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A Cross Relation in Volumes of Activation for Electron-Transfer Reactions

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For the reduction of aqueous $Fe(H_2O)_6^{3+}$ by $Co([9]aneS_3)_2^{2+}$, over a wide range (0.02–0.8 mol kg^{-1}) of ionic strength I, the rate constant k_{12} varies according to $\ln(k_{12}/k_{12}^0) = 2AZ_1Z_2I^{1/2}/(1 + B\mathring{a}I^{1/2})$, where A and B are the Debye–Hückel parameters and $k_{12}^0 = 369 \pm 7$ with $\mathring{a} = 798 \pm 10$ pm for $CF_3SO_3^-$ media at 25 °C. The pressure dependence of the electrode potential difference ΔE gives the volume of reaction $\Delta V_{12}^0 = -17.1 \pm 0.4$ cm^3 mol^{-1} at $I = 0.26$ mol kg^{-1}. The volume of activation ΔV_{12}^* (-15.9 ± 0.3 and -13.7 ± 0.4 cm^3 mol^{-1} for 0.1 mol kg^{-1} $CF_3SO_3^-$ and ClO_4^- media, respectively) agrees well with that calculated from a volume cross relation $\Delta V_{12}^* = {}^1/_2(\Delta V_{11}^* + \Delta V_{22}^* + \Delta V_{12}^0) + C$, derived from the Marcus cross relation for k_{12} (*J. Phys. Chem.* **1968**, *72*, 891), where ΔV_{11}^* and ΔV_{22}^* are for the $Fe(H_2O)_6^{3+/2+}$ and $Co([9]aneS_3)_2^{3+/2+}$ self-exchange reactions and the small contribution C incorporates the pressure dependence of Marcus' f. For the reduction of aqueous $Fe(H_2O)_6^{3+}$ by $Co(sepulchrate)^{2+}$ at 1.8 °C, for which ΔE is large (1.03 V), k_{12} is 130-fold slower, and ΔV_{12}^* (-5.0 cm^3 mol^{-1}) is 4–5 cm^3 mol^{-1} more positive, than predicted by the cross relations. These results suggest the usefulness of the volume cross relation as a mechanistic criterion, at least for reactions with moderate ΔE; in particular, they militate against nonadiabaticity as the cause of the perceived slowness of cross reactions involving the $Fe(H_2O)_6^{3+/2+}$ couple. Conversely, the volume cross relation affords a means of obtaining experimentally inaccessible volumes of activation for adiabatic outer-sphere redox processes in water.

Introduction

We have recently shown[3-7] that the pressure dependences of rate constants for outer-sphere *self-exchange* electron-transfer reactions

$$A^+ + A \xrightarrow{k_{11}} A + A^+ \qquad (1)$$

$$B^+ + B \xrightarrow{k_{22}} B + B^+ \qquad (2)$$

of transition-metal complexes in *aqueous* solution can generally be accounted for essentially quantitatively by an adaptation of Marcus–Hush theory, except in some cases where there are known complications such as large changes in spin multiplicity[8,9] or active involvement of the counterions in the transition state.[10,11] (The theory is less successful for nonaqueous solutions, especially where the permittivity of the solvent is very low.[5,12]) In this article, we address the question of whether this approach can be generalized to cover "cross" reactions, i.e., reactions in which there is net chemical change:

$$A^+ + B \xrightarrow{k_{12}} A + B^+ \qquad (3)$$

In the theory of Marcus as refined by Sutin,[13] the rate constant k_{12} for a cross reaction 3 with equilibrium constant K_{12} is, in principle, calculable from the rate constants for the constituent self-exchange reactions 1 and 2.

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}W \qquad (4)$$

$$\ln f = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z_{11}Z_{22}) + (w_{11} + w_{22})/RT]} \qquad (5)$$

$$W = \exp[(w_{11} + w_{22} - w_{12} - w_{21})/2RT] \qquad (6)$$

Here, w_{ij} are the Coulombic work terms, which effectively cancel in (6) and in the numerator of (5) when the reactants have the same charges and approximately the same radii as the products (as in this study), and Z_{ii} are the collision frequencies (usually taken to be 1×10^{11} L mol^{-1} s^{-1}) for the hypothetically uncharged reactants in solution. [Sutin[13d,e] replaces Z_{ii} with a term that incorporates the formation constant of the A^+/A precursor complex along with the nuclear frequency, but the traditional use of Z_{ii} is adequate when reactions 1–3 are all of the same charge type.] When the electrode potential difference ΔE between couples A^+/A and B^+/B is small, f tends to 1 and eqs 4–6 reduce to eq 7.

