Recrystallization of this mixture from an equal volume of *n*-hexane at −20 °C produced colorless crystals of $[((Me_3Si)_2CH)_2P]_2$ (**2′**), the dimer of the phosphinyl radical **2**. The effective yield of **2** was 41% based on obtaining 2.49 g (3.56 mmol) of **2′**. Upon warming to room temperature, the crystals of **2′** retained their morphology although a definite orange color became perceptible. Gentle warming caused melting and the production of bright red liquid phosphinyl radical **2**. Some NMR data for **2′** are presented in Table I. Compounds **2** and **2′** have been characterized by electron diffraction and low-temperature X-ray crystallography, respectively.[12]

Preparation of $[(Me_3Si)_2CH]_2PH$ (1) from the Phosphinyl Radical $[((Me_3Si)_2CH)_2P]\cdot$ (2). Thiophenol (0.35 g, 3.18 mmol) in 5 mL of *n*-hexane was added dropwise to a stirred solution of $[((Me_3Si)_2CH)_2P]\cdot$ (**2**) (1.11 g, 3.18 mmol) in 10 mL of *n*-hexane. The red color of the phosphinyl radical was completely discharged at the end of the addition. The yield of $[(Me_3Si)_2CH]_2PH$ (**1**) was virtually quantitative. Samples prepared by this method and the $LiAlH_4$ route were identical spectroscopically.

Preparation of $[(Me_3Si)_2N]_2PH$ (3). Freshly recrystallized[24] $[(Me_3Si)_2N]_2PCl$ (9.08 g, 23.5 mmol) in 20 mL of Et_2O was added slowly to a stirred slurry of $LiAlH_4$ (0.662 g, 17.4 mmol) in 50 mL of Et_2O at 0 °C by means of a double-tipped needle. The slurry was stirred at room temperature for 1 h and then quenched with 10 mL of neutral water *very slowly*. Filtration, followed by removal of the aqueous layer and drying of the organic layer, afforded a pale yellow solution. Removal of the solvent followed by distillation under reduced pressure yielded $[(Me_3Si)_2N]_2PH$ (**3**) (6.45 g, 18.3 mmol), bp 60–72 °C (0.02 torr), as a colorless liquid, which solidified upon standing. Yields ranged from 75 to 80%. Some NMR and IR data for **3** are listed in Table I. HRMS: calcd 352.1771; found 352.1781.

Preparation of $(Me_3Si)_2NP(H)N(H)(SiMe_3)$ (5). The aminoiminophosphine $(Me_3Si)_2NP{=}N(SiMe_3)$ (**4**) (12.85 g, 46.2 mmol) in 15 mL of Et_2O was added dropwise at 0 °C to a stirred slurry of $LiAlH_4$ (1.70 g, 44.8 mmol) in 50 mL of Et_2O. The solution was allowed to warm to room temperature for 30 min prior to *slow* quenching of the reaction mixture with neutral, degassed H_2O. The Li and Al salts were filtered off, and the aqueous layer was removed from the organic filtrate by means of a syringe. The organic layer was concentrated under vacuum and the resulting yellow liquid was distilled to give $(Me_3Si)_2NP(H)N(H)(SiMe_3)$ (**5**), bp 55–60 °C (0.03 torr), in 41% yield (5.30 g, 18.9 mmol). The compound is identical with that reported by Niecke and Ringel.[11] Some NMR and IR data for **5** are presented in Table I.

Preparation of $(Me_3Si)_2NP(D)N(H)(SiMe_3)$ (9a) and $(Me_3Si)_2NP(H)N(D)(SiMe_3)$ (9b). These compounds were prepared in a manner identical with that for the perprotio compound **5**. One experiment employed $LiAlH_4$ reduction followed by D_2O quenching of the reaction mixture; the other utilized $LiAlD_4$ reduction and H_2O quenching of the reaction mixture. Both experiments resulted in a 50/50 mixture of **9a** and **9b** on the basis of ^{31}P NMR and IR spectroscopy (Table I).

Attempts To Deprotonate $[(Me_3Si)_2CH]_2PH$ (1) and $[(Me_3Si)_2N]_2PH$ (3) with *n*-BuLi, MeLi, and KH. Compounds **1** and **3** failed to react with *n*-BuLi, *n*-BuLi/TMEDA, MeLi, or KH. The systems were monitored by ^{31}P NMR spectroscopy.

