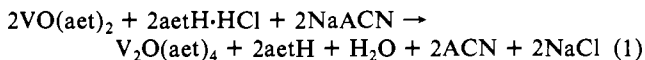
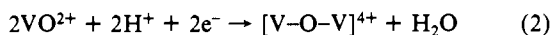


V(III) sulfide polymers, primarily V_2S_3 . Elucidating possible intermediates represents one goal of our synthetic work. We can report that **3** can be cleanly converted to **1** in a controlled fashion under laboratory conditions, a result that suggests a similar reaction involving the conversion 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



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



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.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by NSF Grant CHE 8507748. We thank the Bloomington Academic Computing Service for a gift of computing time. We also thank Brian K. Conroy for his assistance in the molecular orbital calculations.

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

Contribution from the Twin Cities Research Center, Bureau of Mines, U.S. Department of the Interior, Minneapolis, Minnesota 55417

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

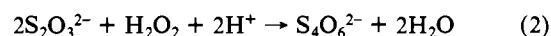
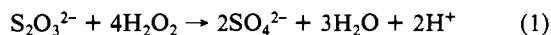
Joseph E. Schiller*

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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 cyanide¹ 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 TLC³ 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 iodometric 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



the right-hand column of Table I. Simultaneous equations using the stoichiometry⁷ in reactions 1 and 2 and the calculated rate

- (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.
- (2) (a) Tarugi, N.; Vitali, G. *Chim. Ital.* **1909**, *63*, 2929. (b) Lunenak-Burmakia, V. A.; Gerasenkova, A. N. *Zh. Neorg. Khim.* **1964**, *9*, 270; *Chem. Abstr.* **1964**, *60*, 9965e.
- (3) Marchant, W. N.; May, S. L.; Simpson, W. W.; Winter, J. K.; Beard, H. R. *BuMines IC 8819*, **1980**, 20 pp. *Inf. Circ. U.S. Bur. Mines* **1980**, *IC 8819*, 1-20.
- (4) Davis, R. E. *J. Am. Chem. Soc.* **1962**, *66*, 956.
- (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.

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Table I. Initial Concentrations and Reaction Rates for Species in the Reaction of H₂O₂ and S₂O₃²⁻ with No Cyanide Present

pH	[S ₂ O ₃ ²⁻], M	[H ₂ O ₂], M	d[S ₂ O ₃ ²⁻]/dt, mol L ⁻¹ s ⁻¹	d[H ₂ O ₂]/dt, mol L ⁻¹ s ⁻¹	d[H ⁺]/dt, ^a mol L ⁻¹ s ⁻¹	% S ₂ O 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.

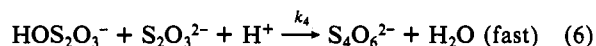
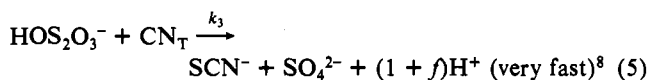
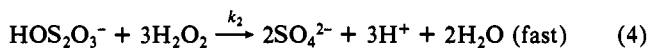
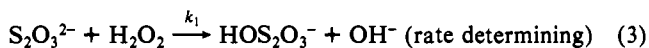
Table II. Initial Concentrations and Reaction Rates for Species in the Reaction of H₂O₂, S₂O₃²⁻, and Cyanide

pH	[S ₂ O ₃ ²⁻], M	[H ₂ O ₂], M	[cyanide], M	d[S ₂ O ₃ ²⁻]/dt, mol L ⁻¹ s ⁻¹	d[H ₂ O 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 S₂O₃²⁻ and H₂O₂ were used to determine the percent of S₂O₃²⁻ 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/S²⁻ specific ion electrode. Initial reaction rates and concentrations for each specie are given in Table II. Data for S₂O₃²⁻-H₂O₂-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 elim-



inated; this simpler case will be discussed first. When the steady-state approximation for HOS₂O₃⁻ 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 [S₂O₃²⁻]/[H₂O₂] ratio if reactions 4 and 6 were correctly assumed to be first order in H₂O₂ and S₂O₃²⁻, respec-

Table III. Rate Constant Expressions and Average Values of *k*₁ and *k*₄/*k*₂ for the H₂O₂-S₂O₃²⁻ Reaction (No Cyanide Present)

pH	nominal ratio [S ₂ O ₃ ²⁻]/ [H ₂ O ₂]	<i>k</i> ₁ , ^a L mol ⁻¹ s ⁻¹	<i>k</i> ₄ / <i>k</i> 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 = (-2/3 TP)/(P' + 3H'/4) = (-3/7 TP)(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 = [S₂O₃²⁻]; P = [H₂O₂]; T' = d[S₂O₃²⁻]/dt; P' = d[H₂O₂]/dt; H' = d[H⁺]/dt.

tively. However, the trend in values of *k*₄/*k*₂ is consistent with a reaction order of about 0.5 for H₂O₂ and S₂O₃²⁻. This indicates that a radical may be involved, and reactions 4 and 6 may be the summation of a series of steps.