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2} \qquad (7)$$

Implicit in eqs 4–6 are several assumptions, notably that the intrinsic energy barrier for the cross reaction is the average of those for the self-exchanges, that all ligand displacements in the course of the reactions are approximately harmonic, and that reactions 1–3 are all adiabatic. It is usually further assumed that the collision frequency Z for (3) can be taken to be $(Z_{11}Z_{22})^{1/2}$. With these limitations in mind, and with assumption that the work terms cancel except in the denominator of (5) and that Z is independent of pressure, one can differentiate eqs 4 and 5 with respect to pressure P to give a cross relationship involving volumes of activation (ΔV_{ij}^*) and reaction (ΔV_{12}^0) and the corresponding

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volume changes associated with the Coulombic work terms $\Delta V_{ii}^{\mathrm{w}}$:[5]

$$\Delta V_{12}^{\ddagger} = [(\Delta V_{11}^{\ddagger} + \Delta V_{22}^{\ddagger} + \Delta V_{12}^{0})/2] + C \qquad (8)$$

$$C = -(RT/2)(\partial \ln f/\partial P)_T = [X\Delta V_{12}^{0} \ln K_{12} - 2(\ln K_{12})^2(\Delta V_{11}^{\ddagger} + \Delta V_{22}^{\ddagger} - \Delta V_{11}^{\mathrm{w}} - \Delta V_{22}^{\mathrm{w}})]/X^2 \qquad (9)$$

$$X = 4[\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT] \qquad (10)$$

In the limiting case of low ΔE, C becomes negligible, and we have

$$\Delta V_{12}^{\ddagger} = {}^1/_2(\Delta V_{11}^{\ddagger} + \Delta V_{22}^{\ddagger} + \Delta V_{12}^{0}) \qquad (11)$$

In principle, then, since $\Delta V_{ii}^{\ddagger}$ values for self-exchange are calculable from theory,[5] $\Delta V_{12}^{\ddagger}$ for any *simple*, *adiabatic*, *outer-sphere* electron-transfer reaction should also be calculable from eqs 8–10 and may serve as a criterion of this type of reaction mechanism (assuming that K_{12} and ΔV_{12}^{0} are known or can be reliably predicted). To test eqs 8–10 in this context, we require aqueous self-exchange reactions for which $\Delta V_{ii}^{\ddagger}$ are known and conform to expectations based on our extension of Marcus theory.[5] To date, only the $Fe(H_2O)_6^{3+/2+}$, $Fe(phen)_3^{3+/2+}$, $Co(sep)^{3+/2+}$, and $Co([9]aneS_3)_2^{3+/2+}$ couples have met these criteria,[4,6,7,14] and of their possible cross reactions, those involving $Fe(phen)_3^{3+/2+}$ are too fast for the high-pressure stopped-flow methodology available to us. We have therefore made detailed high-pressure studies of the following two reactions only:

$$Fe(H_2O)_6^{3+} + Co([9]aneS_3)_2^{2+} \rightarrow Fe(H_2O)_6^{2+} + Co([9]aneS_3)_2^{3+} \qquad (12)$$

$$Fe(H_2O)_6^{3+} + Co(sep)^{2+} \rightarrow Fe(H_2O)_6^{2+} + Co(sep)^{3+} \qquad (13)$$

Even so, as Rudgewick-Brown and Cannon found,[15] reaction 13 is fast enough to restrict the application of the stopped-flow technique to inconveniently low reactant concentrations, since $\Delta E \approx 1.0$ V.[16] Values of ΔV^0 are obtainable from the pressure dependence of ΔE[16,17] or from the molar volumes of the reactants.

Experimental Section

Materials. $[Co(sep)]Cl_3 \cdot H_2O$ was prepared by the method of Sargeson, Harrowfield, et al.[18–20] The salts $[Co([9]aneS_3)_2]X_2$ were made by mixing methanolic solutions of $Co(H_2O)_6X_2$ and 1,4,7-trithiacyclonane (Aldrich).[21] Microanalyses for CHN confirmed the purity of the products. Solutions of $Fe(H_2O)_6^{3+}$ were prepared either directly from iron(III) chloride (Fisher) or perchlorate (Aldrich) or, in the case of the trifluoromethanesulfonate (triflate), indirectly by either anion exchange of Dowex-1 or by precipitating $KClO_4$ from $Fe(ClO_4)_3$ solutions with CF_3SO_3K. These solutions were analyzed for Fe content spectrophotometrically as $Fe(phen)_3^{2+}$ following reduction with hydroxylamine hydrochloride;[22] analysis of $Fe(ClO_4)_3$ solutions required anion exchange of ClO_4^- for Cl^- before reduction. Sodium and potassium triflates were made by neutralization of redistilled CF_3SO_3H (Eastman Kodak) and recrystallized twice from water. NaCl (BDH Assurance) and $NaClO_4 \cdot H_2O$ (Fisher Purified) were used as received; $NaClO_4 \cdot H_2O$ was analyzed by anion exchange for OH^- and subsequent titration with standard acid. $Co(sep)^{3+}$ in triflate media was reduced, with rigorous exclusion of air, with mossy zinc.

