V(III) sulfide polymers, primarily V_2S_3. Elucidating possible intermediates represents one goal of our synthetic work. We can report that **3** can be cleanly converted to **1** in a controlled fashion under laboratory conditions, a result that suggests a similar reaction involving the conversion of VO^{2+} to $[V-O-V]^{4+}$ may be an initial step in the transformation of the crude oil impurities under the industrial conditions. Treatment of **3** with 1 equiv of sodium acenaphthylenide (NaACN) in the presence of aetH·HCl leads to a fairly rapid color change from purple to the brown that is characteristic of **1**. IR comparison of the isolated, recrystallized (DMF) solid with an authentic sample of **1** confirmed the identity of this product. The presumed stoichiometry of this conversion is indicated in eq 1. The simplified form of this equation is given

$$2VO(aet)_2 + 2aetH{\cdot}HCl + 2NaACN \rightarrow V_2O(aet)_4 + 2aetH + H_2O + 2ACN + 2NaCl \quad (1)$$

in eq 2. In essence, reduction of **3** presumably yields $[VO(aet)_2]^-$,

$$2VO^{2+} + 2H^+ + 2e^- \rightarrow [V-O-V]^{4+} + H_2O \quad (2)$$

which, in the presence of a proton source (aetH·HCl), dimerizes to **1** with elimination of H_2O. The $V{=}O^{2+}$ multiple bond would be expected to be seriously weakened and destabilized by lowering of the metal oxidation state.

If we entertain a little further the hypothesis that $[V-O-V]^{4+}$ species are formed from VO^{2+} in the industrial process, it is possible that reaction with H_2S will then yield $[V-S-V]^{4+}$ species followed by an increase in the S content with loss of peripheral ligation. We are currently investigating, therefore, whether $V_2O(aet)_4$ can be converted to $V_2S(aet)_4$.

Substitution of $(NMe_4)Na[VO(edt)_2]{\cdot}2EtOH$ and 2 $(Et_3NH)Cl$ for $VO(aet)_2$ and aetH·HCl in the reaction of eq 1 in MeCN leads to a brown crystalline product. The complex nature of this material has necessitated its elucidation by X-ray crystallography, which shows it to be the mixed-anion salt $(NMe_4)_6[VO(edt)_2]_2[V_2(edt)_4]{\cdot}4MeCN$ containing well-separated anions. The conversion of $[VO(edt)_2]^{2-}$ to $[V_2(edt)_4]^{2-}$ is thus established, but the reason for the incomplete conversion is unclear; the EtOH molecules may be interfering by mopping up reducing equivalents. Addition of excess NaACN leads to a messier reaction and a mixture of products. Further investigation of this reaction must await a nonsolvated form of a $[VO(edt)_2]^{2-}$ salt, but none is currently available. Nevertheless, available results are encouraging and the generality of the NaACN/H^+ reduction procedure for converting VO^{2+} to $[V-O-V]^{4+}$ or non-oxo V(III) species warrants further investigation with other VO^{2+} starting materials, of which there is truly no shortage in the established chemistry of this oxidation level.

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Supplementary Material Available: Tables S1-S4, listing fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles (8 pages); a table of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page. A complete MSC structure report (No. 86016) is available on request from the Indiana University Chemistry Library.

Notes

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A New Reaction of Cyanide with Peroxide and Thiosulfate at pH 7-9