Deprotonation of $(Me_3Si)_2NP(H)N(H)(SiMe_3)$ (5). Compound **5** (0.56 g, 2.0 mmol) in 5 mL of *n*-hexane was treated with *n*-BuLi (1.25 mL of a 1.6 M solution in *n*-hexane). After the reaction mixture was stirred at −78 °C for 30 min, it was quenched with D_2O and allowed to warm slowly to room temperature. Measurement of the ^{31}P NMR spectrum of the solution indicated that an equimolar mixture of **9a** and **9b** had been formed.

Preparation of $[((Me_3Si)_2CH)_2P(Me)H]^+I^-$ (10). Methyl iodide (0.91 g, 6.4 mmol) was added by means of a syringe to a stirred solution of $[(Me_3Si)_2CH]_2PH$ (**1**) (1.12 g, 3.2 mmol) in 5 mL of Et_2O. A white precipitate formed slowly. After 6 h the Et_2O was removed by evacuation and the residual white solid was recrystallized from a CH_2Cl_2/Et_2O mixture at −10 °C. Filtration followed by drying in vacuo afforded 1.12 g (2.27 mmol) of white crystalline $[((Me_3Si)_2CH)_2P(Me)H]^+I^-$ (**10**) in 71% yield. Anal. Calcd for $C_{15}H_{42}IPSi_4$: C, 36.6; H, 8.6. Found: C, 36.3; H, 8.7. Some NMR data for **10** are presented in Table I.

Preparation of $[(Me_3Si)_2CH]_2PHFe(CO)_4$ (11). A mixture of $[(Me_3Si)_2CH]_2PH$ (**1**) (0.397 g, 1.1 mmol) and $Fe_2(CO)_9$ (0.449 g, 1.23 mmol) in 10 mL of *n*-hexane was stirred at room temperature for 24 h. Filtration of the reaction mixture through a medium-porosity frit followed by prolonged pumping to remove all volatiles afforded 0.456 g (0.88 mmol) of pure dark brown liquid $[(Me_3Si)_2CH]_2PHFe(CO)_4$ (**11**) in 80% yield. Anal. Calcd for $C_{18}H_{39}FeO_4PSi$: C, 41.7; H, 7.6. Found: C, 41.7; H, 8.2. Some NMR and IR data for **11** are presented in Table I.

Preparation of $[(Me_3Si)_2CH]_2PHCo_2(CO)_7$ (12). The phosphine $[(Me_3Si)_2CH]_2PH$ (**1**) (0.446 g, 1.28 mmol) was syringed into a stirred solution of $Co_2(CO)_8$ (0.438 g, 1.28 mmol) in 5 mL of *n*-hexane at room temperature. The product, $[(Me_3Si)_2CH]_2PHCo_2(CO)_7$ (**12**), undergoes decomposition upon heating or standing overnight; hence it was possible to characterize this compound only by the NMR and IR spectroscopic data presented in Table I.

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Note Added in Proof. The reaction of $[(Me_3Si)_2CH]_2PCl$ with Na in hydrocarbon solvents has also been studied by: Power, P. P. D.Phil. Thesis, University of Sussex, 1977. We thank Professor Power for bringing this earlier work to our attention.

Registry No. **1**, 83436-92-4; **2**, 63429-86-7; **2′**, 83436-91-3; **3**, 81072-86-8; **4**, 50732-21-3; **5**, 63104-54-1; **9a**, 83928-53-4; **9b**, 83928-54-5; **10**, 83928-55-6; **11**, 83928-52-3; **12**, 83947-19-7; C_6H_5SH, 108-98-5; $[(Me_3Si)_2CH]_2PCl$, 63429-87-8; $[(Me_3Si)_2N]_2PCl$, 53327-45-0; $Fe_2(CO)_9$, 15321-51-4; $Co_2(CO)_8$, 10210-68-1; Co, 7440-48-4.

