at 83–84.5 °C and showed infrared absorptions (pentane solution) at 2018 and 1950 cm^{-1} (C–O stretching) and 1688 cm^{-1} (N–O stretching) (lit.[47] IR (CH_2Cl_2 solution): ν_{CO} = 2020, 1937; ν_{NO} = 1663).

Dicarbonyl(η^5-cyclopentadienyl)nitrosyltungsten, prepared by the method of Crease and Legzdins,[46] melted at 107–108.5 °C and showed infrared absorptions at 2010 and 1938 cm^{-1} (C–O stretching) and 1683 cm^{-1} (N–O stretching) (lit.[47] IR (CH_2Cl_2 solution): ν_{CO} = 2010, 1925 cm^{-1}; ν_{NO} = 1655 cm^{-1}).

Trinitrosyl(trimethylphosphine)manganese was prepared by the reaction of $Mn(NO)_3CO$[49] and trimethylphosphine in xylene solution. After the reaction, the solvent was removed in vacuo. The green residue was sublimed at 50 °C to obtain dark green crystals. The infrared spectrum (pentane solution) showed nitrosyl bands at 1792 and 1680 cm^{-1}.

$W(Cp)(NO)_2H$ was kindly furnished by Prof. Legzdins of the University of British Columbia.

Chloro(η^5-cyclopentadienyl)dinitrosylchromium, prepared by the method of Hoyano et al.,[47] melted and decomposed at 144–145 °C (lit. mp 144 °C).

Dinitrosyliron iodide dimer, prepared by the method of Haymore and Feltham,[50] melted at 95–96 °C and showed infrared absorptions (pentane solution) at 1810 and 1768 cm^{-1} (N–O stretching) (lit.[51] IR (CCl_4 solution): ν_{NO} = 1810, 1769 cm^{-1}).

Dinitrosyliron bromide dimer was prepared by a method analogous to that used for dinitrosyliron iodide. The compound melted at 94–96 °C and showed infrared absorptions (pentane solution) at 1817 and 1767 cm^{-1} (lit.[51] IR (CCl_4 solution): ν_{NO} = 1818.5, 1767 cm^{-1}).

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Registry No. $C_6H_6Cr(CO)_3$, 12082-08-5; $C_7H_7V(CO)_3$, 12083-16-8; $Mo(CO)_5P(NMe_2)_3$, 14971-43-8; $C_5H_5Cr(CO)_2NS$, 66539-91-1; $C_5H_5Mn(CO)_3$, 12079-65-1; $Mo(CO)_5PMe_3$, 16917-96-7; $C_5H_5V(CO)_4$, 12108-04-2; $C_5H_5(Me)Mo(CO)_3$, 12082-25-6; $Me(OMe)CCr(CO)_5$, 20540-69-6; $C_5H_5Cr(CO)_2NO$, 36312-04-6; $C_5H_5Mo(CO)_2NO$, 12128-13-1; $C_5H_5W(CO)_2NO$, 12128-14-2; $C_5H_5Mn(CO)_2CS$, 31741-76-1; $Mo(CO)_5P(OEt)_3$, 15603-75-5; $C_5H_5Co(CO)_2$, 12078-25-0; $Mo(CO)_5P(OMe)_3$, 15631-20-6; $C_7H_8Fe(CO)_3$, 36343-88-1; $W(CO)_5CS$, 50358-92-4; $C_3H_5Fe(CO)_2NO$, 12071-54-4; $C_4H_6Fe(CO)_3$, 12078-32-9; $Mo(CO)_5PCl_3$, 19212-18-1; $Cr(CO)_5CS$, 50358-90-2; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $C(CH_2)_3Fe(CO)_3$, 12078-33-0; $Mo(CO)_6$, 13939-06-5; $HCCo_3(CO)_9$, 15664-75-2; $BrCCo_3(CO)_9$, 19439-14-6; $Mn_2(CO)_{10}$, 10170-69-1; $MeCCo_3(CO)_9$, 13682-04-7; $ClCCo_3(CO)_9$, 13682-02-5; $Mo(CO)_5PF_3$, 15322-05-1; $Cr(CO)_5PF_3$, 18461-42-2; $Co_2(CO)_8$, 10210-68-1; $MeCOMn(CO)_5$, 13963-91-2; $C_3H_5Mn(CO)_5$, 14057-83-1; *cis*-$Mo(CO)_3(PF_3)_3$, 15280-12-3; $Mn(CO)_4NO$, 16104-17-9; $MeRe(CO)_5$, 14524-92-6; $MeMn(CO)_5$, 13601-24-6; $Fe(CO)_5$, 13463-40-6; $Ni(CO)_4$, 13463-39-3; $Fe(CO)_2(NO)_2$, 13682-74-1; $HMn(CO)_5$, 16972-33-1; $Co(CO)_3NO$, 14096-82-3; $HCo(CO)_4$, 16842-03-8; $Mn(NO)_3CO$, 14951-98-5; $IMn(CO)_5$, 14879-42-6; $SiCl_3Mn(CO)_5$, 38194-30-8; $BrMn(CO)_5$, 14516-54-2; $H_2Fe(CO)_4$, 12002-28-7; $ClMn(CO)_5$, 14100-30-2; $CF_3COMn(CO)_5$, 14099-62-8; $CF_3Mn(CO)_5$, 13601-14-4; $SiF_3Mn(CO)_5$, 39945-25-0; $Mn(NO)_3PMe_3$, 73347-69-0; $C_5H_5W(NO)_2H$, 69532-01-0; C_5H_5NiNO, 12071-73-7; $C_5H_5Cr(NO)_2Cl$, 12071-51-1; $Fe_2(NO)_4Br_2$, 15696-30-7; $Cr(NO)_4$, 37355-72-9; $Fe_2(NO)_4I_2$, 15002-08-1.

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Activation Parameters for Homogeneous Outer-Sphere Electron-Transfer Reactions. Comparisons between Self-Exchange and Cross Reactions Using Marcus' Theory

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Experimental rate constants and activation parameters for a number of outer-sphere cross reactions involving cationic transition-metal complexes are compared with the values predicted from the kinetic parameters of the corresponding self-exchange processes using the conventional Marcus treatment. The required free energies, entropies, and enthalpies of the cross reactions were obtained from electrochemical measurements using nonisothermal cells. It was found that the increasingly large disagreements seen between the experimental rate constants and the predicted values at very large thermodynamic driving forces are compatible with the presence of large unfavorable work terms required to form the binuclear collision complex prior to electron transfer. The discrepancies are especially large for reactions involving pairs of aquo complexes. Analysis of the activation parameters suggests that these discrepancies lie chiefly in the entropic component of the activation free energy. It is speculated that a major part of such entropic terms may be due to the need to reorientate solvating water molecules in order to form the highly charged collision complexes from the separated reactants, although these effects may arise partly from the presence of nonadiabatic pathways or from anharmonicity of the free energy barriers.

Introduction

The adiabatic model of outer-sphere electron transfer developed by Marcus and others[1,2] predicts that there should be a simple relationship between the kinetics of homogeneous cross reactions and the corresponding self-exchange processes. This relationship has commonly been formulated as eq 1,

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

$$\log f_{12} = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \tag{1a}$$

where k_{11} and k_{22} are the rate constants for the two constituent self-exchange (homonuclear) reactions, k_{12} and K_{12} are the rate and equilibrium constants, respectively, for the corresponding cross (heteronuclear) reaction, and Z is the bimolecular collision frequency in solution. A number of tests of the applicability of eq 1 to experimental kinetic data have been

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made. It has frequently been observed that eq 1 does provide a reasonable fit to the experimental results; i.e., the observed values of k_{12} are often within an order of magnitude or so of the values k_{12}^{calcd} that are calculated from k_{11} and k_{22} by using eq 1.[3] However, it has recently become clear that there are a disturbingly large number of reactions for which k_{12} and k_{12}^{calcd} are in substantial disagreement.[4-10] For most of these systems, it is found that $k_{12} < k_{12}^{\mathrm{calcd}}$, the difference between k_{12} and k_{12}^{calcd} increasing as the equilibrium constant K_{12} increases.[5-8]

Another puzzling feature of homogeneous outer-sphere redox processes between like-charged ions is that the entropies of activation ΔS^{*} for self-exchange as well as cross reactions are typically large and negative[3b] (ca. −20 to −35 eu) and insensitive to variations in ionic strength.[7b,11] Although such values of ΔS^{*} are predicted by simple electrostatic theory at low ionic strengths, for self-exchange reactions ΔS^{*} is theoretically predicted to increase markedly with increasing ionic strengths to a value close to −10 eu.[3b,11,12]

In view of these striking discrepancies between theory and experiment, it seems worthwhile to examine the ability of the Marcus model to predict not only the relative values of the free energies of activation for corresponding self-exchange and cross reactions but also their individual enthalpic and entropic components. Such an examination should help to pinpoint the factors that are responsible for the observed breakdown of eq 1. Few previous tests have been made of the applicability of the Marcus model to correlate activation parameters for corresponding self-exchange and cross reactions[8,10] because the required enthalpies and entropies of the cross reactions, $\Delta H_{12}°$ and $\Delta S_{12}°$, have been largely unavailable. However, we have recently determined the "standard" (or formal) electrode potentials $E°$ and the reaction entropies $\Delta S_{rc}°$ of a number of cationic transition-metal redox couples by using nonisothermal electrochemical cells.[13] These measurements enable $\Delta H_{12}°$ and $\Delta S_{12}°$ for appropriate pairs of redox couples to be accurately evaluated at ionic strengths that are typically employed for kinetic measurements. In the present paper, these and some additional experimental values of $E°$ and $\Delta S_{rc}°$ are employed to compare experimental free energies, enthalpies, and entropies of activation for a range of outer-sphere cross reactions with the quantities that are predicted from the kinetic parameters of the corresponding self-exchange reactions by using the Marcus model. This analysis provides an additional insight into the limitations of the Marcus and related models in describing the energetics of homogeneous outer-sphere electron-transfer processes.

