁻ which subsequently forms the final products Co^{III}(EDTA)⁻ and Fe^{II}(CN)₆⁴⁻.

The complex *trans*-Co(en)₂SO₃OH₂⁺ 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}O₃²⁻. 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 paper⁴ showed that *trans*-Co(en)₂SO₃OH₂⁺ and its conjugate base *trans*-Co(en)₂SO₃OH 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)₂SO₃OH₂⁺ has been found to undergo internal oxidation-reduction yielding Co_{aq}²⁺ and dithionic acid, H₂S₂O₆, 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, SO₃⁻, is considered⁵ to exist in the protonated form HSO₃ and this will be assumed in this paper. In the absence of radical scavengers, HSO₃ radicals dimerize to form dithionic acid. Thus dithionic acid is formed when sulfurous acid is oxidized by metal oxides,⁶ such as β-MnO₂, 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 scheme⁷



In perchlorate media, Karraker⁸ found that $k_2/k_3 = 22$. The oxidation of Fe²⁺ can be used to estimate the HSO₃ radical, provided chemical yields are corrected for the side reaction with the product Fe_{aq}³⁺.

The initial formation of inner-sphere sulfite-metal complexes (*e.g.*, Fe(HSO₃)²⁺) has been proposed^{6,7} but their stationary concentration appears to be too low to permit spectroscopic detection. The species *trans*-Co(en)₂SO₃OH₂⁺ is thus a convenient model for such complexes for the thermal generation of an HSO₃ radical.

Experimental Section

Materials.—*trans*-Co(en)₂SO₃OH₂ClO₄ was prepared by Baldwin's method.⁹ *Anal.* Calcd for *trans*-Co(en)₂SO₃OH₂ClO₄: 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 -CH₂ and the -NH₂ protons were detectable. Only two peaks of integrated area 1.0:1.0 were observed at +1.7 ppm (-CH₂) and +3.2 ppm (-NH₂) relative to acetaldehyde as an internal reference standard. No conformational splitting of the -CH₂ peak was observed. This spectrum is clear evidence for the *trans* configuration, in agreement with the ir evidence of Hughes and McWhinnie¹⁰ but at variance with the earlier assignment of Baldwin.⁹ The *cis* isomer would have yielded three proton peaks due to -NH₂ in the intensity ratio 1:1:2 and probably two peaks for the -CH₂ 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 Fe²⁺ scavenger which does not itself

(1) H. Taube, *Can. J. Chem.*, **37**, 129 (1959).

(2) N. Sutin, Proceedings of the XIIth Conference on Coordination Chemistry, Aug 20-27, 1969, Science Press, Sydney, Australia, 1969, p 30.

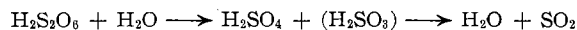
(3) A. W. Adamson and E. Gonick, *Inorg. Chem.*, **2**, 129 (1963).

(4) D. R. Stranks and J. K. Yandell, submitted for publication.

(5) N. Uri, *Chem. Rev.*, **50**, 439 (1952).(6) H. Bassett and W. G. Parker, *J. Chem. Soc.*, 1540 (1951).(7) W. C. E. Higginson and J. W. Marshall, *ibid.*, 447 (1951).(8) D. J. Karraker, *J. Phys. Chem.*, **67**, 871 (1963).(9) M. E. Baldwin, *J. Chem. Soc.*, 3123 (1961).(10) N. M. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **28**, 1659 (1966).

reduce Co(en)₂SO₃OH₂⁺. A solution of Co(en)₂SO₃OH₂⁺ (0.010 *M*) and Fe²⁺ (0.10 *M*) in 2.36 *M* HClO₄ 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* NH₄SCN and the mixture was diluted to 100 ml. The Fe³⁺ was determined as FeNCS₂⁺ at 480 nm using ε(FeNCS₂⁺) 4310 *M*⁻¹ cm⁻¹.

Dithionic acid was identified qualitatively using Co(en)₂-³⁵S₂O₆OH₂⁺. The yield of dithionic acid was determined from the SO₂ evolved from the hydrolysis



A solution of *trans*-Co(en)₂SO₃OH₂⁺ (1.0 × 10⁻³ *M*) in 2.36 *M* HClO₄ 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* K₂Cr₂O₇ in 2 *M* H₂SO₄. The temperature of the reaction mixture was then raised to 98° and the liberated SO₂ trapped in the two bubblers. Only 2% of the SO₂ passed into the second bubbler. The reduction of the K₂Cr₂O₇ concentration by SO₂ was determined at 435 nm using ε(Cr₂O₇²⁻) 470 *M*⁻¹ cm⁻¹.