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During research on a method to treat cyanide-containing waste waters, we investigated the reaction of H_2O_2, $S_2O_3^{2-}$, and cyanide[1] at pH 7-9 that produces thiocyanate and sulfate. To our knowledge, this reaction has not been reported previously. When only H_2O_2 and $S_2O_3^{2-}$ were reacted together (each at $(2.5-10) \times 10^{-3}$ M), a mixture of SO_4^{2-} and $S_4O_6^{2-}$ was produced; low pH and excess $S_2O_3^{2-}$ favored $S_4O_6^{2-}$ formation. The literature erroneously reports $S_3O_6^{2-}$ as the product in neutral solution,[2] while acidic and basic conditions lead to $S_4O_6^{2-}$ and SO_4^{2-}, respectively. Stoichiometric data in this work as well as TLC[3] confirmed that a mixture of SO_4^{2-} and $S_4O_6^{2-}$, not $S_3O_6^{2-}$, was formed. Either H_2O_2 or $S_2O_3^{2-}$ alone reacts with cyanide at an insignificant rate under the conditions used in this work.[4,5] When cyanide was present (8×10^{-4} M or less), H_2O_2 and $S_2O_3^{2-}$ reacted at about the same rate as when cyanide was absent. However, each mole of $S_2O_3^{2-}$ that reacted converted 1 mol of cyanide to SCN^- and yielded 1 mol of SO_4^{2-}. As the cyanide content decreased below about 5×10^{-4} M, parallel reactions to give SCN^-, SO_4^{2-}, and $S_4O_6^{2-}$ were observed until the cyanide was completely gone.

To define the mechanism, H_2O_2 and $S_2O_3^{2-}$ were first studied without cyanide present. Solutions of H_2O_2 and $S_2O_3^{2-}$ (1 L each) were prepared, thermostated at 25 °C, and separately adjusted to the desired pH value. After they were mixed to initiate the reaction, the pH was maintained with standard acid or base. Every 5-10 min, 50-mL aliquots were withdrawn for determination of $S_2O_3^{2-}$ and H_2O_2 by classical iodimetric titration.[6] If the titrations were done rapidly, mutual interference was less than 1%. Experimental data points for concentration and time were computer fitted to a third-order polynomial that calculated instantaneous concentrations and reaction rates for $S_2O_3^{2-}$, H_2O_2, and H^+ throughout the reaction. Table I gives the initial concentrations and rates that were calculated by using the polynomial. Reactions 1 and 2 proceeded in parallel according to the results shown in

$$S_2O_3^{2-} + 4H_2O_2 \rightarrow 2SO_4^{2-} + 3H_2O + 2H^+ \quad (1)$$

$$2S_2O_3^{2-} + H_2O_2 + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O \quad (2)$$

the right-hand column of Table I. Simultaneous equations using the stoichiometry[7] in reactions 1 and 2 and the calculated rate

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(1) At pH 7-9, cyanide exists primarily as HCN with some free CN^- in equilibrium. The term "cyanide" means total cyanide rather than only free CN^- ion.

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(5) In control experiments, reactions of 1×10^{-2} M H_2O_2 with 8×10^{-4} M cyanide at pH 7, 8, and 9 had half-lives for cyanide disappearance of about 1000, 500, and 100 h, respectively. Masson, O. *J. Chem. Soc.* **1907**, *91*, 1449.

(6) Each 50-mL aliquot was analyzed for both $S_2O_3^{2-}$ and H_2O_2 by titrating first with standard I_3^- at pH 4 using starch indicator. Then H_2SO_4, KI, $(NH_4)_2MoO_4$ were added so that H_2O_2 would liberate 1 equiv of I_2 that was titrated with standard $S_2O_3^{2-}$ solution.

Table I. Initial Concentrations and Reaction Rates for Species in the Reaction of H_2O_2 and $S_2O_3^{2-}$ with No Cyanide Present