Kinetics. Rate measurements were made using a thermostated (±0.1 °C) Hi-Tech SP-56 high-pressure stopped-flow spectrophotometer. Sufficient acid was added to the iron(III) solutions to eliminate slow absorbance changes, caused by hydrolytic polymerization, that occurred in reactant solutions after mixing (in addition to changes due to reactions 12 and 13). Since the molal scale is independent of both pressure P and temperature T, either the solutions were made up by weight or molar concentrations were converted to molal using solution density data.[23]

For reaction 12, $Co([9]aneS_3)_2^{2+}$ solutions were prepared daily in N_2-purged water and kept in the dark at 4 °C to avoid aerial oxidation (<2% oxidation to Co^{III} in an 8-h period; cf. ≈10% at 25 °C) until needed, and no solution was left in the stopped-flow instrument for more than 2 h. Concentration ranges (mol kg^{-1}) after mixing were as follows: $[Co([9]aneS_3)_2^{2+}]$, $(0.3–0.8) \times 10^{-4}$; $[Fe^{III}]$, $(0.6–2.0) \times 10^{-4}$; $[Cl^-]$, 0.01–0.10; $[CF_3SO_3^-]$, 0.02–0.08; $[ClO_4^-]$, 0.010–0.78. To minimize loss of $Co([9]aneS_3)_2^{2+}$ and hydrolytic oligomerization of Fe^{III}, the added acid and supporting electrolyte were introduced with the Fe^{III} solution at twice the required postmixing concentration; this, however, led to a significant differential in compressibility between the two reagent solutions at high ionic strengths I, leading to pressure-induced leakage from one syringe into the other. The reaction was therefore followed (at 330 nm and 25 °C) either at low pressure over a wide range of I or at relatively low I and pressures from ≈1 to 200 MPa. In a typical run, six transients were signal-averaged at each of seven pressures, and the averaged transient was then converted to absorbance units. The second-order rate equation for an irreversible reaction with unequal initial concentrations of reactants

$$\ln([Fe^{III}]/[Co^{II}]) = \ln([Fe^{III}]_0/[Co^{II}]_0) + k_{12}([Fe^{III}]_0 - [Co^{II}]_0)t$$

was evaluated iteratively in terms of the product concentration ($[Fe^{II}] = [Co^{III}]$) with adjustment of the infinite-time absorbance to minimize the sum of the squares of the residuals, so giving the optimized value of k_{12}.

For reaction 13, rate measurements were made in triflate media over a temperature range 1.8–24.8 °C at 5.5 MPa and over a pressure range 4–206 MPa at 1.8 °C, with $[H^+] = 0.258$ mol kg^{-1}, ionic strength $I = 0.27$ mol kg^{-1}, $[Fe^{III}]_0 = 1.33–2.23$ mmol kg^{-1}, and $[Co^{II}]_0$ (from spectral change) = 0.114–0.636 mmol kg^{-1}; zero subscripts indicate initial concentrations. For $[Fe^{III}]_0 \approx 10[Co^{II}]_0$, rate constants k_{12} could be calculated on a pseudo-first-order basis using the whole transient; for $[Fe^{III}]_0 \approx 3[Co^{II}]_0$, collection of data was postponed until about 80% completion of reaction to achieve pseudo-first-order behavior (cf. Rudgewick-Brown and Cannon[15]), whereupon the reaction was followed for at least 2 further half-periods. These experiments were possible because absorbance changes of less than 0.01 can be reliably measured on the Hi-Tech instrument; the absorbance changes used were in excess of 0.05.

Electrochemical Measurements. The pressure dependence of the electrode potential E of $Co([9]aneS_3)_2(CF_3SO_3)_2$ vs Ag/AgCl(saturated KCl) was obtained from cyclic voltammograms (+0.500 to 0.0 mV at 10 or 20 mV s^{-1}) as described elsewhere.[16] The solutions in aqueous KCl or CF_3SO_3K were first deoxygenated with N_2.

Results

Kinetics of Reduction of $Fe(H_2O)_6^{3+}$ by $Co([9]aneS_3)_2^{2+}$. This reaction proceeded at a rate that was convenient to stopped-flow spectrophotometry at 25 °C but showed a marked dependence on $[H^+]$ as well as on the nature and identity of the anion(s) present. The $[H^+]$ dependence was shown to arise because $Fe(H_2O)_5OH^{2+}$, formed by the hydrolysis of $Fe(H_2O)_6^{3+}$, is much less reactive than the latter toward $Co([9]aneS_3)_2^{2+}$ (as is generally found with other typical reductants[24]). Table 1 shows that the apparent (measured) values of k_{12} at a particular ionic strength I and pressure P were satisfactorily corrected for this effect by multiplying them by $(1 + K_a/[H^+])$, using literature values[25] of

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[14] sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; phen = 1,10-phenanthroline; $[9]aneS_3$ = 1,4,7-trithiacyclononane.

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Table 1. Variation of the Observed Value of k_{12} with Hydrogen Ion Concentration[a]

$[H^+]$/mol L^{-1}	k_{12}(measd)/10^3 kg mol^{-1} s^{-1}	k_{12}(corr)/10^3 kg mol^{-1} s^{-1}
0.0250	2.49	2.83
0.0250	2.42	2.76
0.0250	2.46	2.79
0.100	2.06	2.76
0.100	2.14	2.88
0.00500	1.72	2.90
0.00500	1.71	2.88
0.00250	1.29	3.05
0.00250	1.27	3.01

[a] 25.0 °C, 1.0 MPa, $I = 0.515$ mol kg^{-1} ($CF_3SO_3^-/H^+/Na^+$); correction to measured k_{12} values for presence of redox-inactive $Fe(H_2O)_5OH^{2+}$ made using $K_a = 3.43 \times 10^{-3}$ mol L^{-1} for these conditions (from ref 25).