Contribution from the Department of Chemistry,
San Diego State University, San Diego, California 92182

Kinetics of the Hexaammineruthenium(II)-(Ethylenediaminetetraacetato)iron(III) Reaction. A Relative Marcus Theory Evaluation

F. MOATTAR, JOHN R. WALTON, and LARRY E. BENNETT*

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Kinetic parameters for the outer-sphere reaction between $Ru(NH_3)_6^{2+}$ and $Fe(EDTA)^-$ have been determined at $I = 1.00$ M: $k = (2.2 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$ (25 °C), $\Delta H^* = 3.6 \pm 0.3$ kcal mol^{-1}, and $\Delta S^* = -17 \pm 1$ eu. With the reported variation of k with I, these results provide the basis for a detailed evaluation of the Marcus cross-reaction relationships for ΔG^*, ΔH^*, and ΔS^*. At $I = 0.00$ M the agreement with extrapolated experimental results is excellent when the work terms are taken properly into account. Major components of the substantial corrections they provide to ΔG_0^*, ΔH_0^*, and S_0^* are attributable to differences in solvation shell polarization relative to the respective self-exchanges. At $I = 0.10$ M, ΔH^* and ΔS^* are less well accounted for than is ΔG^*, with the deviations suggesting an exaggerated shielding of charge by the supporting electrolyte within the Debye–Hückel model for ΔH^w and ΔS^w.

Outer-sphere electron transfer processes have been modeled by Marcus and others[1-4] in terms[5-8] of (a) the kinetic barriers attending a self-exchange and (b) the relationship between the kinetic parameters of a cross reaction and the corresponding self-exchanges, e.g. as expressed in one familiar form

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

Both $Ru(NH_3)_6^{2+}$ and $Fe(EDTA)^{2-}$ have been used as probes of metalloprotein reactivity within this context.[7-11] Another direction has been toward a theoretical evaluation of the enthalpic and entropic barriers for self-exchange and cross reactions.[2,8,11-16] Recent work has focused attention on the failure of the Marcus work terms to cancel completely for cross reactants of like charge at high driving force.[16]

The $Ru(NH_3)_6^{2+}$–$Fe(EDTA)^-$ reaction engages ions of opposite charge whereas the corresponding self-exchanges engage ions of like charge. As a result, even though the driving force is low, the work terms involved do not cancel to yield the relative Marcus expression (1), as they frequently are assumed to do for cross reactants of like charge. The results reported here present the opportunity to test these features of the Marcus theory as they affect ΔH^* and ΔS^* as well as ΔG^*. Thus, the factors determining reactivity for this prototypical system are susceptible to a more comprehensive evaluation than has been done with other reactions of this type.[18-23]

Experimental Section

Materials. Deionized water was redistilled from alkaline permanganate, and all oxygen-sensitive operations were carried out under Cr^{2+}-scrubbed argon with use of syringes. Solutions of $Ru(NH_3)_6^{2+}$ were freshly prepared by amalgamated zinc reduction of spectrally pure, recrystallized[24] $Ru(NH_3)_6Cl_3$ from Matthey Bishop. Aliquots of standardized $Fe^{2+}(aq)$, prepared from either 99.999% iron wire or primary standard ferrous ammonium sulfate, were added under Ar to solutions containing $Na_2(EDTA)$. Air oxidation in the dark yielded $Fe(EDTA)^-$ as did direct preparation from standardized, nonyellow ferric perchlorate solution. Concentrations were confirmed spectrophotometrically.[25]

Table I. Kinetic Results for the $Ru(NH_3)_6^{2+}$–$Fe(EDTA)^-$ Reaction

I = 1.00 M		T = 25.0 °C	
T, °C	$10^{-6}k$, M^{-1} s^{-1}	I, M	$10^{-6}k$, M^{-1} s^{-1}
5.0	1.3	0.050	4.3
15.0	1.8	0.10	3.9
25.0	2.2	0.50	2.8
35.0	2.7	1.00	2.2
$\Delta H^\ddagger = 3.6 \pm 0.3$ kcal mol^{-1}		0.00	6^a
$\Delta S^\ddagger = -17 \pm 1$ eu			

[a] Estimated by extrapolation of log k vs. $I^{1/2}/(1 + I^{1/2})$ plot.

Kinetic Measurements. The disappearance of absorbance at 258 nm, the maximum for $Fe(EDTA)^-$, was measured in a Durrum-Gibson stopped-flow spectrophotometer with a pseudo-first-order excess of $Ru(NH_3)_6^{2+}$ such that plots of ln $(A_t - A_\infty)$ vs. t linear through 3–4 half-lives. The majority of runs were at I = 1.00 M to decrease the rapid rate. The $\sim 10^{-5}$ M $Fe(EDTA)^-$ solutions contained 1.5×10^{-5} M EDTA, 0.10 M $TrisH^+$, and 0.90 M $NaClO_4$ (or $LiClO_4$) adjusted to the indicated pH with $HClO_4$. The $Ru(NH_3)_6^{2+}$ solutions contained 0.10 M $TrisH^+$ and 0.90 M NaCl adjusted with HCl. Runs without $TrisH^+$ gave indistinguishable results. The activation parameters quoted are the result of least-squares analysis over four temperatures. The rate constant at I = 0.00 M was extrapolated from a plot of log k vs. $I^{1/2}/(1 + I^{1/2})$.