pH	$[S_2O_3^{2-}]$, M	$[H_2O_2]$, M	$d[S_2O_3^{2-}]/dt$, mol L^{-1} s^{-1}	$d[H_2O_2]/dt$, mol L^{-1} s^{-1}	$d[H^+]/dt$,[a] mol L^{-1} s^{-1}	% $S_2O_3^{2-}$ reacting by eq 1
7	9.95×10^{-3}	2.52×10^{-3}	-7.9×10^{-7}	-8.8×10^{-7}	-5.0×10^{-7}	18
7	5.04×10^{-3}	4.67×10^{-3}	-7.5×10^{-7}	-8.8×10^{-7}	-3.3×10^{-7}	19
7	2.49×10^{-3}	9.27×10^{-3}	-5.2×10^{-7}	-9.6×10^{-7}	3.0×10^{-8}	38
8	9.83×10^{-3}	2.34×10^{-3}	-6.2×10^{-7}	-7.8×10^{-7}	-1.8×10^{-7}	22
8	4.90×10^{-3}	4.60×10^{-3}	-5.1×10^{-7}	-1.2×10^{-6}	2.4×10^{-7}	53
8	2.50×10^{-3}	9.22×10^{-3}	-5.4×10^{-7}	-1.5×10^{-6}	4.3×10^{-7}	65
9	1.01×10^{-2}	2.45×10^{-3}	-5.6×10^{-7}	-1.1×10^{-6}	2.0×10^{-8}	42
9	4.99×10^{-3}	4.71×10^{-3}	-5.5×10^{-7}	-1.6×10^{-6}	4.4×10^{-7}	69
9	2.51×10^{-3}	9.28×10^{-3}	-5.1×10^{-7}	-1.9×10^{-6}	8.8×10^{-7}	92

[a] $[H^+]$ is kept constant; $d[H^+]/dt$ is determined by the rate of standard acid or base addition required to keep the pH fixed. Positive values of $d[H^+]/dt$ mean H^+ was produced in the reaction, so base was added to maintain the pH.

Table II. Initial Concentrations and Reaction Rates for Species in the Reaction of H_2O_2, $S_2O_3^{2-}$, and Cyanide

pH	$[S_2O_3^{2-}]$, M	$[H_2O_2]$, M	[cyanide], M	$d[S_2O_3^{2-}]/dt$, mol L^{-1} s^{-1}	$d[H_2O_2]/dt$, mol L^{-1} s^{-1}	$d[H^+]/dt$, mol L^{-1} s^{-1}	d[cyanide]/dt, mol L^{-1} s^{-1}
7	1.00×10^{-2}	2.51×10^{-3}	7.9×10^{-4}	-7.7×10^{-7}	-5.9×10^{-7}	-2.3×10^{-7}	2.5×10^{-7}
7	5.09×10^{-3}	4.75×10^{-3}	8.2×10^{-4}	-6.7×10^{-7}	-6.3×10^{-7}	0.0	2.8×10^{-7}
7	2.63×10^{-3}	9.27×10^{-3}	8.1×10^{-4}	-5.5×10^{-7}	-6.0×10^{-7}	3.3×10^{-7}	2.6×10^{-7}
8	1.01×10^{-2}	2.39×10^{-3}	8.0×10^{-4}	-5.3×10^{-7}	-5.2×10^{-7}	3.3×10^{-7}	3.9×10^{-7}
8	5.19×10^{-3}	4.63×10^{-3}	7.9×10^{-4}	-6.0×10^{-7}	-5.2×10^{-7}	3.7×10^{-7}	3.6×10^{-7}
8	2.65×10^{-3}	9.42×10^{-3}	7.1×10^{-4}	-5.6×10^{-7}	-8.3×10^{-7}	4.0×10^{-7}	2.6×10^{-7}
9	1.01×10^{-2}	2.34×10^{-3}	7.9×10^{-4}	-5.6×10^{-7}	-6.6×10^{-7}	2.9×10^{-7}	4.2×10^{-7}
9	5.17×10^{-3}	4.69×10^{-3}	7.9×10^{-4}	-5.1×10^{-7}	-7.4×10^{-7}	2.4×10^{-7}	3.0×10^{-7}
9	2.74×10^{-3}	9.34×10^{-3}	7.5×10^{-4}	-4.1×10^{-7}	-1.1×10^{-6}	3.7×10^{-7}	3.0×10^{-7}

data in Table I for $S_2O_3^{2-}$ and H_2O_2 were used to determine the percent of $S_2O_3^{2-}$ reacting by eq 1 and 2, respectively.