Table 2. Parameters Governing the Kinetic Ionic Strength Effect on Reaction 12 According to Eq 14[a]

anion	P/MPa	A/$kg^{1/2}$ $mol^{-1/2}$	B/nm^{-1}	å/pm	ln(k_{12}^0/kg mol^{-1} s^{-1})
$CF_3SO_3^-$	1.0	1.175	3.286	798 ± 10	5.912 ± 0.018
	40.0	1.153	3.284	788 ± 10	6.164 ± 0.019
ClO_4^-	1.0	1.175	3.286	700 ± 17	6.173 ± 0.039
	40.0	1.153	3.284	685 ± 19	6.408 ± 0.044

[a] 25.0 °C.

the hydrolysis constant K_a, interpolated as necessary; the average and standard deviation of the corrected k_{12} values in Table 1 are $(2.87 \pm 0.10) \times 10^3$ kg mol^{-1} s^{-1}. All other k_{12} data cited in this paper have been corrected in this way. Corrections at other I and P values were equally satisfactory except in cases where P was highest at the same time that $[H^+]$ was very low (2.5–5.0 mmol kg^{-1}), apparently because high pressures favor the formation of hydrolytic polymers that are otherwise negligible in these experiments. Accordingly, we report below only those variable-pressure measurements for which $[H^+]$ was 0.01 mol kg^{-1} or higher.

As with the $Co(phen)_3^{3+/2+}$ self-exchange reaction,[8] the dependence of the rate constant for reaction 12 on the counterion (triflate or perchlorate) is quite adequately accounted for in terms of ionic strength effects, through the extended form of the Brønsted–Bjerrum–Christiansen equation:

$$\ln k_{12} = \ln k_{12}^0 + 2AZ_1Z_2I^{1/2}/(1 + B\mathring{a}I^{1/2}) \qquad (14)$$

Here, Z_1 and Z_2 are the charge numbers of the reactants, and the Debye–Hückel parameters A and B are exactly calculable for a given temperature and pressure, but the ion-size parameter å may be allowed to vary to give the best fit of the data. Table 2 shows that å is characteristic of the anion and is not significantly dependent on the pressure. Figure 1 and supplementary Figures S1–S3 illustrate the effectiveness of eq 14 for reaction 12 in triflate and perchlorate media. Some measurements were also made in chloride media, but the rates were inconveniently fast (some 10-fold faster than for comparable perchlorate systems) and the interpretation was complicated by the significant but undetermined concentrations of Fe^{III} chloro complexes that would have been formed.

Ionic strength effects could not be investigated to high I at pressures above 40 MPa because of the differential compressibility problem noted above. The variable-pressure kinetics studies were therefore limited to ionic strengths just high enough (0.02–0.10 mol kg^{-1}) to provide sufficient $[H^+]$ to prevent hydrolytic oligomerization at 200 MPa. In all cases, ln k_{12} was a linear function of P to within the experimental uncertainty, over a 0–200 MPa range, as is shown in Figure 2 for triflate media at $I = 0.10$ mol kg^{-1} and in the supplementary material for other media. The corresponding volumes of activation are given in Table 3.

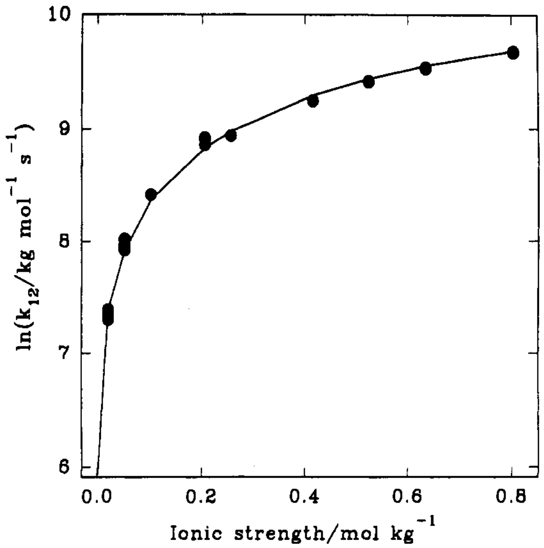

Figure 1. Ionic strength dependence of the rate constant, corrected for Fe^{III} hydrolysis, for the reduction of $Fe(H_2O)_6^{3+}$ by $Co([9]aneS_3)_2^{2+}$ at 25.0 °C and 1.0 MPa. The anion is $CF_3SO_3^-$. The curve is calculated from eq 14 with Debye–Hückel parameters $A = 1.175$ $kg^{1/2}$ $mol^{-1/2}$, $B = 3.286$ nm^{-1}, and å = 798 pm.

