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Kinetics and Mechanism of the Conversion of a Coordinated Thiol to a Coordinated Disulfide by the One-Equivalent Oxidants Neptunium(VI) and Cobalt(III) in Aqueous Perchloric Acid[1a]

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Reaction of excess (2-mercaptoethylamine-N,S)bis(ethylenediamine)cobalt(III), I, with the 1-equiv oxidant Np(VI) (or Co^{3+}(aq)) in aqueous perchloric acid media is shown to lead to (2-aminoethyl-N 2-ammonioethyl disulfide-S^1) bis(ethylenediamine)cobalt(III), II, according to the stoichiometry $5H^+ + 2I + Np(VI) \rightarrow II + Co^{2+}(aq) + Np(V) + 2enH_2^{2+}$. This reaction follows the rate law $-d[I]/dt = k''[I][oxidant]$. For Np(VI) as oxidant k'' is independent of $[H^+]$; at 25 °C, μ = 1.00 M ($LiClO_4$), $k'' = k_0 = 2842 \pm 15\ M^{-1}\ s^{-1}$, $\Delta H^*_0 = 7.57 \pm 0.08$ kcal/mol, and $\Delta S^*_0 = -17.4 \pm 0.3$ eu. For Co^{3+}(aq) as oxidant, $k'' = k_0 + k_{-1}[H^+]^{-1}$ where the inverse acid path is taken to reflect oxidation by $CoOH^{2+}$(aq); at 25 °C, μ = 1.00 M ($LiClO_4$), $k_0 = 933 \pm 32\ M^{-1}\ s^{-1}$, $k_{-1} = 1152 \pm 22\ s^{-1}$, $\Delta H^*_0 = 12.5 \pm 0.7$ kcal/mol, $\Delta H^*_{-1} = 18.0 \pm 0.4$ kcal/mol, $\Delta S^*_0 = -3.1 \pm 2.4$ eu, and $\Delta S^*_{-1} = 15.8 \pm 1.2$ eu. It is proposed that the conversion of I to II proceeds by initial 1-equiv oxidation of the coordinated thiol, reaction of the resultant coordinated thiol radical (RS·) with additional I to form a relatively stable radical ion dimer ($RSSR^{\bar{\cdot}}$), and then internal electron transfer within the dimer to yield Co^{2+}(aq) and II which contains a coordinated disulfide. The possible generality of this mechanism and its relevance to biological metal–thiol–disulfide interactions are noted.

Introduction

The prevalence of metal–thiol interactions in biological electron-transfer systems[2] (e.g., those involving nonheme iron–sulfur proteins,[3] the cytochromes,[4] copper metalloenzymes,[5] vitamin B_{12} dependent enzymes,[6] etc.) has led to considerable interest in the redox chemistry of low-valent sulfur coordinated to transition metal ions. Oxidation of coordinated thiols has been observed to occur by diverse pathways[7] which include (a) metal–sulfur bond fission and formation of the free disulfide,[8] (b) oxidation at sulfur with no cleavage of the metal–sulfur bond (to yield coordinated sulfenic and sulfinic acids),[9] and (c) oxidation of the carbon adjacent to sulfur (to yield a product in which the sulfur has undergone no net oxidation and the metal–sulfur bond remains intact).[10] It is of interest to ask whether a complex containing a coordinated disulfide can be a product of, or intermediate in, the oxidation of a coordinated thiol.[2,11,12] Recent x-ray studies have shown that multidentate ligands containing an aliphatic disulfide linkage can form complexes containing metal–sulfur bonds.[12] However, these studies do not provide information on how such complexes may arise from the oxidation of coordinated thiols. In this paper we present some observations on the oxidation of a coordinated cysteamine which bear directly on this point.[13]

Experimental Section

Reagents and Analyses. Common laboratory reagents, water, and perchloric acid were of the purity previously specified.[14] Solutions of perchloric acid, lithium perchlorate, cobalt(II) perchlorate, neptunium(VI) perchlorate, and neptunium(V) perchlorate were prepared and standardized as previously described.[7,14]

(2-Mercaptoethylamine-N,S)bis(ethylenediamine)cobalt(III) perchlorate was available from previous studies[15] and was recrystallized three times before use. Dowex 50-X2 (H^+-form, 200–400 mesh) cation-exchange resin was kindly donated by the Dow Chemical Co. and cleaned by a previously outlined procedure.[16] Cobalt(III) perchlorate solutions were prepared by the method of Hofman-Bang and Wulff[17] and spectrophotometrically standardized using an extinction coefficient for Co(III) in 1.00 M $HClO_4$ of 34.5 $M^{-1}\ cm^{-1}$ at 602 nm.[18] The total cobalt concentration of solutions was determined by Kitson's method as previously described.[7] Nonmetal elemental analyses were performed by Galbraith Laboratories, Inc.