Experimental Section

Cyclic voltammetry was used along with a nonisothermal cell arrangement to determine the formal potentials E_f of $U_{aq}^{4+/3+}$ ("aq" represents aquo ligands), $Ru(bpy)_3^{3+/2+}$, and $Ru(NH_3)_5py^{3+/2+}$ as a function of temperature, enabling values of $\Delta S_{rc}°$ to be obtained. Details of the method are given in ref 13. Solutions of U_{aq}^{4+} were prepared by exhaustively electrolyzing uranyl perchlorate (G. F. Smith Co.) in 0.5 M $HClO_4$ at a stirred mercury pool at −1000 mV vs. the saturated calomel electrode (SCE) to form U_{aq}^{3+} and then at −650 mV to yield U_{aq}^{4+}. Solutions of $Ru(NH_3)_5py^{2+}$ were prepared by cathodically electrolyzing $Ru(NH_3)_5Cl^{2+}$ in 0.1 M CF_3COONa (pH ~3) at a mercury pool at −700 mV and adding a slight excess of pyridine [$Ru(NH_3)_5py^{2+}$ is formed quantitatively under these conditions[14]]. $Ru(bpy)_3 \cdot Cl_2 \cdot 6H_2O$ was obtained from G. F. Smith Co. Values of E_f for $U_{aq}^{4+/3+}$ were determined by using a hanging mercury drop electrode and for $Ru(NH_3)_5py^{3+/2+}$ by using platinum and glassy carbon indicator electrodes. For $Ru(bpy)_3^{3+/2+}$, 0.1 M CF_3COOH was used as a supporting electrolyte to inhibit the formation of anodic oxide films and oxygen evolution.

Kinetic Formulations and Results

1. Free Energies of Activation. For the present purposes, eq 1 can be usefully rewritten in terms of free energies of activation as in eq 2,[8,15] where $\Delta G_{12}°$ is the "standard" free

$$\Delta G_{12}{}^{*} = 0.5(\Delta G_{11}{}^{*} + \Delta G_{22}{}^{*}) + 0.5(1 + \alpha)\Delta G_{12}° \quad (2)$$

$$\alpha = \Delta G_{12}°/4(\Delta G_{11}{}^{*} + \Delta G_{22}{}^{*}) \quad (2a)$$

energy driving force for the cross reaction (determined at the appropriate ionic strength) and $\Delta G_{11}{}^{*}$, $\Delta G_{22}{}^{*}$, and $\Delta G_{12}{}^{*}$ are the free energies of activation for the self-exchange and cross reactions, respectively. The activation free energies appearing in eq 2 should be corrected for the work of forming the collision complex from the separated reactants since they are actually reorganization energies within such a binuclear assembly.[1] Equation 2 should therefore be written for the experimentally accessible ("apparent") free energies of activation $(\Delta G^{*})_{app}$ in the form[1]

$$(\Delta G_{12}{}^{*})_{app} = 0.5[(\Delta G_{11}{}^{*})_{app} + (\Delta G_{22}{}^{*})_{app}] + 0.5(\Delta G_{12}{}^{W} + \Delta G_{21}{}^{W} - \Delta G_{11}{}^{W} - \Delta G_{22}{}^{W}) + 0.5\Delta G_{12}° + (\Delta G_{12}° + \Delta G_{21}{}^{W} - \Delta G_{12}{}^{W})^2/8[(\Delta G_{11}{}^{*})_{app} + (\Delta G_{22}{}^{*})_{app} - \Delta G_{11}{}^{W} - \Delta G_{22}{}^{W}] \quad (3)$$

The apparent free energies of activation are related to the experimental second-order rate constants k by eq 4,[1,2] where

$$k = Z \exp[-(\Delta G^{*})_{app}/RT] \quad (4)$$

Z is the bimolecular collision frequency. In eq 3, $\Delta G_{12}{}^{W}$ and $\Delta G_{21}{}^{W}$ are the free energies required to form the precursor and successor ("collision") complexes from the separated reactants and products, respectively, and $\Delta G_{11}{}^{W}$ and $\Delta G_{22}{}^{W}$ are the corresponding work terms for the constituent self-exchange reactions. For cross reactions between like-charged ions of similar structure, it is expected that $\Delta G_{12}{}^{W} \approx \Delta G_{21}{}^{W} \approx \Delta G_{11}{}^{W} \approx \Delta G_{22}{}^{W} = \Delta G^{W}$, so that eq 3 can be simplified to eq 5. In principle, the presence of positive values of ΔG^{W} in

$$(\Delta G_{12}{}^{*})_{app} = 0.5[(\Delta G_{11}{}^{*})_{app} + (\Delta G_{22}{}^{*})_{app}] + 0.5(1 + \alpha)\Delta G_{12}° \quad (5)$$

$$\alpha = \Delta G_{12}°/4[(\Delta G_{11}{}^{*})_{app} + (\Delta G_{22}{}^{*})_{app} - 2\Delta G^{W}] \quad (5a)$$

eq 5 can account for the common observation for cation–cation reactions that the observed cross-reaction rate constants k_{12} for large driving forces are substantially smaller than the values k_{12}^{calcd} that are calculated by using eq 1. For small values of $\Delta G_{12}°$, the influence of α on the driving-force term in eq 5 will generally be small since $\alpha\Delta G_{12}°$ is proportional to the

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Table I. Kinetic and Thermodynamic Parameters of Some Self-Exchange Reactions at 25 °C

redox couple	E_f,[a] mV vs. SCE	$\Delta S_{rc}°$,[b] cal deg^{-1} mol^{-1}	k_{11},[c] M^{-1} s^{-1}	k_{11}^{cor},[d] M^{-1} s^{-1}	$(\Delta G_{11}^*)_{cor}$,[e] kcal mol^{-1}	$(\Delta H_{11}^*)_{cor}$,[f] kcal mol^{-1}	$-(\Delta S_{11}^*)_{cor}$,[g] cal deg^{-1} mol^{-1}
$Co_{aq}^{3+/2+}$	1680[h]	~45[k]	3.3 (3)[m]	8	13.5	10.2	11
$Fe_{aq}^{3+/2+}$	500 (0.2)	43	4 (0.5)[n]	15	13.1	8.6	15
$Ru_{aq}^{3+/2+}$	−15 (0.3)	36	~60 (1)[9]	200	11.6	~7.0[u]	~15[u]
$V_{aq}^{3+/2+}$	−475 (0.2)	37	0.015 (2)[o]	0.03	16.8	~12.5	15
$Eu_{aq}^{3+/2+}$	−625 (0.2)	48		(4×10^{-4})	19.3[s]	~15.0[u]	~15[u]
$Cr_{aq}^{3+/2+}$	−660 (1)	49		(2×10^{-6})	22.5[s]	~18.0[u]	~15[u]
$Yb_{aq}^{3+/2+}$	−1425 (0.1)	48		(~0.1)	~15.5[s]	~11[u]	~15[u]
$U_{aq}^{4+/3+}$	−875 (0.5)[i]	48[i]		(0.5)	15.1[s]	~9.0[v]	~20[v]
$Np_{aq}^{4+/3+}$	−80 (1)[j]	52[l]		(~0.02)	~17.0[t]	~11[v]	~20[v]
$Ru(NH_3)_6^{3+/2+}$	−180 (0.2)	18	~3×10^3 (0.1)[11]	~5×10^4	8.3	3.2	17
$Ru(en)_3^{3+/2+}$	−60 (0.1)	13	~3×10^3 (0.1)[11]	~5×10^4	8.3	3.2	17
$Co(en)_3^{3+/2+}$	−460 (1)	37	8×10^{-5} (1)[p]	2.5×10^{-4}	19.6	13.4	22
$Co(phen)_3^{3+/2+}$	145 (0.05)	22	~40 (0.1)[q]	~150	11.7	4.5	24
$Co(bpy)_3^{3+/2+}$	70 (0.05)	22	~20 (0.1)[q]	~80	12.1	7.0	17
$Ru(bpy)_3^{3+/2+}$	1040 (0.1)[i]	0[i]	2×10^9 (1)[r]	~1×10^{10}	~1	~1[w]	~0[w]
$Ru(NH_3)_5py^{3+/2+}$	75 (0.1)[i]	16[i]	4.7×10^5 (1)[10]	1.5×10^6	6.3	2.4	13

[a] Formal potential of redox couple vs. saturated calomel electrode (add 245 mV to convert to electrode potentials vs. NHE). Ionic strength μ is given in parentheses. Data are from ref 13 unless otherwise noted. For most systems, E_f becomes only ~5–10 mV more negative with increasing μ over the range $\mu \approx 0.1$–1.0. [b] Reaction entropy of redox couple Ox + e$^-$(electrode) $\rightleftarrows$ Red.[13,26] Data are from ref 13 unless otherwise noted. Quoted values were obtained at same ionic strengths as E_f. [c] Observed second-order rate constant for acid-independent pathway. Corresponding ionic strength is given in parentheses. [d] Rate constant corrected for the (Debye–Hückel) work $(\Delta G^W)_{DH}$ of forming the collision complex from the separated reactants (eq 8) by $\ln k_{11}^{cor} = \ln k_{11} + (\Delta G^W)_{DH}/RT$. Values of å for insertion into eq 8 were estimated from the sum of the radii of the reactants. Rate constants given in parentheses are estimated values (see text). [e] Free energy of activation corrected for Debye–Hückel work term, determined from k_{11}^{cor} by using eq 3 on the assumption that $Z \approx 6 \times 10^{10}$ M^{-1} s^{-1}.[18] [f] Enthalpy of activation corrected for Debye–Hückel work term, obtained from experimental activation enthalpies by using eq 13 and $(\Delta H_{11}^*)_{cor} = (\Delta H_{11}^*)_{app} - (\Delta G^W)_{DH}$ (see text). [g] Entropy of activation, obtained from experimental activation entropies $\Delta S^{\ddagger}$ by adding 10 eu (eq 12) (see text). [h] D. H. Huchital, N. Sutin, and B. Warnquist, *Inorg. Chem.*, 6, 838 (1967). [i] Present work. [j] J. C. Hindman and E. S. Kritchevsky, *J. Am. Chem. Soc.*, 72, 953 (1950). [k] Estimated value. [l] Calculated from data given by D. Cohen and J. C. Hindman, *J. Am. Chem. Soc.*, 74, 4679 (1952), by noting that $\Delta S_{rc}°$ for the normal hydrogen electrode equals 21 eu [A. J. deBethune, T. S. Licht, and N. Swendeman, *J. Electrochem. Soc.*, 106, 616 (1959)]. [m] H. S. Habib and J. P. Hunt, *J. Am. Chem. Soc.*, 88, 1668 (1966). [n] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, 56, 846 (1952). [o] K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, 80, 5921 (1958). [p] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 65, 1892 (1961). [q] H. M. Neumann, quoted in R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 514 (1968). [r] R. C. Young, F. R. Keene, and T. J. Meyer, *J. Am. Chem. Soc.*, 99, 2468 (1977). [s] Estimated from electrochemical exchange rate data (see text). [t] Estimated from kinetics of $Ru(en)_3^{3+}$–Np_{aq}^{3+} reaction (Table IIB) by using eq 6 (see text). [u] Estimated from value of $(\Delta G_{11}^*)_{cor}$ given by assuming that $(\Delta S_{11}^*)_{cor} = -15$ eu (see text). [v] Estimated by assuming that $(\Delta S_{11}^*)_{cor} = -20$ eu (see text). [w] Estimated value.[8]