Reactions with cyanide present were done as those without except that a closed reaction vessel was used to prevent HCN losses, and separate 50-mL aliquots were withdrawn for cyanide analysis using a Ag/S^{2-} specific ion electrode. Initial reaction rates and concentrations for each specie are given in Table II. Data for $S_2O_3^{2-}$–H_2O_2–cyanide reactions were also computer fitted to a third-order polynomial.

Results in Tables I and II suggested the overall mechanism shown in eq 3–6. With no cyanide present, reaction 5 is eliminated; this simpler case will be discussed first.

$$S_2O_3^{2-} + H_2O_2 \xrightarrow{k_1} HOS_2O_3^- + OH^- \text{ (rate determining)} \quad (3)$$

$$HOS_2O_3^- + 3H_2O_2 \xrightarrow{k_2} 2SO_4^{2-} + 3H^+ + 2H_2O \text{ (fast)} \quad (4)$$

$$HOS_2O_3^- + CN_T \xrightarrow{k_3} SCN^- + SO_4^{2-} + (1 + f)H^+ \text{ (very fast)}^{8} \quad (5)$$

$$HOS_2O_3^- + S_2O_3^{2-} + H^+ \xrightarrow{k_4} S_4O_6^{2-} + H_2O \text{ (fast)} \quad (6)$$

When the steady-state approximation for $HOS_2O_3^-$ is used then k_1 and the ratio k_4/k_2 could be solved in terms of measured quantities. Results are given in Table III. Two different expressions can be derived for k_1, and three independent ones were obtained for k_4/k_2. For each sample time in each kinetic run, calculated values of concentrations and rates were substituted into the expressions for k_1 and k_4/k_2. Rate constants and ratios in Table III are those calculated at zero time by using data in Table I, but throughout each run, values varied generally by less than 10% from those reported. At each pH value, the ratio of k_4/k_2 should have been independent of the $[S_2O_3^{2-}]/[H_2O_2]$ ratio if reactions 4 and 6 were correctly assumed to be first order in H_2O_2 and $S_2O_3^{2-}$, respectively. However, the trend in values of k_4/k_2 is consistent with a reaction order of about 0.5 for H_2O_2 and $S_2O_3^{2-}$. This indicates that a radical may be involved, and reactions 4 and 6 may be the summation of a series of steps.

Table III. Rate Constant Expressions and Average Values of k_1 and k_4/k_2 for the H_2O_2-$S_2O_3^{2-}$ Reaction (No Cyanide Present)

pH	nominal ratio $[S_2O_3^{2-}]/[H_2O_2]$	k_1,[a] L mol^{-1} s^{-1}	k_4/k_2[b]
7	4.0	0.019	0.74
7	1.0	0.019	2.1
7	0.25	0.016	3.6
8	4.0	0.016	0.40
8	1.0	0.018	0.47
8	0.25	0.020	1.2
9	4.0	0.017	0.15
9	1.0	0.021	0.17
9	0.25	0.021	0.19

[a] $k_1 = (-{}^2/_5TP)(P' + 3H'/4) = (-{}^3/_7TP)(P'/3 + T')$. [b] $k_4/k_2 = (2P/T)(2H' + P')/(2P' - H') = (P/2T)(H' + 2T')/(T' - H') = (P/T)(4T' - P')/(2P' - T')$. $T = [S_2O_3^{2-}]$; $P = [H_2O_2]$; $T' = d[S_2O_3^{2-}]/dt$; $P' = d[H_2O_2]/dt$; $H' = d[H^+]/dt$.

In the more complicated case, that is, when cyanide was present, conditions were restricted to zero time in solving for the rate constants because $S_4O_6^{2-}$ converts cyanide to SCN^-. This additional reaction made the rate expression unsolvable in terms of measured quantities except at zero time. Expressions and calculated values of k_1, k_4/k_2, and k_4/k_3 are given in Table IV. The expressions for k_4/k_2 and k_4/k_3 include the sums, differences, and ratios of three or four reaction rates. Experimental uncertainty in each rate caused some of the values of k_4/k_2 and k_4/k_3 to differ by a factor of 2 or more between the independent expressions, so the values given are only an approximation.