In the more complicated case, that is, when cyanide was present, conditions were restricted to zero time in solving for the rate constants because S₄O₆²⁻ 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 [H₂O₂]/[S₂O₃²⁻]. Empirical rate constants⁹ for the reaction

(7) If *x* = mol/(L·min) of S₂O₃²⁻ → SO₄²⁻ and *y* = mol/(L·min) of S₂O₃²⁻ → S₄O₆²⁻, then *x* + *y* = total mol of S₂O₃²⁻/(L·min) reacting, and 4*x* + *y*/2 = mol of H₂O₂/(L·min) reacting.

(8) CN_T⁻ is total cyanide reacting, whether it existed as CN⁻ or HCN. The term *f* = 1/(1 + *K*_{H₂CN}/[H⁺]) is needed, since no H⁺ is produced if CN⁻ reacts, but 1 mol of H⁺ is liberated for each mole of HCN reacting.

(9) Sandved, K.; Holte, J. B. *Forh., K. Nor. Vidensk. Selsk.* 1938, 11, 189.

Table IV. Rate Constant Expressions and Average Values for the H_2O_2 - $\text{S}_2\text{O}_3^{2-}$ -Cyanide Reaction

pH	nominal ratio [$\text{S}_2\text{O}_3^{2-}$]/ 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 $k_4/k_2 = (3P/T)(4T' - 3C' - P')/(6P' - 3C' - 3T') = (3P/(2T)) \cdot (7fC' + H')/(6P' - 3C' - 3T') + 2/3$.
^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 $\text{S}_2\text{O}_3^{2-}$ 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 $\text{S}_2\text{O}_3^{2-}$ reacted). Even though cyanide is more dilute than either H_2O_2 or $\text{S}_2\text{O}_3^{2-}$, 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 $\text{S}_2\text{O}_3^{2-}$, respectively, but ratios of k_2/k_4 are consistent with an order near 0.5. The expected intermediate⁹ 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^- , $\text{S}_2\text{O}_4^{2-}$ (dithionite), did not produce $\text{S}_4\text{O}_6^{2-}$ when added to $\text{S}_2\text{O}_3^{2-}$ solution or SCN^- when added to cyanide solution.

Registry No. $\text{S}_2\text{O}_3^{2-}$, 14383-50-7; H_2O_2 , 7722-84-1; $\text{S}_4\text{O}_6^{2-}$, 15536-54-6; cyanide, 57-12-5.

Contribution from the Department of Chemistry
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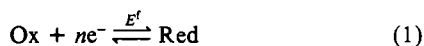
Use of Internal Standards for the Measurement of Reaction Entropies

Carl A. Koval,* Ross M. Gustafson, and Cindy M. Reidsema

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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, $\Delta S^\circ_{\text{rc}}$.^{2,3}



$$\Delta S^\circ_{\text{rc}} = S^\circ_{\text{Red}} - S^\circ_{\text{Ox}} = nF[dE^f/dT]_{\text{nonisothermal}} \quad (2)$$

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Calculation of $\Delta S^\circ_{\text{rc}}$, 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 $\Delta S^\circ_{\text{rc}}$, 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 $\Delta S^\circ_{\text{rc}}$ 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 $\Delta S^\circ_{\text{rc}}$ for the internal standard, $\Delta S^\circ_{\text{rc}}$ 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 $\Delta S^\circ_{\text{rc}}$ is illustrated for $\text{Co}(\text{phen})_3^{3+,2+}$ in water and for $\text{Co}(\text{Cp})_2^{+,0}$ (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 $\Delta S^\circ_{\text{rc}}$ for a couple and the reorganization energy associated with the self-exchange reaction associated with the couple.⁵ Youngblood and Margerum used values of $\Delta S^\circ_{\text{rc}}$ for $\text{Cu}(\text{III},\text{II})$ and $\text{Ni}(\text{III},\text{II})$ 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 $\Delta S^\circ_{\text{rc}}$ has been used to examine the solvation of redox active sites in proteins.⁷ In particular, we comment on the use of $\Delta S^\circ_{\text{rc}}$ 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 hexaamineruthenium(III) chloride (Matthey Bishop) were used as received. Solutions of tris(1,10-phenanthroline)cobalt(II) ion, $\text{Co}(\text{phen})_3^{2+}$, were prepared from a stock solution of $\text{Co}^{II}(\text{ClO}_4)_2$ 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), TBABF₄ (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 $\Delta S^\circ_{\text{rc}}$ Utilizing an Internal Standard. The relationship between the temperature dependence of the difference

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