Equipment and Procedures. The computer-interfaced, specially thermostated, stopped-flow instrumentation used in this study has been described previously.[19] Difficulties associated with the slow oxidation of water by Co^{3+}(aq) in the storage syringe were much less severe than those encountered in our studies using Np(VII) as an oxidant[14,19] and were thus readily overcome using the experimental and calculational techniques described previously.[14,19] Unless otherwise specified, in all kinetic experiments ionic strength was maintained at 1.00 ± 0.01 M with $LiClO_4$. Spectrophotometric measurements were conducted on a Cary Model 14 at room temperature.

Data Analysis. All reactions were conducted under second-order concentration conditions with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ in excess (see Tables I and II for exact concentration conditions). Continuous decay of Co(III) in the storage syringe causes $[Co^{3+}(aq)]_0$ to be an unknown parameter for each individual kinetic experiment, and thus the second-order rate equation was expressed in the form previously presented[14] wherein $[Co^{3+}(aq)]_0$ appears in terms of the adjustable parameters OD_0 and OD_∞. All OD_t–t data, for both Np(VI) and Co(III) oxidations, were analyzed by standard nonlinear least-squares techniques with this expression to obtain optimized values (and standard deviations) of the adjustable parameters k''_{obsd}, OD_0, and OD_∞. Each kinetic experiment was monitored to at least 85% completion, 800–950 OD_t–t data points being collected during this period. Previously described criteria[19] were applied to show that the second-order functional form[14] adequately describes the observed

Table I. Observed Rate Parameters Governing Oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by Np(VI) as a Function of Reactant Concentrations, Acid Concentration, Ionic Strength, and Temperature

T, °C	μ, M	$[H^+]$, M	$[Np(VI)]_0$, mM	$[Co(cys)]_0$,[a] mM	$\bar{k}''_{obsd}$,[b] $M^{-1}\ s^{-1}$	No. of determins
25.0	1.00	1.00	0.952	6.75	2809 ± 9	5
25.0	1.00	1.00	0.476	6.75	2818 ± 21	5
25.0	1.00	0.050	0.476	3.49	3063 ± 15	5
25.0	1.00	0.948	0.952	17.6	2829 ± 23	5
25.0	1.00	0.948	3.18	17.6	2756 ± 11	5
25.0	1.00	1.00	0.222	1.50	2804 ± 19	5
25.0	1.00	1.00	0.438	2.78	2982 ± 17	7[c]
25.0	0.100	0.079	0.938	7.03	842 ± 4	6
25.0	2.00	0.079	0.938	6.89	5270 ± 44	5
3.05	1.00	1.00	0.875	5.55	967 ± 8	7
3.05	1.00	1.00	1.12	7.15	926 ± 2	8
12.0	1.00	1.00	0.875	5.55	1469 ± 10	6
12.0	1.00	1.00	1.12	7.15	1447 ± 10	6
38.4	1.00	1.00	0.875	5.55	4922 ± 48	5
38.4	1.00	1.00	1.12	7.15	4886 ± 34	8

[a] Co(cys) = $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. [b] Error listed as $\pm\sigma_m$, the standard deviation of the mean. [c] λ 430 nm. All other experiments monitored at 600 nm.

Table II. Observed Rate Parameters Governing Oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by Co^{3+}(aq) as a Function of Reactant Concentrations, Acid Concentration, Ionic Strength, and Temperature