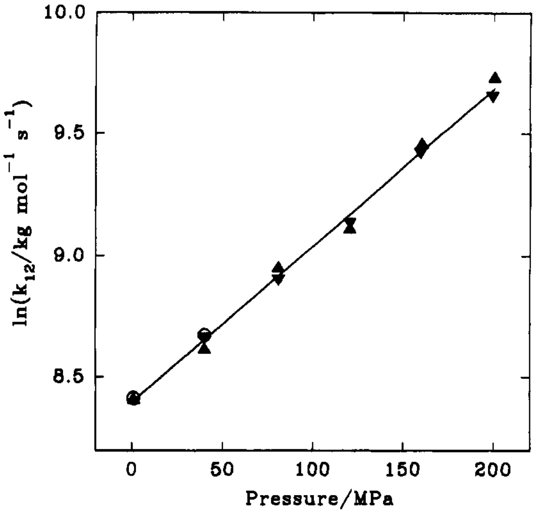

Figure 2. Pressure dependence of the rate constant, corrected for Fe^{III} hydrolysis, for the reduction of $Fe(H_2O)_6^{3+}$ by $Co([9]aneS_3)_2^{2+}$ at 25.0 °C and $I = 0.102$ mol kg^{-1}. The anion is $CF_3SO_3^-$. Triangles: $[H^+] = 0.051$ mol kg^{-1} (two independent series). Open circles: $[H^+] = 0.101$ mol kg^{-1}.

Table 3. Volumes of Activation and Zero-Pressure Rate Constants for Reduction of $Fe(H_2O)_6^{3+}$

reductant	anion	I/mol kg^{-1}	k_{12}/kg mol^{-1} s^{-1}	$\Delta V_{12}^{\ddagger}$/cm^3 mol^{-1}
$Co([9]aneS_3)_2^{2+}$ [a]	$CF_3SO_3^-$	0.102	4.43×10^3	−15.9 ± 0.3
		0.051	2.82×10^3	−15.0 ± 0.3
		0.021	1.49×10^3	−17.1 ± 0.7
	ClO_4^-	0.102	6.89×10^3	−13.7 ± 0.4
		0.021	1.98×10^3	−12.8 ± 0.4
$Co(sep)^{2+}$ [b]	$CF_3SO_3^-$	0.27	6.5×10^4	−5.0 ± 0.5

[a] 25.0 °C. [b] 1.8 °C.

Kinetics of Reduction of $Fe(H_2O)_6^{3+}$ by $Co(sep)^{2+}$. Under the conditions of our experiments, ligand loss from $Co(sep)^{2+}$ (half-period >15 h,[19] corresponding to losses of about 5% over a series of stopped-flow measurements) was negligible when $[Fe^{III}]_0 \approx 10[Co^{II}]_0$ but limited the reliability of rate constants obtained with $[Fe^{III}]_0 \approx 3[Co^{II}]_0$ to ±10%. From 5 to 10 values of the observed pseudo-first-order rate constant k_{obsd} were obtained for each set of conditions, with standard deviations smaller than ±5%,

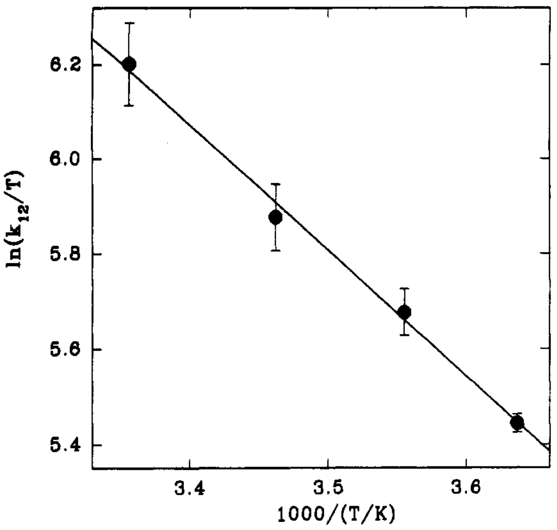

Figure 3. Temperature dependence of the reduction of $Fe(H_2O)_6^{3+}$ by $Co(sep)^{2+}$ at 0.1 MPa, $I = 0.27$ mol kg^{-1}, and $[H^+] = 0.258$ mol kg^{-1}.

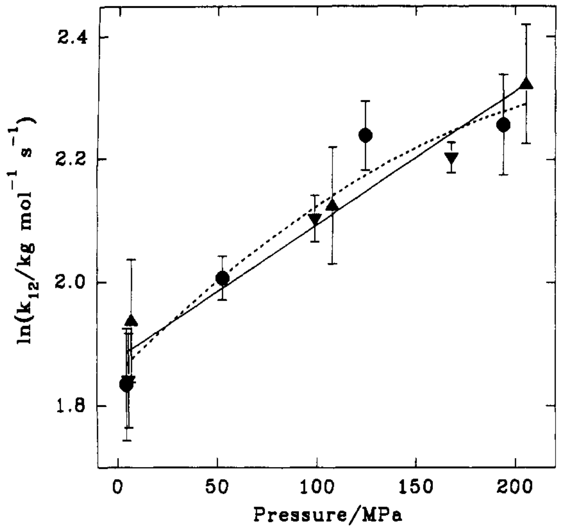

Figure 4. Pressure dependence of the reduction of $Fe(H_2O)_6^{3+}$ by $Co(sep)^{2+}$ at 1.8 °C, $I = 0.27$ mol kg^{-1}, and $[H^+] = 0.258$ mol kg^{-1}. The symbols designate independent experiments.

and were corrected for the very small (<1%) amount hydrolysis of the iron(III) ($pK_a = 3.5$ at 2 °C and 2.9 at 20 °C).