Rate Measurements.—Normally, the rate of disappearance of *trans*-Co(en)₂SO₃OH₂⁺ 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°.

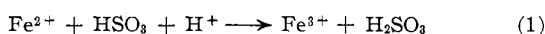
For some reactions, the rate of formation of Co_{aq}²⁺ was measured by analysis of the blue Co(SCN)₄²⁻ species. Aliquot samples (2 ml) from the reaction mixture were added to a chilled solution of 7 *M* NH₄SCN solution (1 ml), a 50:50 ether-amylic alcohol mixture (5 ml) was added, and the optical absorbance 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* HClO₄ (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* BaCl₂ 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 Ba²⁺ was then back-titrated with 0.0842 *M* H₂SO₄ using sodium rhodizonate as an indicator.

Results

Stoichiometry of the Reaction.—The disappearance of 1.00 mol of *trans*-Co(en)₂SO₃OH₂⁺ was accompanied by the formation of 1.00 ± 0.05 mol of Co_{aq}²⁺. Table I shows that in 2.36 *M* HClO₄ at 65°, the first-order rate constant for Co(en)₂SO₃OH₂⁺ consumption was (0.98 ± 0.03) × 10⁻⁴ sec⁻¹ while the rate constant for Co_{aq}²⁺ formation was (1.00 ± .07) × 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



where 1 mol of HSO₃ should be equivalent to 1 mol of Fe³⁺ and 1 mol of SO₂, evolved from the acid medium. A 1.00-mol sample of *trans*-Co(en)₂SO₃OH₂⁺ was allowed to react in the presence of 1.00 mol of Fe²⁺ scavenger and yielded, in a nitrogen-purged environment, 0.94 mol of Fe³⁺ and 0.97 mol of H₂SO₃. The product of reaction 1, Fe³⁺, may also react with HSO₃ to yield SO₄²⁻ and

TABLE I
RATE CONSTANTS FOR THE INTERNAL REDOX
REACTION OF *trans*-Co(en)₂SO₃OH₂⁺ ^a

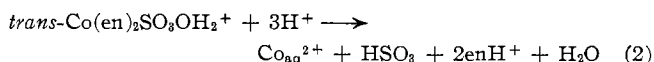
Temp, °C	[HClO ₄], <i>M</i>	10 ⁴ <i>k</i> _{obsd} , sec ⁻¹	10 ⁴ <i>k</i> _{obsd} /α _{H₂O} , sec ⁻¹
73.0	0.0236	0.73	0.73
73.0	0.0377	1.30	1.30
73.0	0.095	2.50	2.50
73.0	0.185	3.45	3.45
73.0	0.48	3.63	3.69
73.0	0.95	3.70	3.50
73.0	2.36	3.22	3.70
73.0	4.72	2.27	3.50
73.0	7.08	1.42	4.63
65.0	2.36	0.98 ^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)₂SO₃OH₂⁺] = 0.003 *M*. ^b When measured by rate of formation of Co_{aq}²⁺, 10⁴*k*_{obsd} = 1.00 ± 0.07 sec⁻¹. ^c Solution contained 0.003 *M* Fe_{aq}²⁺. ^d Solution contained 0.003 *M* Cu_{aq}²⁺.

Fe²⁺ (see the Introduction). The yields of Fe³⁺ and H₂SO₃ must therefore be corrected by the known ratio *k*₂/*k*₃ = 22; thus 1.00 mol of *trans*-Co(en)₂SO₃OH₂⁺ would yield, in the absence of the competing reaction of Fe³⁺, 0.985 mol of Fe³⁺ and 1.01 mol of H₂SO₃. Of these determinations the Fe³⁺ yield is considered more reliable.

A further small source of uncertainty in estimating the stoichiometric yield of HSO₃ is the scavenging effect of traces of oxygen still retained in the nitrogen-purged reaction media. When 1.00 mol of *trans*-Co(en)₂SO₃OH₂⁺ reacted in the presence of 1.00 mol of Fe²⁺ scavenger in an air-saturated medium, the yield of Fe³⁺ fell to 0.64 mol. This indicates that oxygen (10⁻³ *M*) can compete with Fe²⁺ (10⁻² *M*) in scavenging the HSO₃ radical. In the absence of Fe²⁺ scavenger and in the presence of oxygen, no SO₂ was detectable and the HSO₃ radical was converted to sulfate. In the absence of both Fe²⁺ and oxygen, 1.00 mol of *trans*-Co(en)₂SO₃OH₂⁺ yields exclusively dithionic acid, H₂S₂O₆.