T, °C	μ, M	$[H^+]$, M	$[Co^{3+}(aq)]_0$,[a] mM	$[Co(cys)]_0$,[b] mM	$\bar{k}''_{obsd}$,[c] M^{-1} s^{-1}	No. of determins
25.0	1.00	0.884	0.885–0.902	6.98	2 225 ± 15	8
25.0	1.00	0.848	0.802–0.813	19.2	2 272 ± 57	7
25.0	1.00	0.100	0.364–0.432	6.88	12 430 ± 150	9
25.0	1.00	0.884	0.873–0.905	7.05	2 214 ± 28	12[d]
25.0	1.00	0.200	0.331–0.385	4.23	6 718 ± 115	10
25.0	0.139	0.100	0.119–0.134	1.41	8 595 ± 116	12
25.0	2.00	0.100	0.093–0.122	1.41	16 300 ± 750	9
25.0	1.00	0.860	0.353–0.372	2.80	2 272 ± 43	8
25.0	1.00	0.860	0.192–0.206	1.40	2 391 ± 38	10
25.0	1.09	0.500	0.776–0.829	7.02	3 300 ± 25	8
11.1	1.00	0.865	0.734–0.741	4.41	601 ± 3	11
11.1	1.00	0.200	0.546–0.557	4.41	1 553 ± 8	10
11.1	1.00	0.100	0.354–0.371	4.41	2 757 ± 58	10
11.1	1.00	0.500	0.694–0.704	4.41	815 ± 7	9
17.9	1.00	0.870	0.759–0.792	4.46	1 123 ± 11	10
17.9	1.00	0.100	0.456–0.484	4.46	5 560 ± 220	9
17.9	1.00	0.200	0.679–0.701	4.46	3 398 ± 42	10
17.9	1.00	0.500	0.759–0.779	4.46	1 670 ± 31	10
3.3	1.00	0.870	0.621–0.627	4.39	307 ± 29	9
3.3	1.00	0.100	0.287–0.297	4.39	1 247 ± 29	10
3.3	1.00	0.200	0.643–0.648	4.39	772 ± 89	9
3.3	1.00	0.500	0.676–0.687	4.39	404 ± 19	10

[a] Range of initial $[Co^{3+}(aq)]$ encountered during that particular series of experiments. See Experimental Section. [b] Co(cys) = $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. [c] Error listed as $\pm\sigma_m$, the standard deviation of the mean. [d] λ 430 nm. All other experiments monitored at 600 nm.

OD_t–t data, and optimized values of OD_0 and OD_∞ always agreed with observed OD_0 and OD_∞ values to within experimental error. As before,[14,19] replicate measurements showed that the precision in the determination of the observed second-order rate parameter, k''_{obsd}, is limited by factors other than random errors; therefore in this paper we again report the mean values of k''_{obsd}, $\bar{k}''_{obsd}$, calculated for a given set of replicate measurements, along with σ_m, the standard deviation from this mean, and the number of determinations in the set. For Co(III) oxidations the range of $[Co^{3+}(aq)]_0$ values encountered in determining a particular $\bar{k}''_{obsd}$ is also reported; in all cases the continuous variation of $[Co^{3+}(aq)]_0$ and concomitant variation of $[Co^{2+}(aq)]_0$ during a series of experiments had no effect on the values of k''_{obsd} observed during the series. Oxidations by both Np(VI) and Co(III) were monitored at 600 and 430 nm, the resultant values of $\bar{k}''_{obsd}$ being independent of the monitoring wavelength (see Tables I and II). Values of the extinction coefficients of the various reactants and products at these two wavelengths that were used in the second-order data analysis are listed in Table III; values of the stoichiometry factors S and P (defined as previously[14]) were taken as 2.00 (vide infra). Unless otherwise noted, all errors reported in this work are standard deviations. In subsequent calculations of rate and activation parameters, each value of $\bar{k}''_{obsd}$ is weighted as $1/\sigma_m^2$.