$$k_{12} = [k_{obsd}/([Fe^{III}]_0 - [Co^{II}]_0)](1 + K_a/[H^+]) \quad (15)$$

Values of k_{12} were constant to better than ±10% and were in satisfactory agreement with those of Rudgewick-Brown and Cannon,[15] particularly at the higher temperatures. The temperature and pressure dependences of k_{12} are summarized in Figures 3 and 4, in which the straight regression lines correspond to $\Delta H^* = 22.0 \pm 1.1$ kJ mol^{-1}, $\Delta S^* = -72.4 \pm 3.8$ J K^{-1} mol^{-1}, and $\Delta V^* = -5.0 \pm 0.5$ cm^3 mol^{-1}. The broken curve in Figure 4 represents a quadratic least-squares regression,[26] giving $\Delta V^* = -7.5 \pm 1.6$ cm^3 mol^{-1} with compressibility coefficient of activation $\Delta\beta^* = -(2.5 \pm 1.6) \times 10^{-2}$ cm^3 mol^{-1} MPa^{-1}; however, the large error bars for ln k_{12} and the uncertainty in $\Delta\beta^*$ suggest that the linear fit is more appropriate.

Electrochemical Measurements. For redox of $[Co([9]aneS_3)_2](CF_3SO_3)_2$ in 0.26 mol kg^{-1} KCl relative to the Ag/AgCl(saturated KCl) electrode, there was excellent consistency in E values at a given pressure between the upward and subsequent downward legs of a pressure cycle, and E was found to be a linear function of pressure P (i.e., the volume of reaction ΔV was independent of P) within the experimental uncertainty (Figure S8, supplementary material). Measurements in 0.26 mol kg^{-1} CF_3SO_3K (the medium most relevant to the kinetic measurements) or 1.1 mol kg^{-1} KCl tended toward slightly less positive potentials on the latter part of the downward leg because of some concomitant precipitation of a Co complex, and these aberrant data were rejected in preparing Figure 5 and Table 4. Combination of these data with those for the $Fe(H_2O)_6^{3+/2+}$ and $Co(sep)^{3+/2+}$ couples vs Ag/AgCl(saturated KCl)[16] gave ΔE = 0.278 and 1.03 V, with $\Delta V_{12}^0 = -17.1 \pm 0.4$ and -8.9 ± 0.6 cm^3 mol^{-1}, for reactions 12 and 13, respectively, at $I \approx 0.26$ mol kg^{-1}. Voltammetry at lower I (i.e., at lower supporting electrolyte concentrations) was insufficiently precisely reproducible.

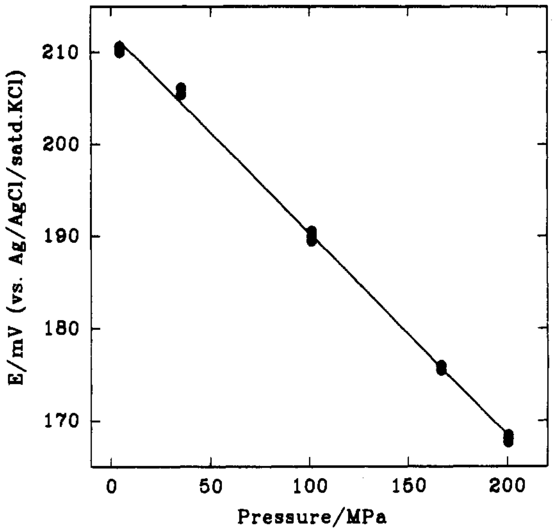

Figure 5. Pressure dependence of the potential of the $Co([9]aneS_3)_2^{3+/2+}$ couple vs Ag/AgCl(saturated KCl) in aqueous CF_3SO_3K (0.26 mol kg^{-1}) at 25.0 °C.

Table 4. Pressure Dependence of the Electrode Potential of the $Co([9]aneS_3)_2^{3+/2+}$ Couple Relative to Ag/AgCl/Saturated KCl at 25 °C

medium	I/mol kg^{-1}	E(0.1 MPa)/mV	ΔV/cm^3 mol^{-1}
CF_3SO_3K	0.26	212.2 ± 0.3	21.1 ± 0.3
KCl	0.26	216.1 ± 0.3	20.6 ± 0.2
KCl	1.1	193.3 ± 0.3	22.3 ± 0.2
		187.6 ± 0.2	21.3 ± 0.2

Discussion

Kinetic Ionic Strength Effects. The treatment of medium effects on electron-transfer kinetics is a perennial problem,[27-31] but for aqueous solutions of moderate I at least, our experience[4,8] has been that the Brønsted–Bjerrum–Christiansen expression (eq 14) provides a good empirical fit of the data if the anion–cation contact distance factor å is regarded as an adjustable parameter. This is confirmed by the present studies, which covered a wider range of I than usual (cf. Figure 1). The derived values of å for the iron(III) oxidation of $Co([9]aneS_3)_2^{2+}$ (Table 2) are physically reasonable, and there is no need to invoke ion pair formation or, in particular, distinct counterion-dependent and -independent pathways (such as occur in the $Fe(CN)_6^{3-/4-}$ [10] and $MnO_4^{-/2-}$ [11]