Equilibrium Measurements. The equilibrium constant for the reaction

$$Fe(EDTA)^- + Ru(NH_3)_6^{2+} = Fe(EDTA)^{2-} + Ru(NH_3)_6^{3+}$$

proved somewhat elusive to the techniques at our disposal. The standard spectrophotometric method,[22,23] employed at 275 nm, was extremely sensitive to small changes in absorbance when equilibrium was approached from the product side. When the electrochemical results for $\Delta S_{rc}°$ for the two couples became available[17,26] for comparison, it seemd clear that they provided more reliable values of $\Delta H°$ and $\Delta S°$.

Results and Discussion

Kinetic determinations over the ranges 4.5 < pH < 6.5 and 0.6×10^{-4} M < $[Ru(NH_3)_6^{2+}]$ < 2.0×10^{-4} M with $[Fe(EDTA)^-]_0 = (0.8–1.0) \times 10^{-5}$ M conformed to the rate law

$$-d[Fe(EDTA)^-]/dt = k[Fe(EDTA)^-][Ru(NH_3)_6^{2+}]$$

with $k = (2.2 \pm 0.2) \times 10^6$ M^{-1} s^{-1} at 25 °C and I = 1.00 M. No evidence for rate saturation was detected under the conditions employed. Table I presents results at other ionic strengths and temperatures, the latter yielding $\Delta H^* = 3.6 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = -17 \pm 1$ eu at I = 1.00 M.

An initial approach to understanding these reactivity characteristics can be made by using the relative Marcus theory.[2,16] For the present case of low $\Delta G_{12}°$, the correction term, α, is negligible, so the relative Marcus relationships are best expressed in the forms[2] (2a)–(2c). The relationships

$$\Delta G_{12}^* = 0.5[\Delta G_{11}^* + \Delta G_{22}^* + \Delta G_{12}°] + 0.5[\Delta G_{12}^w + \Delta G_{21}^w - \Delta G_{11}^w - \Delta G_{22}^w] \qquad (2a)$$

$$\Delta H_{12}^* = 0.5[\Delta H_{11}^* + \Delta H_{22}^* + \Delta H_{12}°] + 0.5[\Delta H_{12}^w + \Delta H_{21}^w - \Delta H_{11}^w - \Delta H_{22}^w] \qquad (2b)$$

$$\Delta S_{12}^* = 0.5[\Delta S_{11}^* + \Delta S_{22}^* + \Delta S_{12}°] + 0.5[\Delta S_{12}^w + \Delta S_{21}^w - \Delta S_{11}^w - \Delta S_{22}^w] \qquad (2c)$$

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$$\Delta G^{\ddagger} = \Delta G^{*} - RT \ln (hZ/kT) \qquad (3)$$

$$\Delta S^{\ddagger} = \Delta S^{*} + R \ln (hZ/kT) - R/2 \qquad (4)$$

$$\Delta H^{\ddagger} = \Delta H^{*} - RT/2 \qquad (5)$$

(3)–(5) (with $Z = 10^{11}$ M^{-1} s^{-1}) reflect the theoretical contributions to $\Delta G^{\ddagger}$ (2.45 kcal mol^{-1}), $\Delta S^{\ddagger}$ (−9.2 eu), and $\Delta H^{\ddagger}$ (−0.3 kcal mol^{-1}) from the formation of a hypothetically uncharged collision complex. The ΔG^{w}, ΔS^{w}, and ΔH^{w} terms arise from the work involved in developing appropriate charge within the collision complexes, for reactant, product, and self-exchange combinations, respectively. These terms, which cannot be expected to cancel in eq 2 for reactants of opposite charge, are usually calculated as the electrostatic work within a dielectric continuum from a Debye–Hückel model,[4] eq 6–8, where a is the metal–metal distance in angstroms.