Preparation of $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]Cl_4\cdot nH_2O\cdot mC_2H_5OH$. Sixteen grams (35 mmol) of $[(en)_2Co(SCH_2CH_2NH_2)][ClO_4]_2$ was dissolved in 300 ml of water containing 1 ml of 1.0 M $HClO_4$. Nine millimoles of Np(VI) in 40 ml of ca. 1 M $HClO_4$ was then rapidly injected into this vigorously stirred solution. The resulting product mixture was adsorbed on a cation-exchange column approximately 4.0 cm in diameter and 50 cm in length. Elution of NpO_2^+, Co^{2+}(aq), and excess $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ was readily accomplished with 0.50, 1.0, and 2.0 M $HClO_4$, respectively. Elution of $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]^{4+}$ was accomplished with 6.0 M HCl, only the most concentrated portion of this band (total volume ca. 100 ml) being collected. Dilution of this fraction to ca. 1600 ml with absolute ethanol led to a red precipitate which redissolved upon warming the mixture to ca. 40 °C. Slow cooling of this solution to 0 °C yielded a red, hygroscopic solid which was removed by filtration and then dried under vacuum, over silica gel, at room temperature. The weight of the dried solid was 2.0 g, corresponding to an overall 40% yield (as the tetrahydrate). Anal. Calcd for $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]Cl_4\cdot 4H_2O$: C, 17.59; H, 6.83; N, 15.38; S, 11.74; Cl, 25.96; Co, 10.79. Found: C, 17.53; H, 6.21; N, 15.29; S, 11.52; Cl, 26.26; Co, 10.89. In an analogous fashion, the product mixture resulting from reaction of 37 mmol of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with 10 mmol of Co^{3+}(aq) was worked up to yield ca. 3.0 g of a red, hygroscopic solid. The elemental analyses and ^1H NMR spectrum of this material indicate that it contains entrapped ethanol. Anal. Calcd for $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]Cl_4\cdot H_2O\cdot 0.25C_2H_5OH$: C, 20.26; H, 6.50; N, 16.68; S, 12.73; Cl, 28.15; Co, 11.70. Found: C, 20.01; H, 6.35; N, 16.65; S, 12.50; Cl, 28.10; Co, 11.37.

Table III. Extinction Coefficients (M^{-1} cm^{-1}) of Various Reactants and Products at 600 and 430 nm

Ion	ϵ_{600}	ϵ_{430}
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ [a]	44.0	95.6
$[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]^{4+}$ [a]	9.0	56.0
Co^{2+}(aq)[a]	0.35[b]	0.98[b]
Np(VI)[a]	2.5	7.4
Np(V)[a]	3.7	5.0
Co^{3+}(aq) at $[H^+]$ = 0.884 M	34.5[c]	24.6
Co^{3+}(aq) at $[H^+]$ = 0.50 M	33.5	
Co^{3+}(aq) at $[H^+]$ = 0.20 M	29.5	
Co^{3+}(aq) at $[H^+]$ = 0.10 M	29.3	

[a] Extinction coefficient taken to be independent of $[H^+]$ over the range 0.050–1.00 M. [b] Value taken from D. W. Weiser, Ph.D. Dissertation, University of Chicago, June 1956. [c] Reference 18.

Results and Discussion

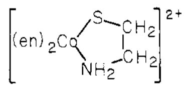
Stoichiometry. In a typical stoichiometry experiment, 0.94 mmol of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (hereafter referred to as I) dissolved in 20 ml of 0.10 M $HClO_4$ was rapidly mixed with 0.154 mmol of Np(VI) in 1.0 ml of 1.0 M $HClO_4$. Ion-exchange chromatography of the product mixture resulting from this reaction gave rise to four well-separated bands: (1) elution with 0.5 M $HClO_4$ yielded a green band containing 0.150 mmol of NpO_2^+; (2) elution with 1.0 M $HClO_4$ yielded a pink band containing 0.139 mmol of Co^{2+}(aq); (3) elution with 2.0 M $HClO_4$ yielded a brown band containing 0.632 mmol of I; (4) elution with 6.0 M HCl yielded a red band containing 0.141 mmol of cobalt. Hereafter this red reaction product will be referred to as II, and thus the stoichiometry of the Np(VI)–I reaction may be represented as

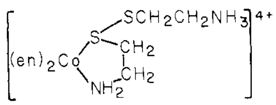
$$2\text{I} + \text{Np(VI)} \rightarrow \text{II} + \text{Np(V)} + Co^{2+}(aq) \quad (1)$$

Equivalent experiments employing Co^{3+}(aq) as oxidant show that the stoichiometry of the Co^{3+}(aq)–I reaction is analogous to that of the Np(VI)–I reaction and may be represented as

$$2\mathrm{I} + Co^{3+}(aq) \rightarrow \mathrm{II} + Co^{2+}(aq) \quad (2)$$

Product Identification. Several lines of evidence establish that the red reaction product II is $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]^{4+}$, a cobalt(III) complex containing a coordinated disulfide:

I =


II =


(1) The stoichiometry experiments described above show that II is 2 equiv oxidized beyond I. One oxidation equivalent arises from the added oxidant (Np(VI) or Co^{3+}(aq)) and one oxidation equivalent arises from another molecule of I which is in turn converted to Co^{2+}(aq).