The consistency and agreement in Tables III and IV support the overall mechanism described; k_1 is independent of pH, cyanide, and $[H_2O_2]/[S_2O_3^{2-}]$. Empirical rate constants[9] for the reaction

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(7) If x = mol/(L·min) of $S_2O_3^{2-} \rightarrow SO_4^{2-}$ and y = mol/(L·min) of $S_2O_3 \rightarrow S_4O_6^{2-}$, then $x + y$ = total mol of $S_2O_3^{2-}$/(L·min) reacting, and $4x + y/2$ = mol of H_2O_2/(L·min) reacting.

(8) CN_T is total cyanide reacting, whether it existed as CN^- or HCN. The term $f = 1/(1 + K_{HCN}/[H^+])$ is needed, since no H^+ is produced if CN^- reacts, but 1 mol of H^+ is liberated for each mole of HCN reacting.

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Table IV. Rate Constant Expressions and Average Values for the H_2O_2–$S_2O_3^{2-}$–Cyanide Reaction

pH	nominal ratio $[S_2O_3^{2-}]/H_2O_2$	k_1,[a] L mol^{-1} s^{-1}	k_4/k_2[b]	k_4/k_3[c]
7	4.0	0.020	3	0.05
7	1.0	0.020	4	0.1
7	0.25	0.018	2	0.07
8	4.0	0.020	0.7	0.01
8	1.0	0.022	0.8	0.04
8	0.25	0.019	2	0.05
9	4.0	0.022	0.2	0.008
9	1.0	0.018	0.8	0.04
9	0.25	0.018	1	0.05

[a] $k_1 = (1/6TP)(H' - 4T' + (f - 2)C') = -{}^3/_7TP(C' + T' + P'/3)$. [b] $k_4/k_2 = (3P/T)(4T' - 3C' - P')/(6P' - 3C' - 3T') = (3P/(2T))(7(fC' + H')/(6P' - 3C' - 3T') + 2/3)$. [c] $k_4/k_3 = (C/T)((T' - {}^3/_7(C' + T' + P'/3))/C') = (C/4T)((H' + {}^6/_7(C' + T' + P'/3) + (f - 2)C')/C')$. T, P, T', P', H' are as defined in Table III. C = [cyanide]; C' = d[cyanide]/dt.

of H_2O_2 and $S_2O_3^{2-}$ are within 10–20% of k_1 values that are calculated on the basis of the mechanism proposed here. The ratio k_4/k_2 decreases as the pH increases, since higher pH favors SO_4^{2-} formation. Values of k_4/k_2 in Table IV (with cyanide present) are near those in Table III (with only H_2O_2 and $S_2O_3^{2-}$ reacted). Even though cyanide is more dilute than either H_2O_2 or $S_2O_3^{2-}$, it reacts almost as rapidly (see Table II). Thus, k_3 is much larger than k_2 or k_4 (see Table IV). Reactions 4 and 6 were assumed to be first order in H_2O_2 and $S_2O_3^{2-}$, respectively, but ratios of k_2/k_4 are consistent with an order near 0.5. The expected intermediate[9] in the peroxide–thiosulfate reaction is written as $HOS_2O_3^-$, but it was never identified explicitly. However, the unprotonated form of $HOS_2O_3^-$, $S_2O_4^{2-}$ (dithionite), did not produce $S_4O_6^{2-}$ when added to $S_2O_3^{2-}$ solution or SCN^- when added to cyanide solution.

Registry No. $S_2O_3^{2-}$, 14383-50-7; H_2O_2, 7722-84-1; $S_4O_6^{2-}$, 15536-54-6; cyanide, 57-12-5.

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Use of Internal Standards for the Measurement of Reaction Entropies

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Several years ago, Gagné et al. recommended the use of ferrocene as an internal standard for the measurement and reporting of formal reduction potentials, E^f, in nonaqueous solvents.[1] The procedure eliminates systematic errors associated with the use of nonaqueous reference electrodes and has been widely adopted. The subsequent availability of values of E^f vs. ferrocene has allowed meaningful comparisons of oxidizing and reducing strengths for numerous compounds.