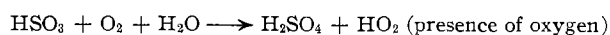
The overall stoichiometry of the primary reaction can then be written



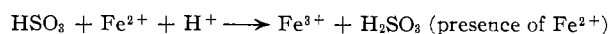
The subsequent reactions of the HSO₃ radical can then be represented as either



or



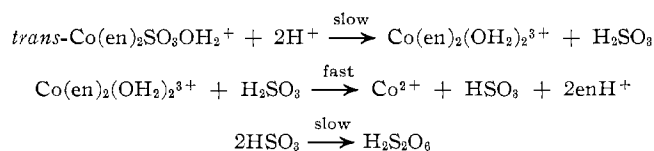
or



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

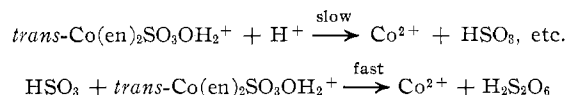
Absence of Alternative Redox Reactions.—It was possible that the stoichiometry observed could arise

from an initial hydrolysis of the sulfito ligand to yield sulfurous acid which then rapidly reduced the diaquo product



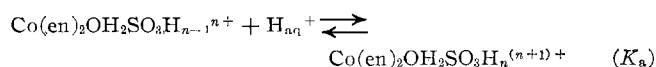
This possible reaction scheme was eliminated by the following check experiments. A perchloric acid solution (2.36 *M*), containing *cis*-Co(en)₂(OH₂)₂³⁺ (0.020 *M*) and Na₂SO₃ (0.100 *M*), was heated at 75° in a sealed vessel for 3 hr. No Co²⁺ was detected above a concentration 10⁻⁴ *M*. The half-time for the internal redox reaction of Co(en)₂SO₃OH₂⁺ was 36 min under the same conditions. After 3 hr, 0.0194 *M* Co²⁺ should have been produced by the alternative reaction scheme. An analogous experiment with *trans*-Co(en)₂(OH₂)₂³⁺ and excess Na₂SO₃ in 2.36 *M* HClO₄ again yielded no detectable Co²⁺ 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 HSO₃ radicals. An alternative reaction mechanism could be



Since Fe²⁺ is an efficient scavenger for HSO₃ radicals, then the presence of Fe²⁺ should eliminate the reaction of the HSO₃ radical with the sulfito complex. The rate constant for disappearance of Co(en)₂SO₃OH₂⁺ should then be halved in the presence of Fe²⁺, if this reaction scheme operated. Table I shows that, within experimental error, the observed rate constant is unaltered by the addition of Fe²⁺. The alternative reaction scheme based on secondary HSO₃ radical attack on the *trans*-Co(en)₂SO₃OH₂⁺ substrate can therefore be excluded. This observation also establishes that Fe²⁺ can be used as a radical scavenger without reducing Co(en)₂SO₃OH₂⁺. Table I also shows that the rate constant is unaffected by the addition of Cu²⁺ which is another radical scavenger for HSO₃.

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



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

The *trans*-Co(en)₂SO₃OH₂⁺ 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 ligand⁴ is 9.45 at 25°. It is assumed therefore that above pH 1 the species *trans*-Co(en)₂SO₃OH₂⁺ is not protonated and that *n* = 1 in the equation. The rate data are consistent with an acidity constant for *trans*-Co(en)₂OH₂SO₃H²⁺ of *K*_a = 0.065. There is no evidence that the nonprotonated *trans*-Co(en)₂OH₂SO₃⁺ undergoes the internal redox reaction at temperatures below 82°.