(2) Elemental analyses of precipitated samples of II support the proposed formulation (see Experimental Section). It should be especially noted that the observed N:Cl:S:Co ratios (5.91:4.01:1.94:1.00 for the product of Np(VI) oxidation and 6.18:4.12:2.02:1.00 for the product of Co^{3+}(aq) oxidation) are in excellent agreement with the predicted ratio of 6:4:2:1. Thus II has one extra nitrogen atom and one extra sulfur atom (and most probably two extra carbon atoms) over I, indicating that II is composed of I plus the elements of cysteamine. Also, since there is no spectral evidence (see below) for II containing a coordinated chloride, the observed Cl:Co ratio indicates that II carries an effective 4+ formal charge.

(3) The fact that 6.0 M HCl is required to elute II from Dowex 50-X2 ion-exchange resin is consistent with the proposed 4+ formal charge.

(4) The uv–visible spectra of I and II (shown in Figure 1) are similar, indicating that on going from I to II there is no drastic change in the spectrochemical environment about cobalt(III). In this connection it is important to note that the spectrum of II exhibits the intense ligand-to-metal charge-transfer (LTMCT) band characteristic[20] of metal–sulfur bonding. The shift of the d–d absorption band from 482 nm for I to 492 nm for II is rationalized in terms of the disulfide providing a weaker ligand field than the thiol. The shift of the LTMCT band from 282 nm for I to 275 nm for II is rationalized in terms of the disulfide being a weaker reducing agent than the thiol. It is also important to note that the spectra of II determined immediately after oxidation of I by either Np(VI) or Co^{3+}(aq) in perchlorate media are identical with one another and with the spectra of redissolved solid samples of II (as the chloride salt). It is therefore unlikely that the solid samples of II contain coordinated chloride.

(5) Further evidence for the formulation of II as a complex containing coordinated cysteamine arises from the observation that the reaction of II with various reducing agents yields I. Thus, the addition of excess cysteamine to a 6 M HCl solution of II at room temperature quantitatively produces I within a few minutes:

$$\mathrm{II} + HSCH_2CH_2NH_3^+ \rightarrow \mathrm{I} + H_3NCH_2CH_2SSCH_2CH_2NH_3^{2+} \quad (3)$$

This reaction may be viewed as a 2-equiv reduction of the coordinated disulfide or as a thiol–disulfide interchange.[2,21] The reduction of II by Sn(II) in 6 M HCl may be determined quantitatively by spectrophotometrically monitoring the production of I at 600 nm (see Figure 1). At the end point of this titration 0.50 ± 0.02 mol of Sn(II) is consumed per mole of II originally present; the slope of the titration graph shows that during the titration 2.0 ± 0.1 mol of I is produced per mole of Sn(II) consumed. Thus the spectrophotometrically monitored reaction of II with Sn(II) may be formulated as

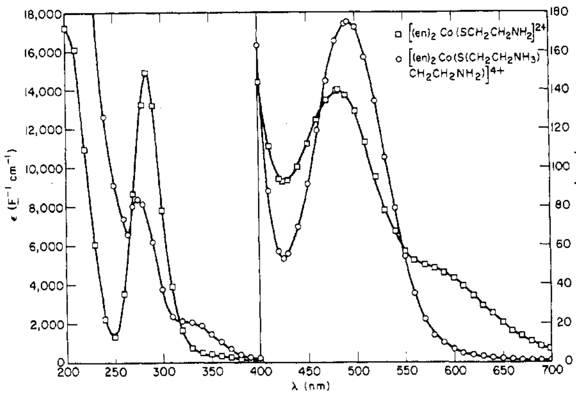


Figure 1. Visible and ultraviolet absorption spectra of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]^{4+}$ in 1.0 M $HClO_4$ (except for the visible spectrum of the latter which is in 6 M HCl).

$$\mathrm{II} + 0.5\mathrm{Sn(II)} \rightarrow \mathrm{I} + 0.5\mathrm{Sn(IV)} + 0.5(H_3NCH_2CH_2S)_2^{2+} \quad (4)$$

After the spectrophotometric end point, cysteamine is presumably reduced by excess Sn(II)

$$(H_3NCH_2CH_2S)_2^{2+} + \mathrm{Sn(II)} \rightarrow \mathrm{Sn(IV)} + 2HSCH_2CH_2NH_3^+ \quad (5)$$

a reaction which is not observable at 600 nm. Reaction 4 could itself involve two steps, i.e., the equimolar reduction of II to yield I plus cysteamine, followed by reaction 3 to give the overall observed 2:1 stoichiometry.