square of $\Delta G_{12}°$ (eq 5a), so that eq 5 will approximately reduce to eq 2 under these conditions, irrespective of the value of ΔG^W. However, as $\Delta G_{12}°$ increases, the effect of α upon the driving-force term will increase so that the presence of positive values of ΔG^W will act to enlarge progressively the values of $(\Delta G_{12}^*)_{app}^{calcd}$ obtained from eq 5, yielding $k_{12} < k_{12}^{calcd}$ since eq 1 does not include work terms. However, the typical values of the work terms $(\Delta G^W)_{DH}$ obtained from the Debye–Hückel model are not sufficiently large to explain the extent of the observed discrepancies.[8] Nevertheless, it seems quite plausible that another large component of ΔG^W, $\Delta G^W{}_s$, could arise from the mutual solvent ordering accompanying the approach of the two cationic reactants. Consequently eq 5 and 5a can conveniently be rewritten in terms of "Debye–Hückel-corrected" free energies of activation $(\Delta G^*)_{cor}$:

$$(\Delta G_{12}^*)_{cor} = 0.5[(\Delta G_{11}^*)_{cor} + (\Delta G_{22}^*)_{cor}] + 0.5(1 + \alpha)\Delta G_{12}° \quad (6)$$

$$\alpha = \Delta G_{12}°/4[(\Delta G_{11}^*)_{cor} + (\Delta G_{22}^*)_{cor} - 2\Delta G^W{}_s] \quad (6a)$$

where

$$(\Delta G^*)_{cor} = (\Delta G^*)_{app} - (\Delta G^W)_{DH} = \Delta G^* + \Delta G^W{}_s \quad (7)$$

and[11]

$$(\Delta G^W)_{DH} = Z_1 Z_2 e^2 N/\epsilon_s å(1 + Bå\mu^{1/2}) \quad (8)$$

where Z_1 and Z_2 are the charges of the two reactants, e is the electronic charge, N is Avogadro's number, ϵ_s is the (static) dielectric constant, B is the Debye–Hückel parameter,[16] μ is the ionic strength, and å is the distance between the centers of the reacting ions in the collision complex.

We shall employ eq 6 and 6a as a convenient means of examining the relationship between the experimental activation free energies of corresponding self-exchange and cross reactions in terms of the Marcus model and also as the basis for exploring the behavior of the individual enthalpic and entropic components. Although the hypothesis embodied in the use of the term $\Delta G^W{}_s$ in eq 6a cannot be proven, it turns out that the algebraic forms of eq 6 and 6a are nicely consistent with most of the available experimental data, as shown below.

In Table I are summarized values of rate parameters for the acid-independent pathways of a number of homogeneous self-exchange reactions between various cationic complexes. The listed values of $(\Delta G_{11}^*)_{cor}$ (or $(\Delta G_{22}^*)_{cor}$) were obtained in the following ways. For reactions for which the self-exchange rate constants k_{11} have been determined, values of $(\Delta G_{11}^*)_{cor}$ were obtained by using eq 4, 7, and 8, on the assumption that $Z = 6 \times 10^{10}$ M^{-1} s^{-1}.[18,19] For $Ru_{aq}^{3+/2+}$, $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, and $Ru(NH_3)_5py^{3+/2+}$ self-exchange, the listed values of k_{11} are literature values that were obtained by using eq 1 from the rates of cross reactions having small driving forces using structurally similar reactants.[9-11] The justification for this procedure is that eq 1 has been found

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(18) Calculated by using the expression[1,11] $Z = N(8\pi k_B T m_r^{-1})^{1/2}(10^{-3}r^2)$, where m_r and r are the effective reduced mass and the distance between the metal centers in the collision complex, respectively. Inserting the typical values (for the present reactants) $m_r = 100$ and $r = 7 \times 10^{-8}$ cm yields $Z \approx 6 \times 10^{10}$ M^{-1} s^{-1}.

(19) Values of å used to calculate $(\Delta G^W)_{DH}$ from eq 5 were obtained from the sum of the radii of the two reacting ions.

Table II. Free Energies of Activation and Driving Forces for Cross Reactions

oxidant	reductant	$-\Delta G_{12}°$,[a] kcal mol^{-1}	k_{12},[b] M^{-1} s^{-1}	k_{12}^{cor},[c] M^{-1} s^{-1}	$(\Delta G_{12}*)_{cor}$,[d] kcal mol^{-1}	$(0.5\alpha_0 \cdot \Delta G_{12}°)$,[e] kcal mol^{-1}	$(0.5\alpha \cdot \Delta G_{12}°)$,[f] kcal mol^{-1}	ΔG^W_s,[g] kcal mol^{-1}
(A) Reactions between Aquo Cations								
Co_{aq}^{3+}	Fe_{aq}^{2+}	27.2	50 (1)[27]	150	11.7	3.3	12.0	10.2
Co_{aq}^{3+}	V_{aq}^{2+}	49.5	9×10^{5} (3)[28]	2×10^{6}	6.1	10.1	19.6	7.3
Co_{aq}^{3+}	Cr_{aq}^{2+}	53.9	1.3×10^{4} (3)[28]	3×10^{4}	8.6	10.1	17.6	7.6
Co_{aq}^{3+}	U_{aq}^{3+}	58.9	1.1×10^{6} (2)[7a]	3×10^{6}	5.9	15.2	21.1	4.1
Fe_{aq}^{3+}	Ru_{aq}^{2+}	11.9	2.3×10^{3} (1)[9]	7×10^{3}	9.5	0.7	3.1	
Fe_{aq}^{3+}	V_{aq}^{2+}	22.5	1.8×10^{4} (1)[7b]	6×10^{4}	8.2	2.1	4.5	8.2
Fe_{aq}^{3+}	Eu_{aq}^{2+}	25.9	7×10^{3} (1)[29]	2×10^{4}	8.8	2.6	5.6	8.8
Fe_{aq}^{3+}	Cr_{aq}^{2+}	26.7	2.3×10^{3} (1)[h]	7×10^{3}	9.5	2.5	5.1	8.9
Fe_{aq}^{3+}	U_{aq}^{3+}	31.7	4×10^{5} (2)[7a]	8×10^{5}	6.7	4.5	8.5	6.3
Ru_{aq}^{3+}	V_{aq}^{2+}	10.6	2.8×10^{2} (1)[9]	9×10^{2}	10.7	0.5	1.8	
Np_{aq}^{4+}	V_{aq}^{2+}	9.1	1.3 (1)[30]	4	13.9	0.3	1.7	
V_{aq}^{3+}	Eu_{aq}^{2+}	3.5	9×10^{-3} (2)[31]	2×10^{-2}	17.0	0	0.7	
V_{aq}^{3+}	U_{aq}^{3+}	9.2	85 (2)[32]	250	11.4	0.3	0	
Eu_{aq}^{3+}	Cr_{aq}^{2+}	0.8	$\sim 2 \times 10^{-5}$ (0.5)[31]	8×10^{-5}	~20.3	0	−0.2	
Cr_{aq}^{3+}	U_{aq}^{3+}	5.0	6.2×10^{-2} (2)[7c]	0.15	15.8	0.1	−0.5	
(B) Reactions Involving Nonaquo Cations								
$Ru(NH_3)_6^{3+}$	V_{aq}^{2+}	6.8	1.5×10^{3} (0.48)[33]	$\sim 2 \times 10^{4}$	8.8	0.23	−0.4	
$Ru(NH_3)_6^{3+}$	Eu_{aq}^{2+}	10.3	2.3×10^{3} (1)[i]	7×10^{3}	9.5	0.5	0.8	
$Ru(NH_3)_6^{3+}$	Cr_{aq}^{2+}	11.1	2×10^{2} (0.2)[j]	2×10^{3}	10.2	0.5	0.3	
$Ru(NH_3)_6^{3+}$	Yb_{aq}^{2+}	28.7	4.5×10^{7} (1)[i]	1.5×10^{8}	3.5	4.3	6.0	3.4
$Ru(NH_3)_6^{3+}$	Np_{aq}^{3+}	−2.3	0.3 (1)[34]	~2	14.3	0	0.5	
$Ru(NH_3)_6^{3+}$	U_{aq}^{3+}	16.0	1.5×10^{5} (1)[35]	9×10^{5}	6.6	1.4	2.9	5.9
$Ru(en)_3^{3+}$	Np_{aq}^{3+}	0.5	8.5 (1)[34]	40	12.5	0	0.1	
$Ru(en)_3^{3+}$	U_{aq}^{3+}	18.8	8.4×10^{5} (1)[35]	4×10^{6}	5.7	1.9	3.4	5.3
$Ru(NH_3)_5py^{3+}$	V_{aq}^{2+}	12.7	3×10^{5} (1)[8]	1×10^{6}	6.5	0.9	1.3	
$Ru(NH_3)_5py^{3+}$	Eu_{aq}^{2+}	16.1	5.4×10^{4} (1)[8]	1.5×10^{5}	7.6	1.3	2.8	6.6
$Ru(NH_3)_5py^{3+}$	$Ru(NH_3)_6^{2+}$	5.9	1.4×10^{6} (1)[8]	4×10^{6}	5.7	0.3	1.4	
Fe_{aq}^{3+}	$Ru(NH_3)_6^{2+}$	15.7	3.5×10^{5} (0.1)[36]	$\sim 6 \times 10^{6}$	5.5	1.4	2.7	5.3
Ru_{aq}^{3+}	$Ru(NH_3)_6^{2+}$	3.8	1.4×10^{4} (1)[9]	4×10^{4}	8.4	0.1	0.3	
Fe_{aq}^{3+}	$Ru(en)_3^{2+}$	12.9	1.4×10^{5} (0.1)[36]	$\sim 3 \times 10^{6}$	6.0	1.0	1.8	4.6
Fe_{aq}^{3+}	$Ru(NH_3)_5py^{2+}$	9.8	5.8×10^{4} (1)[10]	1.7×10^{5}	7.6	0.6	2.8	
$Co(phen)_3^{3+}$	$Ru(NH_3)_6^{2+}$	7.5	1.5×10^{4} (0.1)[8]	$\sim 1 \times 10^{5}$	7.9	0.4	1.7	
$Co(bpy)_3^{3+}$	$Ru(NH_3)_6^{2+}$	5.8	1.1×10^{4} (0.1)[8]	$\sim 1 \times 10^{5}$	7.9	0.2	0.6	
$Co(phen)_3^{3+}$	$Ru(NH_3)_5py^{2+}$	1.6	2×10^{3} (1)[8]	6×10^{3}	9.5	0	1.3	
$Co(en)_3^{3+}$	V_{aq}^{2+}	0.3	7×10^{-4} (1)[k]	2.5×10^{-3}	18.3	0	0.2	
$Co(en)_3^{3+}$	Eu_{aq}^{2+}	3.8	$\sim 5 \times 10^{-3}$ (1)[l]	2×10^{-2}	17.4	0	−0.2	
$Co(en)_3^{3+}$	Cr_{aq}^{2+}	4.6	3×10^{-4} (1)[k]	1×10^{-3}	18.8	0.1	0.1	
$Co(en)_3^{3+}$	U_{aq}^{3+}	9.6	0.13 (0.2)[m]	2.5	14.2	0.3	1.6	
$Co(en)_3^{3+}$	Yb_{aq}^{2+}	22.2	4.5×10^{2} (0.18)[37]	$\sim 1 \times 10^{4}$	9.2	1.8	2.7	5.7
$Co(phen)_3^{3+}$	V_{aq}^{2+}	14.3	4×10^{3} (1)[8]	$\sim 1 \times 10^{4}$	9.2	0.9	2.1	~8
$Co(bpy)_3^{3+}$	V_{aq}^{2+}	12.6	1.1×10^{3} (2)[38]	2×10^{3}	10.2	0.7	2.0	
$Ru(bpy)_3^{3+}$	Fe_{aq}^{2+}	12.4	7.2×10^{5} (1)[39]	2×10^{6}	6.1	1.4	5.2	5.0