$$(\Delta G^{w})_{DH} = 4.23\frac{z_1 z_2}{a} \exp(-0.329 a I^{1/2}) \qquad (6)$$

$$(\Delta S^{w})_{DH} = [z_1 z_2 \exp(-0.329 a I^{1/2})]\left(0.868 I^{1/2} + \frac{19.5}{a}\right) \qquad (7)$$

$$(\Delta H^{w})_{DH} = (\Delta G^{w})_{DH} + T(\Delta S^{w})_{DH} \qquad (8)$$

Since all necessary parameters are available independently, a test of the relative theory, insofar as its inclusion of the work terms is appropriate, can be made by comparing calculated values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ with those observed. For use in eq 2, we have calculated $\Delta G_{12}^{\circ} = -1.24$ kcal mol^{-1}, $\Delta S_{12}^{\circ} = -22.1$ eu, and $\Delta H_{12}^{\circ} = -7.83$ kcal mol^{-1} using absolute entropy differences, ΔS_{rc}°, of 18.5 and −3.6 eu[17,26] and $E_{1/2}^{\circ}$ = 66 and 120 mV[17,26,27] for the $Ru(NH_3)_6^{3+/2+}$ and $Fe(EDTA)^{-/2-}$ couples at $I = 0.10$ M. Other contributing parameters and the results necessary for the comparison are listed in Table II at two ionic strengths. The numbers without parentheses are for the ionic strength at which the experimental data are available (at or near $I = 0.10$ M) where, however, the Debye–Hückel model from which the work terms are calculated is less than rigorous. This model is expected to offer the greatest accuracy at $I = 0.00$ M, but experimental results are not directly available there.

Recent studies, however, provide an experimental basis for the present comparison to be made at $I = 0.00$ M with reasonable confidence. For three reactions involving cations, little variation in $\Delta S^{\ddagger}$ with ionic strength was found over the ranges studied.[15,29] (In the case of $Ru(NH_3)_4bpy^{3+/2+}$, seven determinations were reported between $I = 0.10$ and 0.002 M[15].) Also, the extrapolated value[24] of $\Delta G^{\ddagger} = 14.0$ kcal mol^{-1} at I = 0.0 M for $Ru(NH_3)_6^{3+/2+}$ is in good agreement with that predicted from the ionic strength variation[15] of $Ru(NH_3)_4bpy^{3+/2+}$. On these grounds we have tentatively assigned the variation in $\Delta G^{\ddagger}$ entirely to $\Delta H^{\ddagger}$ for the $Ru(NH_3)_6^{3+/2+}$ couple. (Even should its $\Delta S^{\ddagger}$ prove to be as much as 5 eu more negative at $I = 0.00$ M than at $I = 0.10$ M, the conclusions reached below would not be vitiated.)

A similar extrapolation to $I = 0.00$ M for the $Fe(EDTA)^{-/2-}$ self-exchange does not rest upon comparable experimental precedent for anionic reactants.[30] However, the activation parameters were determined at $I = 0.05$ M[28] and the estimation at $I = 0.0$ M involves only a small change in $\Delta G^{\ddagger}$.

Since one basis for the non-Debye–Hückel dependence of $\Delta S^{\ddagger}$ is likely to be ion association with the higher concentrations of supporting electrolyte, any generalization of the evidence for cationic reactants to oppositely charged reactants must await experimental test. Nevertheless, for the $Ru(NH_3)_6^{2+}$–$Fe(EDTA)^{-}$ reactant pair, the sensitivity of $\Delta G^{\ddagger}$ to variations in I between 0.05 and 1.00 M is so slight (Table I) that it seems unlikely that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at $I = 0.00$ M would differ significantly, for present purposes, from the values obtained by an analogous extrapolation. Thus, with the extrapolation for $Ru(NH_3)_6^{3+/2+}$ having the largest change (in $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$) and the most direct experimental support, we have tabulated numbers in parentheses that appear appropriate for comparison at $I = 0.00$ M.

It can be seen from Table II that the calculated activation parameters are all three in remarkably good agreement with the observed values at zero ionic strength when the work terms are included but are seriously at odds with experiment without the work terms. At $I = 0.10$ M the work term corrections to $\Delta H_{12}^{\ddagger}$(calcd) and $\Delta S_{12}^{\ddagger}$(calcd) represent an improvement, but only for $\Delta G_{12}^{\ddagger}$(calcd) can the agreement with experiment be described as adequate, and that is perhaps somewhat fortuitous, given the constraints of the model. At low ionic strength, then, we find quantitative support for the Debye–Hückel work term model being applicable within the relative theory (as expressed by eq 2).