Kinetics. All kinetic experiments were conducted with the initial ratio of I to oxidant greater than 2.0 (due to the stoichiometries of eq 1 and 2) and less than 20 (to avoid excessive light absorption by the excess I). The exact concentration conditions employed are listed in Tables I and II for Np(VI) and Co^{3+}(aq), respectively. Information presented in the Experimental Section and in Tables I and II shows that the second-order rate equation[14] adequately describes the observed OD_t–t data for all concentration conditions investigated. Thus the rate law governing reactions 1 and 2 (at constant $[H^+]$) may be expressed as

$$-d[\mathrm{I}]/dt = \bar{k}''_{obsd}[\mathrm{I}][\mathrm{oxidant}] \quad (6)$$

The data of Table I show that for Np(VI) as oxidant, $\bar{k}''_{obsd}$ is independent of $[H^+]$ over the range 0.050–0.95 M. Thus $\bar{k}''_{obsd} = k_0$ and the rate law for reaction 1 may be expressed as

$$-d[\mathrm{I}]/dt = k_0[\mathrm{I}][\mathrm{Np(VI)}] \quad (6a)$$

where, at 25 °C and $\mu = [H^+] = 1.00$ M, $k_0 = 2842 \pm 15$ $M^{-1}\ s^{-1}$ (average of 32 independently determined values of $\bar{k}''_{obsd}$ weighted as $1/\sigma_k^2$). Nonlinear least-squares analysis[22] of the temperature dependence of k_0 ($=\bar{k}''_{obsd}$; see Table I) according to the Eyring formalism leads to $\Delta H^*_0 = 7.57 \pm 0.08$ kcal/mol and $\Delta S^*_0 = -17.4 \pm 0.3$ eu; the average difference between observed values of k_0 and values calculated from these activation parameters is 2.2%. The ionic strength dependence of k_0 (Table I) is consistent with the formulation of the rate-determining step of reaction 1 as one involving two positively charged species.

The data of Table II show that, for Co^{3+}(aq) as oxidant, $\bar{k}''_{obsd}$ is strongly dependent upon $[H^+]$ and this dependency may be expressed as $\bar{k}''_{obsd} = k_0 + k_{-1}/[H^+]$ for all temperatures investigated. Thus the rate law for reaction 2 may be expressed as

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = (k_0 + k_{-1}/[\mathrm{H}^+])[\mathrm{I}][\mathrm{Co(III)}] \quad (6b)$$

where, at 25 °C and μ = 1.00 M, k_0 = 933 ± 32 M^{-1} s^{-1} and k_{-1} = 1152 ± 22 s^{-1}. Nonlinear least-squares analysis[22] of the temperature dependence of reaction 2 (see Table II) according to the expression

$$\bar{k}''_{\mathrm{obsd}} = (kT/h)e^{-\Delta H^*_0/RT}e^{\Delta S^*_0/R} + (kT/h[\mathrm{H}^+])e^{-\Delta H^*_{-1}/RT}e^{\Delta S^*_{-1}/R} \quad (7)$$

leads to ΔH^*_0 = 12.5 ± 0.7 and ΔH^*_{-1} = 18.0 ± 0.4 kcal/mol and ΔS^*_0 = −3.1 ± 2.4 and ΔS^*_{-1} = 15.8 ± 1.2 eu; the average difference between observed values of $\bar{k}''_{\mathrm{obsd}}$ and values calculated from these activation parameters is 4.1%. The ionic strength dependence of $\bar{k}''_{\mathrm{obsd}}$ at $[H^+]$ = 0.100 M is consistent with the formulation of the rate-determining step of reaction 2 as one involving two positively charged species.

Rate laws such as (6b) are characteristic for both substitution and redox reactions involving Co^{3+}(aq);[23,24] the terms k_0 and $k_{-1}/[H^+]$ are interpreted as representing the reactions of Co^{3+}(aq) and $CoOH^{2+}$(aq), respectively.[23,24] Thus k_{-1} is a composite rate parameter equal to the product of K_h, the hydrolysis constant for Co^{3+}(aq), and k_{CoOH}, the specific rate constant governing reaction of $CoOH^{2+}$(aq) with substrate

$$k_{-1} = K_h k_{\mathrm{CoOH}} \quad (8)$$

While no accurate value of K_h has yet been determined, Davies and Warnqvist in their review of Co^{3+}(aq) chemistry[23] gave K_h = (2 ± 1) × 10^{-3} (μ = 1.00 M, 25 °C) as the best estimate available. From Sutcliffe and Weber's original data,[25] $\Delta H_h°$ is estimated as 10 ± 2 kcal/mol and $\Delta S_h°$ computed to be 22 ± 8 eu.[23] Using these hydrolysis data, k_{CoOH} (25 °C, μ = 1.00 M), ΔH^*_{CoOH}, and ΔS^*_{CoOH} may be calculated as (6 ± 3) × 10^5 M^{-1} s^{-1}, 8 ± 2 kcal/mol, and −8 ± 8 eu, respectively.