[a] Free energy driving force for cross reaction, determined from the formal potentials listed in Table I by using $\Delta G_{12}° = F(E_{f(Ox)} - E_{f(Red)})$. [b] Observed second-order rate constants for acid-independent pathway. Corresponding ionic strength given in parentheses. Superscripts denote data sources. [c] Rate constant corrected for the Debye–Hückel work of forming the collision complex from the separated reactants. See footnote *d* to Table I. [d] Free energy of activation determined from k_{12}^{cor} by using eq 3 on the assumption that $Z \approx 6 \times 10^{10}$ M^{-1} s^{-1}.[18] [e] α_0 determined from eq 6a by using the values of $(\Delta G^*)_{cor}$ for the appropriate self-exchange reactions (Table I) and assuming that $\Delta G^W_s = 0$. [f] Determined from eq 6 by inserting appropriate values of $(\Delta G_{11}*)_{cor}$ and $(\Delta G_{22}*)_{cor}$ (Table I) and $(\Delta G_{12}*)_{cor}$ and $\Delta G_{12}°$ (this table). [g] Apparent work required to form collision complex from separated reactants; determined from listed values of α_0 and α by using eq 9 (see text). [h] G. Dultz and N. Sutin, *J. Am. Chem. Soc.*, 86, 829 (1964). [i] M. Faraggi and A. Feder, *Inorg. Chem.*, 12, 236 (1973). [j] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, 86, 1686 (1964). [k] T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, 95, 5545 (1973). [l] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, 86, 1019 (1964). [m] R. T. Wang and J. H. Espenson, *J. Am. Chem. Soc.*, 93, 380 (1971).

to be consistently successful under these conditions.[8] Values of the "Debye–Hückel-corrected" rate constants k_{11}^{cor} are also given in Table I. These were obtained from k_{11} by using the relation $\ln k_{11}^{cor} = \ln k_{11} + (\Delta G^W)_{DH}/RT$. For the aquo couples, $Eu_{aq}^{3+/2+}$, $Cr_{aq}^{3+/2+}$, $Yb_{aq}^{3+/2+}$, $U_{aq}^{4+/3+}$, and $Np_{aq}^{4+/3+}$, no quantitative values of k_{11} are apparently available. However, self-consistent estimates of $(\Delta G_{11}*)_{cor}$ for these reactions were obtained in the following two ways. The electrochemical exchange rates for these and other aquo redox couples have been determined at the mercury–water interface and have been found to yield a consistent correlation with the rates of corresponding homogeneous self-exchange and cross reactions.[20,21] This can be expressed as $(\Delta G^*)^e_{cor} = 0.47(\Delta G^*)^h_{cor} - 0.5$ kcal,[21] where $(\Delta G^*)^e_{cor}$ and $(\Delta G^*)^h_{cor}$ are the corresponding electrochemical and homogeneous free energies of activation, respectively, that have been corrected for the appropriate electrostatic work terms. The listed values of $(\Delta G_{11}*)_{cor}$ for $Eu_{aq}^{3+/2+}$, $Cr_{aq}^{3+/2+}$, $Yb_{aq}^{3+/2+}$, and $U_{aq}^{4+/3+}$ were obtained in this manner. A justification for using this method is that the resulting estimates of $(\Delta G_{11}*)_{cor}$ are consistently within ca. 0.5 kcal of the values estimated from the kinetics of cross reactions having small driving forces with the use of eq 6 (see below). The listed value of $(\Delta G_{11}*)_{cor}$ for $Np_{aq}^{4+/3+}$ was determined from the kinetics of the $Ru(en)_3^{3+}$–Np_{aq}^{3+} reaction

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(20) M. J. Weaver, *Inorg. Chem.*, **15**, 1733 (1976).

(21) M. J. Weaver, *J. Phys. Chem.*, **84**, 568 (1980).

(Table IIB) by using the latter method, since the electrochemical exchange rate for this couple is not available.

Table IIA lists the available kinetic parameters for the acid-independent pathways of a number of cross reactions between the various aquo couples listed in Table I. Again, values of the "Debye–Hückel-corrected" free energies of activation $(\Delta G_{12}^*)_{\text{cor}}$ were obtained from the experimental rate constants k_{12} by using eq 4, 7, and 8. Table IIB summarizes the corresponding available data involving the remaining, nonaquo, redox couples that are listed in Table I. Also included in Table II are the corresponding free energies of reaction $\Delta G_{12}°$ for the cross reactions. These latter quantities were determined from the difference in the formal potentials E_f at 25 °C that are given in Table I for the appropriate pairs of redox couples. These values of E_f were obtained in this laboratory by means of cyclic voltammetry[13] using suitably noncomplexing media at ionic strengths that are comparable to those employed for the corresponding kinetic measurements.[22] [Although some values of E_f were determined at ionic strengths that are different from those employed for gathering the kinetic data, this is of little consequence since the variation of E_f with ionic strength μ is typically small ($\lesssim$10 mV) in the range of ionic strength ($\mu \approx 0.1$–1) used for the kinetic measurements[13] and will tend to cancel when the pair of E_f values used to calculate $\Delta G_{12}°$ are determined at similar ionic strengths.]

The experimental values of $(\Delta G_{12}^*)_{\text{cor}}$ for each cross reaction given in Table II were then compared with the predictions of eq 6 and 6a by using the following approach. The quantity $0.5\alpha\Delta G_{12}°$ was calculated for each cross reaction by inserting into eq 6 the appropriate values of $(\Delta G_{12}^*)_{\text{cor}}$, $(\Delta G_{11}^*)_{\text{cor}}$, $(\Delta G_{22}^*)_{\text{cor}}$, and $\Delta G_{12}°$ that are listed in Tables I and II. The same quantity, which we shall label $0.5\alpha_0\Delta G_{12}°$, was also determined from $(\Delta G_{11}^*)_{\text{cor}}$, $(\Delta G_{22}^*)_{\text{cor}}$, and $\Delta G_{12}°$ but with the use of eq 6a by assuming that $\Delta G^{\text{W}}{}_{\text{s}} = 0$. The resulting values of $0.5\alpha\Delta G_{12}°$ and $0.5\alpha_0\Delta G_{12}°$ are listed in adjacent columns in Table II. From eq 6 and 6a, it is seen that the difference between these two quantities $0.5\Delta G_{12}°(\alpha - \alpha_0)$ equals the difference between the experimental value of $(\Delta G_{12}^*)_{\text{cor}}$ and the values $(\Delta G_{12}^*)_{\text{cor}}^{\text{calcd}}$ that are calculated from the self-exchange and driving force parameters by using eq 6 and 6a and assuming that $\Delta G^{\text{W}}{}_{\text{s}} = 0$. For most cross reactions with small enough driving forces so that the "quadratic term" $0.5\alpha_0\Delta G_{12}°$ is small (e.g., $\lesssim$0.5 kcal mol^{-1}), inspection of Table II reveals that $0.5\alpha\Delta G_{12}° \approx 0.5\alpha_0\Delta G_{12}°$, at least within the expected accuracy of the activation free energies used (probably ±0.5–1 kcal mol^{-1}). In other words, $(\Delta G_{12}^*)_{\text{cor}} \approx (\Delta G_{12}^*)_{\text{cor}}^{\text{calcd}}$ so that the eq 1 will be approximately obeyed, in accordance with earlier conclusions.[3,8] (Admittedly, for a few of these reactions, eq 1 was employed to obtain one or both of the self-exchange parameters used in Table II.) This result is expected since the relative values of $0.5\alpha\Delta G_{12}°$ and $0.5\alpha_0\Delta G_{12}°$ will be very insensitive to the magnitude of $\Delta G^{\text{W}}{}_{\text{s}}$ under these conditions. However, for cross reactions with larger values of $\Delta G_{12}°$, it is seen that $0.5\alpha_0\Delta G_{12}° < 0.5\alpha\Delta G_{12}°$ [i.e., $(\Delta G_{12}^*)_{\text{cor}}^{\text{calcd}} < (\Delta G_{12}^*)_{\text{cor}}$], as expected if $\Delta G^{\text{W}}{}_{\text{s}} > 0$ in eq 6a since

$$\Delta G^{\text{W}}{}_{\text{s}} = (\Delta G_{12}°/8)(1/\alpha_0 - 1/\alpha) \qquad (9)$$

Estimates of $\Delta G^{\text{W}}{}_{\text{s}}$ obtained from eq 9 for reactions with suitably large values of the quadratic driving-force term $0.5\alpha_0\Delta G_{12}°$ (>1 kcal mol^{-1}) are also given in Table II. For most reactions involving two aquo reactants, $\Delta G^{\text{W}}{}_{\text{s}} \approx 6$–9 kcal mol^{-1} (Table IIA). For reactions involving only one aquo reactant, $\Delta G^{\text{W}}{}_{\text{s}} \approx 4$–6 kcal mol^{-1} (Table IIB).