This conclusion is based on the closure of rather large gaps between calculated and experimental values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, in each case by a combination of four markedly different work terms. To conclude from this that each of these work terms is individually substantiated, however, would be lending more weight to the comparisons than is justified. As eq 2a–2c clearly reveal, it is *differences* in work between the self-exchanges and the cross reaction that are accounted for by the procedure followed. (This is reminiscent of a related aspect of the relative theory; its success in correlating cross reactions with the corresponding self-exchange couples does not substantiate the theoretical evaluation of an individual self-exchange.)

With this reservation in mind, it is of interest to examine the rather large *changes* in individual work terms that accompany a change in charge type (Table II). Encounter complex formation for the self-exchanges has an unfavorable ΔS^{w} but a favorable ΔH^{w}, which can be understood as a result of increased solvent orientation about a collision complex of increased charge. When the ions colliding are of opposite charge, as in the cross reaction, ΔS^{w} is favorable but ΔH^{w} is actually unfavorable as the result of solvent release. According to the Debye–Hückel model, in both instances the enthalpy component associated with solvent polarization slightly outweighs the opposing enthalpy of electrostatic interaction. Thus, the resultant ΔG^{w} is modulated very significantly by this solvation effect and is in the direction expected from a naive consideration of charge alone only because $T\Delta S^{w}$ outweighs ΔH^{w} at 298 K.[31] (Studies of $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$[23] and $Co(NH_3)_6^{3+}$–SO_4^{2-}[32] are consistent with the qualitative predictions of this model, i.e. a positive ΔS with ΔH being near zero.)

When attention is then turned to the net work term corrections to be applied in eq 2, it can first be noted that the extrapolated value of $\Delta H^{\ddagger}$ for the cross reaction at $I = 0.00$ M is actually higher than is calculated without the work terms.

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Table II. Parameters for the $Ru(NH_3)_6^{2+}$–$Fe(EDTA)^-$ Reaction at $I = 0.10$ M and $I = 0.00$ M[a,b]

reactants	$\Delta G^\ddagger$, kcal mol^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	ref	$(\Delta G^w)_{DH}$, kcal mol^{-1}	$(\Delta H^w)_{DH}$, kcal mol^{-1}	$(\Delta S^w)_{DH}$, eu
$Ru(NH_3)_6^{3+/2+}$	12.7 (14.0)	4.5 (5.8)	−27 (−27)	15	1.8 (3.7)	−0.9 (−1.3)	−9.2 (−17)
$Fe(EDTA)^{-/2-}$	11.4 (11.9)	4.0 (4.5)	−25 (−25)	28	0.5 (0.9)	−0.2 (−0.5)	−2.3 (−4.8)
$Ru(NH_3)_6^{3+}$–$Fe(EDTA)^{2-}$					−1.6 (−3.4)	0.8 (1.2)	8.0 (15.7)
$Ru(NH_3)_6^{2+}$–$Fe(EDTA)^-$					−0.5 (−1.1)	0.3 (0.4)	2.7 (5.2)
obsd	8.5 (8.2)	3.3 (3.0)	−17 (−17)	c			
calcd with DH cor	9.2 (7.7)	1.4 (3.0)	−26 (−16)		−2.2 (−4.6)	1.1 (1.8)	11 (21)
calcd without DH cor	11.4 (12.3)	0.35 (1.2)	−37 (−37)				

[a] Values in parenthese refer to $I = 0.0$ M. Numbers derived from experimental results were obtained from the extrapolation of plots of log k vs. $I^{1/2}/(1 + I^{1/2})$ to obtain $\Delta G^\ddagger$ at $I = 0.0$ M (e.g., see footnote 24; the value for $Fe(EDTA)^{-/2-}$ was estimated from the experimental value[28] determined at $I = 0.05$ M). Values of $\Delta H^\ddagger$ at $I = 0.0$ M without Debye–Hückel correction were calculated from $\Delta G^\ddagger$ on the basis of the assumption that $\Delta S^\ddagger$ does not vary significantly with ionic strength; see text. [b] Calculations were made by using eq 3–9, $\Delta G^\circ = -1.24$ kcal mol^{-1}, $\Delta H^\circ = -7.83$ kcal mol^{-1}, $\Delta S^\circ = -22.1$ eu, and values for the radii of $Ru(NH_3)_6^{3+/2+}$ and $Fe(EDTA)^{-/2-}$ of 3.4 and 4.0 Å, respectively. [c] This work.