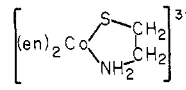
Extensive compilations of kinetic data involving oxidation by Co^{3+}(aq) and $CoOH^{2+}$(aq) have been reported[23] with the intent of supporting the hypothesis that oxidation by these species is limited by the rate of substitution on the cobalt(III) center. Our data on the oxidation of I are consistent with these compilations: e.g., the ratio of $10^{-3}k_{CoOH}/k_0$ = 0.62 falls within the range of values reported[23] for oxidation and substitution reactions of iron(III) and cobalt(III); our value of ΔG^*_{CoOH} = 10.4 kcal/mol falls within the range of values 9.0–12.0 kcal/mol reported[23] for oxidations by $CoOH^{2+}$(aq).

Mechanism. The empirical form of the rate law defines the composition of the activated complexes as one molecule each of oxidant and I. The detailed mechanisms (e.g., outer sphere, inner sphere, substitution controlled), however, are not necessarily the same for the oxidants Np(VI) and Co(III). For example the value of ΔS^*_0 = −3.1 ± 2.4 eu for the hydrogen ion independent path of the Co(III) oxidation is consistent with the concept that an outer-sphere activated complex is formed[23] while no such implication is reasonably based on the value of ΔS^* for Np(VI) as the oxidant. A plausible mechanism for the oxidation of I to II, which does not depend upon the detailed mechanism of the rate-determining step, may be proposed on the basis of results obtained from recent pulse radiolytic studies on the oxidation of free thiols by hydroxy radicals.[27] The reaction of OH· with a thiol, RSH, initially yields a thiol radical, RS·, which in the presence of excess thiol is rapidly converted to the relatively stable radical ion dimer RSSR·⁻

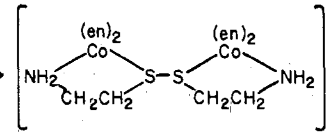
$$\mathrm{RSH + OH\cdot \rightarrow RS\cdot + H_2O} \quad (9a)$$

$$\mathrm{RS\cdot + RSH = RSSR\cdot^- + H^+} \quad (9b)$$

By analogy, the following sequence may be proposed for the reaction of excess I with a 1-equiv oxidant

I + oxidant → reduced oxidant +  (10a)

III

I + III →  (10b)

IV

The cobalt(III) radical ion dimer, IV, presumably then decays by internal electron transfer, the resultant labile cobalt(II) escaping to solution as Co^{2+}(aq) and leaving behind the newly formed sulfur–sulfur bond

$$\mathrm{IV + 5H^+ \rightarrow II + Co^{2+}(aq) + 2enH_2^{\,2+}} \quad (11)$$

The reaction of a 1-equiv oxidant with a coordinated thiol to yield a coordinated disulfide via a radical ion dimer intermediate and induced electron transfer may have considerable generality as well as applicability to biologically important systems. Thus, this mode of metal–thiol–disulfide interaction is not necessarily limited to systems containing the Co(II)–Co(III) couple but may also function in systems containing the Fe(II)–Fe(III) and Cu(I)–Cu(II) couples. The lability of these latter systems allows the coordinated disulfide product to be released to solution, thus generating a general mechanism for metal ion catalyzed thiol–disulfide interconversion.

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Registry No. I, 42901-32-6; $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]Cl_4$, 59230-66-9; Sn^{2+}, 22541-90-8; neptunyl(2+), 18973-22-3; Co^{3+}, 22541-63-5.