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Table 5. Comparison of Measured and Calculated Rate Constants and Volumes of Activation for Reduction of $Fe(H_2O)_6^{3+}$ ^{a}

		reductant	
P/MPa	param	$Co([9]aneS_3)_2^{2+}$	$Co(sep)^{2+}$
0.1	T/°C	25.0	1.8
	I/mol kg^{-1}	0.10	0.28
	k_{11}/kg mol^{-1} s^{-1} ^{b}	9.5×10^4	5.0
	k_{22}/kg mol^{-1} s^{-1} ^{c}	1.12^{d,e}	0.34^{d,e}
	w_{11}/kJ mol^{-1} ^{f}	10.6	11.4
	w_{22}/kJ mol^{-1} ^{f}	15.6	14.1
	ΔE/V	0.278^{g}	1.03^{h}
	k_{12}(calcd)/kg mol^{-1} s^{-1}	4.4×10^4	8.4×10^6
	k_{12}(meas)/kg mol^{-1}	4.5×10^3 ^{g}	6.4×10^4 ^{g}
	f	0.36	5.5×10^{-6}
100	ΔV_{11}^{*}/cm^3 mol^{-1} ^{b}	−4.8	−6.4
	ΔV_{22}^{*}/cm^3 mol^{-1} ^{c,d,i}	−11.1	−11.1
	w_{11}/kJ mol^{-1} ^{f}	10.2	10.9
	w_{22}/kJ mol^{-1} ^{f}	15.0	13.5
	k_{11}/kg mol^{-1} s^{-1} ^{b}	11.5×10^4	6.6
	k_{22}/kg mol^{-1} s^{-1} ^{c,d,e,i}	1.75	0.55
	ΔV_{11}^{w}/cm^3 mol^{-1} ^{f}	−2.8	−2.5
	ΔV_{22}^{w}/cm^3 mol^{-1} ^{f}	−4.2	−3.7
	ΔV_{12}^{0}/cm^3 mol^{-1}	−17.1^{g}	−8.9^{h}
	ΔV_{12}^{*}(calc)/cm^3 mol^{-1}	−14.7^{j}	−9.5^{j}
	ΔV_{12}^{*}(meas)/cm^3 mol^{-1}	−15.9^{g} −13.7^{d,g}	−5.0^{g}
	C/cm^3 mol^{-1}	1.8	3.7

^{a} Triflate media, except as indicated. Data relevant to the high-pressure measurements are presented for $P = 100$ MPa, as this was the midpoint of the experimental pressure range. ^{b} Reductant couple; ref 4. ^{c} $Fe(H_2O)_6^{3+/2+}$. ^{d} Perchlorate medium. ^{e} Calculated from data of ref 32 for the stated I and T. ^{f} Calculated as in ref 5. ^{g} This work. ^{h} Reference 16. ^{i} Reference 6; $I = 0.5$ mol kg^{-1}. ^{j} From eqs 8–10.

self-exchange reactions) to explain the anion effect. The apparent linearity of the dependence of k_{12} on the counterion concentration (here, in effect, I) at relatively high I values, such as is often found for redox reactions, is fortuitous and must not be interpreted as evidence for a two-path mechanism unless I is held constant while the counterion concentration is varied (cf. Spiccia and Swaddle[11]). The infinite-dilution values k_{12}^{0} of the rate constant are subject to substantial errors because of the steepness of the extrapolation (Figure 1) and do not warrant detailed interpretation; nevertheless, the data of Table 2 give infinite-dilution values of ΔV_{12}^{*} of $-15._6$ and $-14._6$ cm^3 mol^{-1} for the triflate and perchlorate experiments, respectively, indicating that ΔV_{12}^{*} is not strongly dependent on I (cf. Table 5).

Cross Relations for the Reduction of $Fe(H_2O)_6^{3+}$ by $Co([9]aneS_3)_2^{2+}$. Table 5 shows that the full Marcus cross relation (eqs 4–6) predicts a value of k_{12} for reaction 12 that is too large by a factor of 10. This might be regarded as close enough, in view of the compounding of uncertainties in the calculation, but in fact the direction and magnitude of the discrepancy are typical of many cross reactions of moderate to high ΔE and of reactions involving the $Fe(H_2O)_6^{3+/2+}$ couple in particular.[13e,33–39] The calculated ΔV_{12}^{*}, however, comes satisfyingly close to the measured values and is in fact bracketed by the data for triflate and perchlorate media (the calculation uses, of necessity, ΔV_{11}^{*} for a triflate medium for the Co^{II} complex and ΔV_{22}^{*} for a perchlorate solution of rather higher I for the Fe^{III}). Indeed, the factor C (which, like the Marcus f from which it is derived, becomes important only at higher ΔE) could be neglected in this case; i.e., the simple volume cross relation of eq 11 is adequate for reaction 12. In principle, ΔV_{ii}^{*} and ΔE, and hence also ΔV_{12}^{*}, should be somewhat pressure dependent (more so in nonaqueous solvents than in water),[5] but the experimental uncertainties in k_{12} usually obscure this and, besides, the problem is avoided if eqs 8–11 are applied at the midpoint of the experimental pressure range (here, 100 MPa—cf. Table 5).