Thus, the successful correction of the calculated ΔG^* by −4.6 kcal (which is equivalent to a rate enhancement factor of $\sim 2 \times 10^3$) is substantially attributable, within the model, to the calculated ΔS^* being 20 eu lower when the work terms are included. These observations are intimately linked to the conclusion that release of solvation is an integral and exceedingly important aspect of reaction between oppositely charged ions, especially in comparison to the increased solvent polarization that is integral to reaction between similarly charged ions in the respective self-exchanges.

With this recognition of the importance of solvent polarization in the work term contributions, the failure of the model to represent ΔH^* and ΔS^* at $I = 0.10$ M can begin to be addressed. The contrast with the apparent success at $I = 0.00$ M suggests that the model fails to represent adequately the interactions with the more concentrated media. The reported variation of the dielectric constant with ionic strength[33] does not seem sufficient to be responsible. An interesting point is the opposite sense of the deviations from those for reactions between ions of like charge. For example, the observed values of ΔH^* and ΔS^* are *more* positive than calculated for our reaction but *less* positive for the self-exchanges $Ru(NH_3)_6^{3+/2+}$ and $Fe(EDTA)^{-/2-}$.[34] The deviations are comparable for the two categories (~2 kcal mol^{-1} and ~10 eu) and substantially compensatory in the net effects of ΔH and ΔS on ΔG as would be consistent with a solvation effect.[35] Since the same couples (with the same intrinsic barriers) are involved, on the basis of the previous discussion on solvation (see also ref 31a) the view could be taken that there is a greater polarization of the medium on encounter formation between ions of like charge than the Debye–Hückel model predicts whereas ions of opposite charge release more solvent than predicted. Thus, the ions would be acting as if they each had a greater effective charge than the model gives them credit for at appreciable ionic strengths. This could be understood if the ion atmosphere were screening the charges to a lesser extent than is implied by the conventional use of $I^{1/2}$ in eq 6–8 (which corresponds to the Debye–Hückel limiting law for point charges). The "extended" or "finite-ion-size" modification of this model has the effect of modulating this screening by a factor of $1/(1 + BaI^{1/2})$.[36] It would appear that a similar modulation of $I^{1/2}$ in eq 7–9 would be appropriate.

By using such a formulation, we have calculated $\Delta G^* = 8.3$ kcal mol^{-1}, $\Delta H^* = 1.7$ kcal mol^{-1}, and $\Delta S^* = 22$ eu, which are in better agreement with the results at $I = 0.10$ M. Nevertheless, this extension of the model can account for only a part of the deviations noted. That this may prove to be a deficiency of the Debye–Hückel model itself is left open by its failure to describe recent kinetic variations as the ionic strength is increased.[15,29] Until a better model under these conditions becomes available, we shall simply note the qualitative indication that the importance of solvent polarization (among other concomitant aspects of ion–ion interaction) is likely to be underestimated by eq 7 and 8 at appreciable ionic strength.

This suggestion should not be allowed to detract from the principal conclusion that an adequate account of ΔG_{12}^*, ΔH_{12}^*, and ΔS_{12}^* for the $Ru(NH_3)_6^{2+}$–$Fe(EDTA)^-$ reaction at zero ionic strength can be given without invoking aspects beyond (a) the self-exchange characteristics, (b) the ground-state thermodynamic differences, and (c) the work term differences. If fortuitous cancellations are assumed to be absent, this has the effect of establishing our understanding at the same level as for the self-exchanges.

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Registry No. $Ru(NH_3)_6^{2+}$, 19052-44-9; $Fe(EDTA)^-$, 15275-07-7.

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(34) The translational entropy change (−9.2 eu), the solvation shell reorganizational enthalpy, $\Delta H_o^* = \Delta G_o^* = (\Delta z)^2 e/8E_{op}r$ (ref 4, p 128), and the Coulombic terms from Table II provide the basis for a calculation, along the lines of ref 15, of the following self-exchange parameters: $\Delta H^* = 7.5$ kcal mole^{-1}, $\Delta S^* = -18$ eu for $Ru(NH_3)_6^{3+/2+}$; $\Delta H^* = 5.9$ kcal mol^{-1}, $\Delta S^* = -11$ eu for $Fe(EDTA)^{-/2-}$. These can be compared with the experimental values in Table II.

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