2. Entropies and Enthalpies of Activation. In view of the apparent marked deviations of the experimental free energies of activation from the conventional form of the Marcus cross relation as expressed in eq 1 or 2, it is of particular interest to compare the behavior of the constituent enthalpies and entropies of activation with the predictions of the Marcus model.

Expressions similar to eq 2 can be written for the corresponding entropies and enthalpies of activation as in eq 10 and 11,[8,15] where α is defined by eq 2a. Since it is conventional

$$\Delta S_{12}^* = 0.5(\Delta S_{11}^* + \Delta S_{22}^*)(1 - 4\alpha^2) + 0.5(1 + 2\alpha)\Delta S_{12}° \qquad (10)$$

$$\Delta H_{12}^* = 0.5(\Delta H_{11}^* + \Delta H_{22}^*)(1 - 4\alpha^2) + 0.5(1 + 2\alpha)\Delta H_{12}° \qquad (11)$$

to compute entropies and enthalpies of activation from rate data by using the preexponential factor k_BT/h rather than Z, the quantities ΔS^* and ΔH^* appearing in eq 10 and 11 are related to the former quantities $\Delta S^‡$ and $\Delta H^‡$ by eq 12 and 13.[8,15]

$$\Delta S^* = \Delta S^‡ - R \ln (hZ/k_BT) + 0.5R \qquad (12)$$

$$\Delta H^* = \Delta H^‡ + 0.5RT \qquad (13)$$

Equations 10 and 11 can be written in a form compatible with eq 6 by noting that ΔS^* and ΔH^* are reorganizational parameters that may differ from the "Debye–Hückel-corrected" entropies and enthalpies of activation $(\Delta S^*)_{\text{cor}}$ and $(\Delta H^*)_{\text{cor}}$ by the work terms $\Delta S^{\text{W}}{}_{\text{s}}$ and $\Delta H^{\text{W}}{}_{\text{s}}$, respectively, such that $(\Delta S^*)_{\text{cor}} = \Delta S^* + \Delta S^{\text{W}}{}_{\text{s}}$ and $(\Delta H^*)_{\text{cor}} = \Delta H^* + \Delta H^{\text{W}}{}_{\text{s}}$. Therefore

$$(\Delta S_{12}^*)_{\text{cor}} - \Delta S^{\text{W}}{}_{\text{s}} = 0.5[(\Delta S_{11}^*)_{\text{cor}} + (\Delta S_{22}^*)_{\text{cor}} - 2\Delta S^{\text{W}}{}_{\text{s}}](1 - 4\alpha^2) + 0.5(1 + 2\alpha)\Delta S_{12}° \qquad (14)$$

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(22) Some of the formal potentials E_f listed in Tables I and II differ significantly from the values that are commonly quoted in inorganic literature. These discrepancies can often be traced to the frequent indiscriminate use of "standard" electrode potentials $E°$ that refer to widely varying ionic strengths or of older data that were obtained in strongly complexing media. For example, the often-quoted "$E°$" for $\text{Eu}_{\text{aq}}{}^{3+/2+}$ of –430 mV vs. NHE[23] (≡–670 mV vs. SCE) was determined in a formic acid medium.[23] Determinations of E_f for this couple in "noncomplexing" (perchlorate) media yield substantially less negative values ($E_f \approx -620$ mV vs. SCE; $\mu = 0.2$–1.0[13,24,25]).

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(26) The quoted values of $\Delta S_{\text{rc}}°$ are essentially equal to $\bar{S}_{\text{Red}}° - \bar{S}_{\text{Ox}}°$, where $\bar{S}_{\text{Red}}°$ and $\bar{S}_{\text{Ox}}°$ are the partial molal entropies of the reduced and oxidized species, respectively.[13] Therefore $\Delta S_{\text{rc}}°$ should be carefully distinguished from other, commonly quoted, "reaction entropies" which refer, for example, to isothermal cells containing the NHE and to values obtained by arbitrarily assuming that $\bar{S}_{\text{H}^+}° = 0$.[13]

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$$(\Delta H_{12}^*)_{\text{cor}} - \Delta H^{\text{W}}_{\text{s}} = 0.5[(\Delta H_{11}^*)_{\text{cor}} + (\Delta H_{22}^*)_{\text{cor}} - 2\Delta H^{\text{W}}_{\text{s}}](1 - 4\alpha^2) + 0.5(1 + 2\alpha)\Delta H_{12}^{\circ} \quad (15)$$

where α is given by eq 6a, and $-\Delta G^{\text{W}}_{\text{s}} = -\Delta H^{\text{W}}_{\text{s}} + T\Delta S^{\text{W}}_{\text{s}}$. Since relatively large values of $\Delta G^{\text{W}}_{\text{s}}$ were required in order to fit the experimental free energies of activation with eq 6, it is of interest to compare the predictions of eq 14 and 15 with the experimental entropies and enthalpies of activation, respectively, in order to ascertain if the major contributions to $\Delta G^{\text{W}}_{\text{s}}$ arise from $\Delta S^{\text{W}}_{\text{s}}$ and/or $\Delta H^{\text{W}}_{\text{s}}$.

Table III lists the cross reactions considered in Table II for which activation parameters have been determined. The listed values of $(\Delta H_{12}^*)_{\text{cor}}$ were obtained from the experimental quantities $\Delta H^{\ddagger}$ by using eq 13 to yield $(\Delta H_{12}^*)_{\text{app}}$ and then by assuming that $(\Delta H_{12}^*)_{\text{cor}} = (\Delta H_{12}^*)_{\text{app}} - (\Delta G^{\text{W}})_{\text{DH}}$. This presumes that the Coulombic work of forming the collision complexes from the separated reactants is entirely of enthalpic origin at the high ionic strengths encountered. Support for this assertion is that the dependence of the rate constant upon ionic strength for a number of outer-sphere redox reactions has been found to be due almost entirely to the enthalpic term.[7b,11] The listed values of $(\Delta S^*)_{\text{cor}}$ were therefore obtained directly from the conventional experimental quantities $\Delta S^{\ddagger}$ by using eq 12 (which simply involved the addition of 10 eu to $\Delta S^{\ddagger}$).

Activation parameters $(\Delta H_{11}^*)_{\text{cor}}$ and $(\Delta S_{11}^*)_{\text{cor}}$ for the corresponding self-exchange reactions are given in Table I. Since some of these latter quantities have not been directly determined, it was necessary to estimate them from the listed values of $(\Delta G_{11}^*)_{\text{cor}}$. It was assumed that $(\Delta S_{11}^*)_{\text{cor}} = -15$ eu for $\text{Ru}_{\text{aq}}^{3+/2+}$, $\text{Eu}_{\text{aq}}^{3+/2+}$, $\text{Cr}_{\text{aq}}^{3+/2+}$, and $\text{Yb}_{\text{aq}}^{3+/2+}$ since this value has been observed for both $\text{Fe}_{\text{aq}}^{3+/2+}$ and $\text{V}_{\text{aq}}^{3+/2+}$ self-exchange. For $\text{U}_{\text{aq}}^{4+/3+}$ and $\text{Np}_{\text{aq}}^{4+/3+}$ exchange, $(\Delta S_{11}^*)_{\text{cor}}$ was taken as −20 eu, since these values are more compatible with cross-reaction data (see below). Although these estimates are admittedly somewhat arbitrary, experimental values of $(\Delta S_{11}^*)_{\text{cor}}$ for such small cationic reactants tend to fall within the narrow range ca. −15 to −20 eu (Table I), and such values are suggested by the experimental values of $(\Delta S_{12}^*)_{\text{cor}}$ for cross reactions with small driving forces (see below). For $\text{Ru(bpy)}_3^{3+/2+}$, $(\Delta S_{11}^*)_{\text{cor}}$ was assumed to be ~0 eu.[8]

For comparison of these kinetic parameters with the predictions of eq 14 and 15, values of the entropic and enthalpic driving forces ΔS_{12}° and ΔH_{12}° are required. The values of $\Delta S_{\text{rc}}^{\circ}$ for the various redox couples of interest here are given in Table I.[26] They were obtained in media having ionic strengths comparable to those used for the kinetic measurements. (Most couples exhibit only small decreases in $\Delta S_{\text{rc}}^{\circ}$ as the ionic strength is increased in the range $\mu = 0.1$–1.0 in "noncomplexing" electrolytes.) The differences between $\Delta S_{\text{rc}}^{\circ}$ for appropriate pairs of redox couples allow ΔS_{12}° for the required cross reactions to be determined. These values of ΔS_{12}° are listed in Table III, along with the corresponding values of ΔH_{12}° which were obtained from the relation $\Delta H_{12}^{\circ} = \Delta G_{12}^{\circ} + T\Delta S_{12}^{\circ}$ with $T = 298$ K.