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(1) (a) A portion of this investigation was conducted under the auspices of the U.S. Energy Research and Development Administration. (b) Rosary College. (c) Argonne National Laboratory. (d) University of Cincinnati.
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Empirical Bonding Relationships in Metal–Iron–Sulfide Compounds

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A bond valence–bond length relationship for bonds between sulfur and iron, where high-spin iron is coordinated by sulfur only, has been derived using the method of Brown and Shannon. This relationship, $V = 1/3\sum_i(R_i/2.515)^{-6.81}$, is constrained so that the sum of the bond valences around iron is equal to its electrostatic valence, V. The calculated valence is especially useful in structures where direct metal–metal interactions give rise to mobile electrons. The Mössbauer isomer shift, δ, for iron tetrahedrally coordinated by sulfur has been related to the electrostatic valence by the equation $\delta = 1.4 - 0.4V$. The predicted values for isomer shifts and magnetic moments are compared to the measured values for several metal–iron–sulfide and organometallic compounds. This approach interrelates the valence, Mössbauer isomer shift, effective magnetic moment, and electrical conductivity in metal–Fe–S compounds.

Introduction

A series of Ba–Fe–S compounds has been synthesized in our laboratories, and their physical properties have been studied.[1-5] The properties have been shown to depend on the oxidation states of iron and these need not necessarily correspond to the values expected on the basis of stoichiometry. Robin and Day[6] have surveyed the mixed-valence chemistry and its influence on the physical properties of a large number of compounds but have excluded sulfides because the ease of electron delocalization in such covalent metal–ligand bonds makes the effects difficult to distinguish from those due to the presence of mixed-valence states. We have developed a relationship between bond valence–bond length and Mössbauer isomer shift that permits the determination of the oxidation state of iron in metal–Fe–S compounds.

A set of empirical bond valence–bond length functions was derived by Brown and Shannon[7] for several cations in oxides based on the equation

$$V = s_0 \sum_{i=1}^{\mathrm{CN}} (R_i/R_0)^{-N}$$

where V is the valence, R_i is the bond distance, and CN is the coordination number. The constants s_0, R_0, and N were adjusted so that the equation will predict the valence of an ion at a given site using only the observed bond distances. This is of particular use in structures where the cation is in mixed coordination and/or mixed valence states or the electrons are mobile so that an average oxidation state exists in the crystal.

This approach is used in the metal–iron–sulfur system to determine the oxidation state of the high-spin iron ion. These valences are then used to predict various physical properties which are compared to the values observed in these materials, i.e., Mössbauer isomer shift (δ), magnetic moment (μ), room-temperature electrical resistivity (ρ), and the valence based on stoichiometry. The average Fe–S distance is 2.370 Å in compounds which contain Fe^{2+} in tetrahedral coordination,[2,8,9] and the average Fe–S distance is 2.233 Å[10,11] in compounds which contain Fe^{3+} in tetrahedral coordination. These two average distances and oxidation states were used in the Brown and Shannon formula to determine the arbitrary constants R_0 and N. The constant s_0 was chosen as $^1/_3$; i.e., the R_0 thus calculated is a hypothetical value for Fe^{2+} in an octahedral environment. The resultant equation for the iron–sulfur compounds is

$$V = {}^1/_3 \sum_i (R_i/2.515)^{-6.81}$$

or

$$V = 178.2 \sum_i R_i^{-6.81} \tag{1}$$

The Mössbauer isomer shift, δ, has been related to the electrostatic valence of iron in many materials. Isomer shift values of 0.60 and 0.20 mm/s are typical values for high-spin Fe^{2+} and Fe^{3+}, respectively,[4] in metal–iron–sulfide compounds when iron is tetrahedrally coordinated by sulfur. Intermediate isomer shift values are interpreted to mean delocalization of electrons and an averaged electrostatic valence. The isomer shift may be written as

$$\delta = A - C|\Psi(0)|^2$$

where $\Psi(0)$ is the electronic wave function at a radius of zero, i.e., in the vicinity of the atomic nucleus of the iron. Only s wave functions are nonzero at the nucleus and thus affect the isomer shift. An increase in s-electron density at the iron nucleus on going from a $3d^6$ to a $3d^5$ configuration arises as a consequence of the decrease in shielding of the 3s and 4s electrons by the removal of the d electron. The change in the valence, ΔV, in going from Fe^{2+} to Fe^{3+} is one d electron which would increase $|\Psi(0)|^2$ and decrease δ. Thus as V increases, $|\Psi(0)|^2$ increases, which can be written as

$$V \approx K|\Psi(0)|^2 + \text{constant}$$

assuming a linear variation of $|\Psi(0)|^2$ with V. Rewriting the equation for the isomer shift yields

$$\delta = A' - C'V$$

The constants A' and C' can be evaluated from typical values