It appears, then, that our adaptation of the Marcus cross relation to volumes of activation for adiabatic outer-sphere aqueous redox processes proceeding with net chemical change can give ΔV_{12}^{*} values that are accurate to within 1–2 cm^3 mol^{-1}. Furthermore, since ΔV_{ii}^{*} for the two constituent self-exchange reactions can themselves be calculated with similar accuracy from basic physical data,[4–6] we can predict ΔV_{12}^{*} from those same data if K_{12} and ΔV_{12}^{0} are known (if ΔE is small, eq 11 is applicable and only ΔV_{12}^{0} is needed). At present, there is no reliable general theory for these latter parameters, but they can be obtained relatively easily with good precision from electrochemical measurements.[16] In the same way, measurements of ΔV_{12}^{*} in conjunction with ΔE, ΔV_{12}^{0}, and ΔV_{11}^{*} can lead to estimates of ΔV_{22}^{*} for experimentally inaccessible self-exchange reactions.

Conversely, the success of eqs 8–11 confirms that reaction 12 proceeds by a normal, adiabatic, outer-sphere electron-transfer mechanism. We may conclude that ΔV_{12}^{*} is a useful criterion for such a mechanism but with the caveat that ΔE should not be large. We see below that, for the analogous $Fe(H_2O)_6^{3+}$/high-spin-Co^{II} reaction 13, which has a high "driving force" (ΔE = 1.03 V), predicted values of k_{12} are decidedly too high and ΔV_{12}^{*} too negative.

Cross Relations for the Reduction of $Fe(H_2O)_6^{3+}$ by $Co(sep)^{2+}$. As noted by Rudgewick-Brown and Cannon,[15] the cross relation predicts a rate constant for reaction 13 that is clearly too high—by a factor of 130, according to Table 5—with a very small value of the Marcus f factor. Furthermore, the measured ΔV_{12}^{*} of −5.0 cm^3 mol^{-1} is some 4–5 cm^3 more positive than predicted by eqs 8–10. If ΔV_{12}^{*} is taken to be pressure dependent, its zero-pressure value is 2.5 cm^3 mol^{-1} closer to that predicted, but the comparison must be made at the midrange pressure of 100 MPa, where ΔV_{12}^{*} is again −5.0 cm^3 mol^{-1}. In any event, because the driving force is large, i.e., $f \ll 1.0$, the C factor cannot be ignored, so that eq 11 is inadequate.

Prominent among the several explanations that have been advanced to explain the apparent slowness of many Fe(aq)$^{3+/2+}$ cross reactions in terms of eqs 4–7[33–39] has been the suggestion that these reactions may be nonadiabatic while the Fe$^{III/II}$ self-exchange itself is adiabatic. If that were the case, however, we would expect the observed ΔV_{12}^{*} to be more *negative* than predicted—in principle, by an amount $\Delta V_{NA} \approx -2RT\alpha\beta\sigma/3$, where α is the nonadiabatic distance scaling factor, β is the isothermal compressibility of the solvent, and σ is the mean Fe–Co separation at the instant of electron transfer (taken here to be the sum of the effective radii of the reactant ions, ≈800 pm).[5] For reaction 13, a reasonable choice of α (10 nm^{-1})[5,13d] gives $\Delta V_{NA} \approx -6$ cm^3 mol^{-1}. In fact, the observed ΔV_{12}^{*} is too *positive*. Thus, although the data of Figure 4 may not be as good as one would wish to provide a convincing test case, the point is made that ΔV_{12}^{*} measurements can provide evidence for or against suspected nonadiabaticity[5,8,9] and, in the case of redox involving $Fe(H_2O)_6^{3+/2+}$, that evidence is against it.

It might be thought that the use of the classical Marcus pre-exponential factor Z and the assumption that it is independent of pressure could invalidate eqs 8–10, particularly when $f \ll 1$, and so account for the aberrant ΔV_{12}^{*} value of reaction 13. If, however, we replace Z with the currently preferred factor $4000\pi N\nu_n\kappa_{el}\sigma^2\delta\sigma$ (SI units),[5,13d] in which ν_n is the nuclear frequency, κ_{el} is the electronic transmission coefficient (=1, for an adiabatic reaction), and $\delta\sigma$ is the range in σ over which the probability of electron transfer is significant (which may be taken

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to be proportional to σ), the additional contributions to $\Delta V_{12}^{\ddagger}$ for reactions 12 and 13 arising from the pressure dependence of σ are less than +0.03 and +0.3 cm^3 mol^{-1}, respectively, and these are smaller than the corresponding experimental uncertainties.

The most probable explanation for the faster rates of cross reactions predicted by eqs 4–6 is that some of the other implicit assumptions of Marcus theory noted in the Introduction fail at high driving forces. The progressive worsening of agreement between theory and experiment as ΔE increases was noted by Sutin and co-workers[33,34] and is not restricted to $Fe(aq)^{3+/2+}$ systems—the latter may appear to be prominent deviants simply by virtue of the abundance of data for them in the appropriate range of ΔE. The exact cause(s) of the discrepancies, and more particularly the implications for $\Delta V_{12}^{\ddagger}$, are not clear at this time.

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Supplementary Material Available: Figures showing graphical presentations of the pressure and ionic strength dependences of rate constants for reaction 12 and the pressure dependence of the potential of the $Co([9]aneS_3)_2^{3+/2+}//Ag/AgCl$ cell in aqueous KCl (8 pages). Ordering information is given on any current masthead page.