For each cross reaction in Table III, the experimental parameters $(\Delta G_{12}^*)_{\text{cor}}$, $(\Delta H_{12}^*)_{\text{cor}}$, and $(\Delta S_{12}^*)_{\text{cor}}$ are listed alongside the calculated parameters $(\Delta G_{12}^*)_{w=0}^{\text{calcd}}$, $(\Delta H_{12}^*)_{w=0}^{\text{calcd}}$, and $(\Delta S_{12}^*)_{w=0}^{\text{calcd}}$. The latter values were obtained by inserting the corresponding self-exchange parameters into eq 6, 15, and 14, setting $\Delta S^{\text{W}}_{\text{s}}$ and $\Delta H^{\text{W}}_{\text{s}}$ equal to zero, and determining α from eq 6a by assuming that $\Delta G^{\text{W}}_{\text{s}} = 0$.

Inspection of Table III reveals that for reactions with small values of ΔS_{12}° and ΔH_{12}° as well as ΔG_{12}°, the corresponding values of $(\Delta S_{12}^*)_{\text{cor}}$ and $(\Delta S_{12}^*)_{w=0}^{\text{calcd}}$ and $(\Delta H_{12}^*)_{\text{cor}}$ and $(\Delta H_{12}^*)_{w=0}^{\text{calcd}}$, in addition to $(\Delta G_{12}^*)_{\text{cor}}$ and $(\Delta G_{12}^*)_{w=0}^{\text{calcd}}$, are typically in good agreement. As the overall driving force $-\Delta G_{12}^{\circ}$ increases, the progressively smaller values of $(\Delta G_{12}^*)_{w=0}^{\text{calcd}}$ that are seen relative to $(\Delta G_{12}^*)_{\text{cor}}$ are typically reflected both in values of $(\Delta H_{12}^*)_{w=0}^{\text{calcd}}$ that are markedly smaller than $(\Delta H_{12}^*)_{\text{cor}}$ and in values of $(\Delta S_{12}^*)_{w=0}^{\text{calcd}}$ that are less negative than $(\Delta S_{12}^*)_{\text{cor}}$.

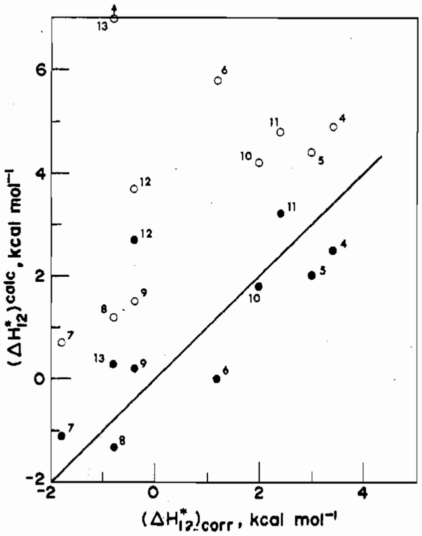

Figure 1. Experimental $(\Delta H_{12}^*)_{\text{cor}}$ for cross reactions corrected for Debye–Hückel work terms plotted against $(\Delta H_{12}^*)^{\text{calcd}}$ calculated from eq 15. In Figures 1 and 2, data are taken from Table IV; labels for each point follow the numbering scheme for reactions in Table IV. Calculated activation parameters were obtained by assuming that $\Delta G^{\text{W}}_{\text{s}} = -T\Delta S^{\text{W}}_{\text{s}}$ (closed circles) and $\Delta G^{\text{W}}_{\text{s}} = \Delta H^{\text{W}}_{\text{s}}$ (open circles). $\Delta G^{\text{W}}_{\text{s}}$ was taken to be 6 kcal mol^{-1} for aquo–aquo reactions and 5 kcal mol^{-1} for aquo–nonaquo reactions (see text). Reactions 1–3 involving $\text{Co}_{\text{aq}}^{3+/2+}$ were omitted for clarity. The solid straight line has a slope of unity and passes through the origin.

In view of the more complex form of eq 14 and 15 compared with eq 6, it is necessary to determine the appropriate values of ΔS^{W} and ΔH^{W} by trial fits of the experimental activation parameters $(\Delta S_{12}^*)_{\text{cor}}$ and $(\Delta H_{12}^*)_{\text{cor}}$ with the estimates obtained from eq 14 and 15 using various values of $\Delta S^{\text{W}}_{\text{s}}$, $\Delta H^{\text{W}}_{\text{s}}$, and $\Delta G^{\text{W}}_{\text{s}}$. From the forms of eq 14 and 15, it is seen that these work terms will only markedly affect the derived activation parameters when ΔG_{12}° is sufficiently large so that α is significantly greater than zero (eq 6a). Table IV lists the cross reactions from Table III for which this condition holds. Three sets of activation parameters are given for each system in Table IV. The first two sets are the experimental and calculated values that are also given in Table III. The third set of activation parameters in Table IV, labeled $(\Delta G_{12}^*)^{\text{calcd}}$, $(\Delta H_{12}^*)^{\text{calcd}}$, and $(\Delta S_{12}^*)^{\text{calcd}}$, are determined from eq 6, 15, and 14 with the inclusion of trial estimates of the appropriate work terms $\Delta G^{\text{W}}_{\text{s}}$, $\Delta H^{\text{W}}_{\text{s}}$, and $\Delta S^{\text{W}}_{\text{s}}$. For the aquo–aquo reactions, $\Delta G^{\text{W}}_{\text{s}}$ was taken to be 6 kcal mol^{-1}, whereas for the nonaquo–aquo reactions $\Delta G^{\text{W}}_{\text{s}}$ was chosen to be 5 kcal mol^{-1}. As expected from the estimates of $\Delta G^{\text{W}}_{\text{s}}$ that were derived from eq 9 and listed in Table II, the inclusion of such work terms is seen to make the resulting estimates of $(\Delta G_{12}^*)^{\text{calcd}}$ in markedly closer agreement with $(\Delta G_{12}^*)_{\text{cor}}$ than are $(\Delta G_{12}^*)_{w=0}^{\text{calcd}}$. Two pairs of values of $(\Delta H_{12}^*)^{\text{calcd}}$ and $(\Delta S_{12}^*)^{\text{calcd}}$ are given for each reaction in Table IV. The left values were determined by assuming that $\Delta G^{\text{W}} = -T\Delta S^{\text{W}}_{\text{s}}$ and the right values by assuming that $\Delta G^{\text{W}}_{\text{s}} = \Delta H^{\text{W}}_{\text{s}}$. These results are also given in graphical form in Figures 1 and 2, which are plots of $(\Delta H_{12}^*)_{\text{cor}}$ vs. $(\Delta H_{12}^*)^{\text{calcd}}$ and $(\Delta S_{12}^*)_{\text{cor}}$ vs. $(\Delta S_{12}^*)^{\text{calcd}}$, respectively. Apart from the $\text{Co}_{\text{aq}}^{3+}$–$\text{Fe}_{\text{aq}}^{2+}$ and $\text{Co}_{\text{aq}}^{3+}$–$\text{Cr}_{\text{aq}}^{2+}$ reactions, it is seen that considerably better fits between the experimental and calculated activation parameters are obtained by using the former assumption (i.e., the closed rather than open points in Figures 1 and 2). Essentially the same results were obtained by choosing different values of

Table III. Activation Parameters for Some Cross Reactions at 25 °C: Comparisons with Self-Exchange Parameters Using the Marcus Theory

oxidant	reductant	$-\Delta G_{12}^\circ$,[a] kcal mol^{-1}	$-\Delta H_{12}^\circ$,[b] kcal mol^{-1}	ΔS_{12}°,[c] cal deg^{-1} mol^{-1}	$(\Delta G_{12}^*)_{cor}$,[d] kcal mol^{-1}	$(\Delta H_{12}^*)_{cor}$,[e] kcal mol^{-1}	$(\Delta S_{12}^*)_{cor}$,[f] cal deg^{-1} mol^{-1}	$(\Delta G_{12}^*)_{w=0}^{calcd}$, kcal mol^{-1} [g]	$(\Delta H_{12}^*)_{w=0}^{calcd}$, kcal mol^{-1} [h]	$(\Delta S_{12}^*)_{w=0}^{calcd}$, cal deg^{-1} mol^{-1} [h]
Co_{aq}^{3+}	Fe_{aq}^{2+}	27.2	~27	~0	11.7	8.0	-13	3.2	0.3	-9
Co_{aq}^{3+}	Cr_{aq}^{2+}	53.9	~55.5	~-5	8.6	9.2	+2	1.1	-0.7	-6
Co_{aq}^{3+}	U_{aq}^{3+}	58.9	~60	~-3	5.9	1.2	-16	0	0.3	+1
Fe_{aq}^{3+}	Ru_{aq}^{2+}	11.9	9.8	7	9.5	6.4	-10	7.1	3.6	-12
Fe_{aq}^{3+}	V_{aq}^{2+}	22.5	20.7	6	8.2	3.4	-16	5.8	2.6	-11
Fe_{aq}^{3+}	Eu_{aq}^{2+}	25.9	27.4	-5	8.8	3.0	-19	5.8	1.6	-14
Fe_{aq}^{3+}	U_{aq}^{3+}	31.7	33.2	-5	6.7	1.2	-18	2.7	-1.2	-13
Np_{aq}^{4+}	V_{aq}^{2+}	9.1	4.6	15	14.0	9.6	-14	12.7	9.5	-11
V_{aq}^{3+}	Eu_{aq}^{2+}	3.5	6.8	-11	17.0	11.0	-20	16.3	10.4	-20
V_{aq}^{3+}	U_{aq}^{3+}	9.2	12.5	-11	11.4	9.4	-7	11.6	5.1	-22
$Ru(NH_3)_6^{3+}$	V_{aq}^{2+}	6.8	12.5	-19	8.8	-0.8	-32	9.4	2.3	-24
$Ru(NH_3)_6^{3+}$	Np_{aq}^{3+}	-2.3	7.9	-34	14.3	3.0	-38	13.8	3.0	-36
$Ru(NH_3)_6^{3+}$	U_{aq}^{3+}	16.0	25.0	-30	6.6	-1.8	-28	5.1	-2.8	-26
$Ru(en)_3^{3+}$	Np_{aq}^{3+}	0.5	12.2	-39	12.5	0.5	-40	12.4	1.0	-38
$Ru(en)_3^{3+}$	U_{aq}^{3+}	18.8	29.3	-35	5.7	-0.8	-21	4.2	-3.6	-26
$Ru(NH_3)_5py^{3+}$	V_{aq}^{2+}	12.7	19.0	-21	6.5	-0.4	-23	6.1	-0.1	-21
$Ru(NH_3)_5py^{3+}$	Eu_{aq}^{2+}	16.1	25.7	-32	7.6	-0.4	-27	6.0	-1.1	-24
Fe_{aq}^{3+}	$Ru(NH_3)_6^{2+}$	15.7	8.2	25	5.5	2.0	-12	4.3	2.5	-6
Fe_{aq}^{3+}	$Ru(en)_3^{2+}$	12.9	3.9	30	6.0	2.4	-12	5.2	4.0	-4
Fe_{aq}^{3+}	$Ru(NH_3)_5py^{2+}$	9.8	1.7	27	7.6	4.4	-10	5.4	4.5	-3
$Co(phen)_3^{3+}$	$Ru(NH_3)_6^{2+}$	7.5	6.3	4	7.9	3.2	-15	6.6	1.2	-18
$Co(phen)_3^{3+}$	$Ru(NH_3)_5py^{2+}$	1.6	-0.2	6	9.5	8.0	-5	8.2	3.5	-16
$Co(en)_3^{3+}$	Yb_{aq}^{2+}	22.2	25.5	-11	9.2	-0.4	-32	8.2	2.3	-20
$Co(phen)_3^{3+}$	V_{aq}^{2+}	14.3	18.8	-15	9.2	3.4	-19	8.0	0.9	-24
$Co(bpy)_3^{3+}$	V_{aq}^{2+}	12.6	17.1	-15	10.2	3.4	-23	8.8	2.6	-21
$Ru(bpy)_3^{3+}$	Fe_{aq}^{2+}	12.4	25.3	-43	6.1	-0.8	-23	2.2	-3.2	-18