A second useful property associated with redox couples is the temperature dependence of the formal reduction potential, dE^f/dT, measured in a nonisothermal cell. This quantity can be used to estimate entropy changes associated with a single redox couple, ΔS°_{rc}.[2,3]

$$\mathrm{Ox} + ne^- \overset{E^f}{\rightleftharpoons} \mathrm{Red} \tag{1}$$

$$\Delta S^\circ_{rc} = S^\circ_{Red} - S^\circ_{Ox} = nF[\mathrm{d}E^f/\mathrm{d}T]_{\mathrm{nonisothermal}} \tag{2}$$

Calculation of ΔS°_{rc}, the reaction entropy for the redox couple, requires extrathermodynamic assumptions, which have been discussed in detail by Yee et al.[4] The most problematic of these assumptions from an experimental point of view is the requirement of a temperature-independent junction potential between the working and reference compartments of the nonisothermal cell. While it is possible to construct cells in which the temperature dependence of the junction potential is negligible,[4] these junctions can become temperature dependent or simply change with time. These experimental difficulties represent a potential source of systematic error in the reporting of values of ΔS°_{rc}, and indeed, difficulties associated with construction of reliable nonisothermal cells may inhibit many from making these measurements.

Herein, we report a simple procedure for measuring ΔS°_{rc} that eliminates the need for nonisothermal cell measurements. This is achieved by recording the reduction potential for the sample redox couple, E^f_{sam}, vs. the reduction potential of an internal standard, E^f_{std}, at a variety of temperatures in a single-compartment thermostated cell. By choice of a value of ΔS°_{rc} for the internal standard, ΔS°_{rc} for the sample redox couple can be readily calculated. We suggest the use of ferrocene as an internal standard for measurements in nonaqueous solvents and the use of ruthenium hexaammine in aqueous solutions. The internal standard procedure for measuring ΔS°_{rc} is illustrated for $Co(phen)_3^{3+,2+}$ in water and for $Co(Cp)_2^{+,0}$ (cobaltocene) in acetonitrile.

Values of reaction entropies can be related to the electron-transfer reactivity associated with a redox couple in a variety of ways. Even though the reasons are unclear, there is an unmistakable correlation between the magnitude of ΔS°_{rc} for a couple and the reorganization energy associated with the self-exchange reaction associated with the couple.[5] Youngblood and Margerum used values of ΔS°_{rc} for Cu(III,II) and Ni(III,II) oligiopeptide complexes to demonstrate changes in the number of coordinated water molecules for the oxidized and reduced states of the complexes.[6] Similarly, measurement of ΔS°_{rc} has been used to examine the solvation of redox active sites in proteins.[7] In particular, we comment on the use of ΔS°_{rc} values obtained by the internal standard method to obtain thermodynamic parameters associated with electron-transfer cross-reactions.

Experimental Section

Water, acetonitrile, and supporting electrolytes were purified as described in previous publications.[8,9] Ferrocene (Strem), cobaltocenium tetrafluoroborate (Strem) and hexaammineruthenium(III) chloride (Matthey Bishop) were used as received. Solutions of tris(1,10-phenanthroline)cobalt(II) ion, $Co(phen)_3^{2+}$, were prepared from a stock solution of $Co^{II}(ClO_4)_2$ and 1,10-phenanthroline.[8]

Electrochemical measurements were made by utilizing a BAS-100 electrochemical analyzer. Working electrodes were either platinum or glassy carbon and were polished prior to use. The auxiliary electrode was platinum foil or gauze. Saturated sodium chloride calomel (SSCE) and silver/silver nitrate (0.01 M), $TBABF_4$ (0.5 M) reference electrodes were used in the aqueous and nonaqueous experiments, respectively. Cell temperatures were maintained with a Lauda constant-temperature bath.

Results and Discussion

Measurement of ΔS°_{rc} Utilizing an Internal Standard. The relationship between the temperature dependence of the difference

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