Above 2 *M* HClO₄, values of *k*_{obsd} fall with increasing acid concentration. This reduction is associated with the known¹¹ reduction in water activity as the perchloric acid concentration is increased. Table I shows that the values of (*k*_{obsd}/*a*_{H₂O}) remain constant, within experimental error, from 1 to 6 *M* HClO₄. Hence the rate law may be expressed in the form

$$-d[\text{Co(en)}_2\text{SO}_3\text{OH}_2^+]/dt = k'[\text{Co(en)}_2\text{SO}_3\text{HOH}_2^{2+}]a_{\text{H}_2\text{O}}$$

At 73°, *k*' = (3.61 ± 0.11) × 10⁻⁴ sec⁻¹. The value of *k*_{obsd}, as determined by the rate of disappearance of Co(en)₂SO₃OH₂⁺, rises above 6 *M* HClO₄ 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*-Co(en)₂(OH₂)₂³⁺. As the water activity is further reduced in the region of 10 *M* HClO₄, 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* HClO₄ wherein protonation of the sulfito complex is complete. Over the range 65–82°, Δ*H*[‡] = 32.8 ± 0.5 kcal mol⁻¹ and at 73°, Δ*S*[‡] = 9 ± 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 H₂S₂O₆ + H₂O → H₂SO₃ + H₂SO₄ exhibits a first-order rate constant *k* = 1.7 × 10⁻⁴ sec⁻¹ in 2.36 *M* HClO₄. This rate constant is one-sixth of the value for the internal redox reaction. It was also confirmed that the oxidation of Fe²⁺ 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 HSO₃ radicals from *trans*-Co(en)₂SO₃OH₂⁺.

Discussion

The one-electron reduction of spin-paired (t_{2g}⁶) cobalt(III) complexes may be considered to involve electron transfer from the reductant to the d_{z²} orbital of cobalt. For an inner-sphere reduction, the ligand

(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 ΔH^\ddagger be reduced to an accessible value, the energy of the *d*_{z² 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)₂SO₃OH₂⁺ seems to be consistent with this general mechanism.}

In *trans*-Co(en)₂SO₃OH₂⁺, the aquo ligand is unusually labile and ΔH^\ddagger for dissociative release of this ligand has the unusually low value⁴ 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 -SO₃ and -OH₂ ligands are substantially dissociated from the cobalt(III) center.

Acid catalysis of the internal oxidation-reduction of *trans*-Co(en)₂SO₃OH₂⁺ is also consistent with the partial dissociation of the -SO₃ 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 ΔH^\ddagger . The value of the corresponding acidity constant for Co(en)₂OH₂SO₃H⁺, *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 H₂SO₃ (*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

(12) S. F. Lincoln and D. R. Stranks, *Australian J. Chem.*, **21**, 37, 67 (1968).

water molecule. One water molecule could be involved in the hydration of the emerging HSO₃ 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 ΔH^\ddagger would be held at a moderate value. This function of water would be analogous to S_N2 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⁺ reduction¹³ 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*-OH₂ ligand to X is associated with anomalously high rates of reduction. Likewise *trans*-Co(en)₂SO₃OH₂⁺ is the only sulfito complex of cobalt(III) which has been reported to undergo disproportionation. Species like *trans*-Co(NH₃)₄ASO₃⁺,¹⁴ Co(CN)₅SO₃⁴⁻,¹⁵ and *trans*-Co(en)₂(SO₃)₂⁻⁴ all undergo conventional aquation and substitution reactions. In sulfito complexes of iron(III), there is also some evidence that sulfitoquo complexes are prone to disproportionation. Danilczuk and Swinarski¹⁶ found that the species Fe(SO₃)₃³⁻ was quite stable in the presence of excess free sulfite ion. The Fe(SO₃)₃³⁻ complex could contain no aquo ligands if the sulfito ligands were bidentate. However FeSO₃⁺ and Fe(SO₃)₂⁻, both of which must contain aquo ligands and which are probably *trans* to the sulfito ligands, establish the equilibrium: Fe^{III}(SO₃)_{*n*}^{3-2*n*} ⇌ Fe_{aq}²⁺ + (*n*/2)S₂O₆²⁻. As in the *trans*-Co(en)₂SO₃OH₂⁺ complex, the production of dithionate, *via* HSO₃ radicals, seems to require aquo ligands *trans* to the reducing sulfito ligand.

Acknowledgment.—The authors wish to thank the Australian Research Grants Committee for support of this project.

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(14) J. Halpern, R. A. Palmer, and L. M. Blakely, *ibid.*, **88**, 2877 (1966).

(15) H. H. Chen, M. S. Tsao, R. W. Gaver, R. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).

(16) E. Danilczuk and A. Swinarski, *Roczniki Chem.*, **35**, 1563 (1961).