[a] Free energy driving force for cross reaction, determined from formal potentials E_f listed in Table I by using $\Delta G_{12}^\circ = F(E_{f(Ox)} - E_{f(Red)})$, where $E_{f(Ox)}$ and $E_{f(Red)}$ are the formal potentials of the couples undergoing oxidation and reduction, respectively. [b] Enthalpy driving force for cross reaction, determined from listed values of ΔG_{12}° and ΔS_{12}° by using $\Delta H_{12}^\circ = \Delta G_{12}^\circ + T\Delta S_{12}^\circ$. [c] Entropy driving force for cross reaction, determined from reaction entropies for appropriate redox couples listed in Table I by using $\Delta S_{12}^\circ = [(\Delta S_{rc}^\circ)_{Red} - (\Delta S_{rc}^\circ)_{Ox}]$, where $(\Delta S_{rc}^\circ)_{Red}$ and $(\Delta S_{rc}^\circ)_{Ox}$ are the reaction entropies for the couples undergoing reduction and oxidation, respectively.[26] [d] "Debye-Hückel-corrected" free energy of activation, taken from Table II. [e] "Debye-Hückel-corrected" enthalpy of activation, obtained from experimental activation energies by using eq 13 and $(\Delta H_{11}^*)_{cor} = (\Delta H_{11}^*)_{app} - (\Delta G^W)_{DH}$ (see text). See Table II for data sources. [f] Entropy of activation, obtained from experimental activation entropies by using eq 12. See Table II for data sources. [g] Free energy of activation for cross reaction, calculated from the values of $(\Delta G_{11}^*)_{cor}$ and $(\Delta G_{22}^*)_{cor}$ listed in Table I, along with ΔG_{12}°, by using eq 6 with α determined from eq 6a on the assumption that $\Delta G^W{}_s = 0$. [h] Enthalpy of activation for cross reaction, determined by using eq 15 from values for corresponding self-exchange reactions given in Table I by assuming that $\Delta H^W{}_s = 0$ and calculating α from eq 6a on the assumption that $\Delta G^W{}_s = 0$. (See text.) [i] Entropy of activation for cross reaction, determined by using eq 14 from values for corresponding self-exchange reactions given in Table I by assuming that $\Delta S^W{}_s = 0$ and calculating α from eq 6a on the assumption that $\Delta G^W{}_s = 0$. (See text.)

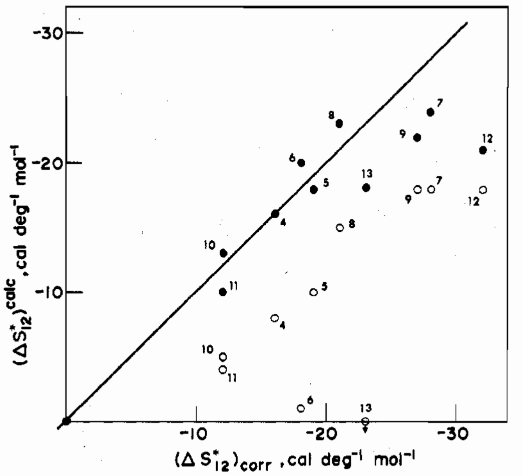

Figure 2. Experimental $(\Delta S_{12}^*)_{cor}$ for cross reactions corrected for Debye–Hückel work terms plotted against $(\Delta S_{12}^*)^{calcd}$ calculated from eq 14. See the caption of Figure 1 for additional information.

$\Delta G^W{}_s$ within the range of the estimates given in Table IIA,B. Reasonable fits were also obtained by assigning both entropic and enthalpic components to $\Delta G^W{}_s$, but only when the predominant contributor was assumed to be $\Delta S^W{}_s$.

Discussion

The foregoing results indicate that the increasingly marked discrepancies between the observed rate constants of outer-sphere cross reactions and the predictions of eq 1 that are observed as the thermodynamic driving force becomes extremely large are consistent with the presence of a significant component of the overall free energy of activation which does not respond to changes in the driving force. A simple, albeit not the only, explanation of such behavior is to consider that this part of the activation free energy is associated with the work ΔG^W of forming the binuclear collision complex prior to the rate-determining electron-transfer step, resulting in eq 6, 6a, 14, and 15. However, the derived values of ΔG^W are typically much larger than the Debye–Hückel estimates $(\Delta G^W)_{DH}$ and appear to arise chiefly from unexpectedly large and negative values of the entropic component ΔS^W (ca. −15 to −25 eu). It is tempting to speculate that this entropy term has the same origin as the similarly large and negative entropies of activation ΔS^* that are typically observed for self-exchange reactions (∼−15 to −20 eu). Since the reorganization entropy within the binuclear complex is theoretically predicted[3b,12] and experimentally confirmed[40] to be close to zero for self-exchange processes, the observed negative values of ΔS^* for bimolecular reactions could also reflect the unfavorable entropic work required to form the binuclear complex from the separated reactants.

It remains to consider the possible origins of such large entropic terms. A common feature of all the reactions considered here is that they involve small multicharged cationic reactants. Consequently, it has been suggested that the negative activation entropies are largely the result of concentrating charge in the dielectric medium.[40] Indeed, the ionic entropy of the transition state appears to be related to its net charge.[3a,41] The high polarizing field within the vicinity of the collision complex could result in a substantial mutual ordering of solvent molecules when this complex is formed from the separated reactants. Such a notion finds support in the observation that

Table IV. Activation Parameters for Some Cross Reactions Having Driving Forces: Effect of Including Entropic and Enthalpic Work Terms on Marcus Predictions

	oxidant	reductant	$(\Delta G_{12}^*)_{cor}$,[a] kcal mol^{-1}	$(\Delta H_{12}^*)_{cor}$,[b] kcal mol^{-1}	$(\Delta S_{12}^*)_{cor}$,[c] cal deg^{-1} mol^{-1}	$(\Delta G_{12}^*)_{w=0}^{calcd}$, kcal mol^{-1} [d]	$(\Delta H_{12}^*)_{w=0}^{calcd}$, kcal mol^{-1} [d]	$(\Delta S_{12}^*)_{w=0}^{calcd}$, cal deg^{-1} mol^{-1} [d]	$(\Delta G_{12}^*)^{calcd}$, kcal mol^{-1} [e]	$(\Delta H_{12}^*)^{calcd}$,[f] kcal mol^{-1}	$(\Delta S_{12}^*)^{calcd}$,[g] cal deg^{-1} mol^{-1}
1	Co_{aq}^{3+}	Fe_{aq}^{2+}	11.7	8.0	−13	3.2	0.3	−9	6.0	0.3, 5.5	−19, −2
2	Co_{aq}^{3+}	Cr_{aq}^{2+}	8.6	9.2	2	1.1	−0.7	−6	6.1	−0.3, 7.3	−21, 4
3	Co_{aq}^{3+}	U_{aq}^{3+}	5.9	1.2	−16	0	0.3	1	11.0	2.6, 21.5	−28, 35
4	Fe_{aq}^{3+}	V_{aq}^{2+}	8.2	3.4	−16	5.8	2.6	−11	7.2	2.5, 4.9	−16, −8
5	Fe_{aq}^{3+}	Eu_{aq}^{2+}	8.8	3.0	−19	5.8	1.6	−14	7.3	2.0, 4.4	−18, −10
6	Fe_{aq}^{3+}	U_{aq}^{3+}	6.7	1.2	−18	2.7	−1.2	−13	6.0	0, 5.8	−20, −1
7	$Ru(NH_3)_6^{3+}$	U_{aq}^{3+}	6.6	−1.8	−28	5.1	−2.8	−26	6.1	−1.1, 0.7	−24, −18
8	$Ru(en)_3^{3+}$	U_{aq}^{3+}	5.7	−0.8	−21	4.2	−3.6	−26	5.6	−1.3, 1.2	−23, −15
9	$Ru(NH_3)_5py^{3+}$	Eu_{aq}^{2+}	7.6	−0.4	−27	6.0	−1.1	−24	6.8	0.2, 1.5	−22, −18
10	Fe_{aq}^{3+}	$Ru(NH_3)_6^{2+}$	5.5	2.0	−12	4.3	2.5	−6	5.6	1.8, 4.2	−13, −5
11	Fe_{aq}^{3+}	$Ru(en)_3^{2+}$	6.0	2.4	−12	5.2	4.0	−4	6.1	3.2, 4.8	−10, −4
12	$Co(en)_3^{3+}$	Yb_{aq}^{2+}	9.2	−0.4	−32	8.2	2.3	−20	8.9	2.7, 3.7	−21, −18
13	$Ru(bpy)_3^{3+}$	Fe_{aq}^{2+}	6.1	−0.8	−23	2.2	−3.2	−18	5.5	0.3, 11.7	−18, 21

[a] "Debye–Hückel-corrected" free energy of activation (from Table II). [b] "Debye–Hückel-corrected" enthalpy of activation (from Table III). [c] Entropy of activation (from Table III). [d] Calculated activation parameters for cross reactions, obtained by using eq 6, 15, and 14 on the assumption that $\Delta G^W{}_s$, $\Delta H^W{}_s$, and $\Delta S^W{}_s = 0$ (from Table III.) [e] Calculated free energy of activation for cross reaction, obtained from eq 6 and 6a as for $(\Delta G^*)_{w=0}^{calcd}$ but on the assumption that $\Delta G^W{}_s = 6$ and 5 kcal mol^{-1} for aquo–aquo and nonaquo–aquo reactions, respectively (see text). [f] Calculated enthalpy of activation for cross reaction, obtained from eq 15 and 6a by assuming that $\Delta G^W{}_s = -T\Delta S^W{}_s$ (left values) or $\Delta G^W{}_s = \Delta H^W{}_s$ (right values) (see text). [g] Calculated entropy of activation for cross reaction, obtained from eq 14 and 6a by assuming that $\Delta G^W{}_s = -T\Delta S^W{}_s$ (left values) or $\Delta G^W{}_s = \Delta H^W{}_s$ (right values) (see text).

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(40) H. Fischer, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).

(41) T. W. Newton and F. B. Baker, *Adv. Chem. Ser.*, No. **71**, 268 (1967).

the values of the reaction entropies $\Delta S_{rc}°$ for such redox couples (i.e., the entropy change resulting from decreasing the cationic charge by one unit) are frequently much larger than the values predicted from the dielectric-continuum (Born) model.[13]

For a number of cross reactions with extremely large driving forces, the derived estimates of $\Delta G^{W}{}_{s}$ are close to the overall free energy of activation $(\Delta G_{12}^{*})_{cor}$ (Table II). This suggests that the rate-determining step under these conditions is the formation of the collision complex rather than the electron-transfer step itself.[42] In this case estimates of $\Delta G^{W}{}_{s}$ would refer to the formation of the transition state prior to the ground-state collision complex itself, so that the actual values of $\Delta G^{W}{}_{s}$ could be substantially smaller than these estimates.

A major assumption that was made in obtaining eq 5 and 6 and also eq 14 and 15 from eq 3 is that the work terms for the corresponding self-exchange and cross reactions are the same. Although this should be approximately the case for cross reactions between structurally similar reactants such as the aquo–aquo reactions considered here, it is less likely to be valid for the amine–aquo cross reactions since amine ligands appear to induce less solvent ordering in the vicinity of multicharged cations compared with aquo ligands.[13] However, from the form of eq 3 it is seen that if the work terms for the cross reactions, $\Delta G_{12}{}^{W}$ and $\Delta G_{21}{}^{W}$, are both equal to the mean of the work terms for the self-exchange reactions, $\Delta G_{11}{}^{W}$ and $\Delta G_{22}{}^{W}$, then these terms will still only appear in the quadratic driving force term in eq 5 and 6.[43] The fact that the values of ΔG^{W} for aquo–amine reactions are typically smaller than for aquo–aquo reactions may reflect a smaller degree of solvent ordering around the amine redox center. Indeed, the markedly larger values of $\Delta S_{rc}°$ that are observed for aquo compared with ammine and other redox couples suggest that the aquo complexes induce an unusual degree of solvent ordering in the trivalent oxidation state.[13] Marked differences have also been observed in the degree of solvent ordering in the transition states for heterogeneous electron transfer for otherwise similar aquo and ammine complexes.[44,45]

Such large and negative apparent entropies of activation are also expected if nonadiabatic mechanisms are followed, i.e., if the probability κ of electron tunneling in the transition state is small.[2a,3c,46] Such an effect would indeed appear as an apparent negative entropic work term in eq 14 if the values of κ for self-exchange and cross reactions are comparable. This possibility has been discussed by Chou et al.[8] Nonadiabatic pathways have been suggested to explain the especially slow electron-transfer rates of reactions involving lanthanide and actinide redox couples since the transferred f electrons are shielded from the surrounding environment.[46] However, cross reactions between f- and d-electron reactants do not exhibit any obviously larger discrepancies with eq 6, 14, and 15 compared to reactions involving electron transfer between d-acceptor and -donor orbitals (Tables II–IV). This provides one argument against the occurrence of strongly nonadiabatic pathways, suggesting that cross reactions involving f-electron couples are adiabatic or not especially nonadiabatic. However, nonadiabatic factors may be responsible for some of the large apparent values of $\Delta G^{W}{}_{s}$ observed for reactions involving Co(III)/Co(II) couples, for example.[47]

An extensive comparison of experimental rate constants for outer-sphere pathways with the predictions of eq 1 and of some experimental activation parameters with the predictions of eq 10 and 11 has recently been given by Chou, Creutz, and Sutin.[8] Similar discrepancies in the rate constants with the Marcus predictions were observed in ref 8 and in the present work. A number of possible explanations for these discrepancies were considered by Chou et al., including noncancellation of work terms and nonadiabatic factors. By comparing the experimental activation parameters with the values calculated from eq 10 and 11 by using the limited $\Delta S_{rc}°$ data then available, Chou et al. tentatively concluded that the unexpectedly small rate constants for the cross reactions originate primarily from the enthalpic rather than the entropic component of the activation free energies.[8] This apparent disparity with the present conclusions arises partly from the use of different values of $\Delta S_{rc}°$ in ref 8 and in the present work; the $\Delta S_{rc}°$ data employed here are considered to be more reliable.[13] However, the chief reason for the disparity arises from the hypothesis embodied in eq 14 and 15 that the discrepancies between the calculated and observed activation parameters arise entirely from work terms that are independent of the driving force. Thus, the observation that a major portion of the differences between a set of observed activation parameters and the values calculated from eq 14 and 15 lies in the enthalpic (or entropic) terms does not necessarily imply that the factor responsible for the difference is of enthalpic (or entropic) origin. This is because a contribution to α arising from either an entropic or enthalpic contribution to $\Delta G^{W}{}_{s}$ (eq 6a) will effect *both* the activation entropies $(\Delta S_{12}^{*})^{calcd}$ and enthalpies $(\Delta H_{12}^{*})^{calcd}$ calculated from eq 14 and 15. Although both $(\Delta H_{12}^{*})^{calcd}_{w=0}$ and $(\Delta S_{12}^{*})^{calcd}_{w=0}$ typically differ markedly from the experimental quantities $(\Delta H_{12}^{*})_{cor}$ and $(\Delta S_{12}^{*})_{cor}$ in Table IV, insertion of an entropic rather than enthalpic work term usually leads to a markedly better fit between the calculated and experimental activation parameters.

Chou et al. also considered the possibility that the observed differences between the experimental results and the Marcus model are due to anharmonicity of the potential energy barriers but concluded that the expected magnitude of this effect was insufficient to account for the observed size of the discrepancies.[8] One piece of evidence which prompts further consideration of anharmonicity factors is obtained from some recently observed kinetic data for the electrooxidation of $Cr_{aq}{}^{2+}$, $Eu_{aq}{}^{2+}$, and $V_{aq}{}^{2+}$ at the mercury–water interface.[48] It was found that all three reactions are accelerated with increasing anodic overpotential (i.e., thermodynamic driving force) to a markedly smaller extent than predicted by the harmonic Marcus model,[48] i.e., exhibit the same type of driving-force-dependent deviations from theory seen for homogeneous reactions. On the other hand, discrepancies between experiment and theory that are substantially smaller and are in the opposite direction were observed for the electroreduction rates of $Cr_{aq}{}^{3+}$ and $Eu_{aq}{}^{3+}$ at cathodic overpotentials.[48,49] The observed anodic electrochemical behavior could be due to the presence of strongly anharmonic *free* energy surfaces, apparently arising from the need for additional orientation of solvent molecules in the vicinity of the dipositive aquo reactant prior to electron transfer.[48] It is interesting to note that most of the homogeneous cross reactions listed in Table II that yield rate constants markedly smaller than anticipated from the Marcus model involve the oxidation of aquo cations.

The present results therefore suggest that the conventional dielectric-continuum models of electron transfer[1,2] provide an incomplete description of the role of the solvent in some outer-sphere reactions. These models presume that at high

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[43] Any inapplicability of this condition will lead to a significant failure in eq 1 even at small driving forces if the work terms are sufficiently large.

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ionic strengths essentially all the solvent reorganization that is required for electron transfer occurs after formation of the precursor complex. In contrast, the present findings suggest that a sizable solvent contribution to the overall activation free energy arises from the formation of the precursor complex from the separated reactants, although the estimates of $\Delta G^{W}{}_{s}$ obtained from eq 6 and 6a will be markedly too large if nonadiabatic and anharmonic factors are indeed important. Whatever the detailed reasons for the observed behavior, it seems plausible that specific solvation factors can play an important role in determining the kinetics of cationic redox reactions in aqueous solution. The further acquisition of kinetic and thermodynamic data, both in solution and at electrode surfaces, for redox reactions involving systematic variations in ligand structure and thermodynamic driving force should provide valuable additional information on this important question.

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Registry No. Co^{3+}, 22541-63-5; Co^{2+}, 22541-53-3; Fe^{3+}, 20074-52-6; Fe^{2+}, 15438-31-0; Ru^{3+}, 22541-88-4; Ru^{2+}, 22541-59-9; V^{3+}, 22541-77-1; V^{2+}, 15121-26-3; Eu^{3+}, 22541-18-0; Eu^{2+}, 16910-54-6; Cr^{3+}, 16065-83-1; Cr^{2+}, 22541-79-3; Yb^{3+}, 18923-27-8; Yb^{2+}, 22541-96-4; U^{4+}, 16089-60-4; U^{3+}, 22578-81-0; Np^{4+}, 22578-82-1; Np^{3+}, 21377-65-1; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(en)_3^{3+}$, 21393-87-3; $Ru(en)_3^{2+}$, 21393-86-2; $Co(en)_3^{3+}$, 14878-41-2; $Co(en)_3^{2+}$, 23523-25-3; $Co(phen)_3^{3+}$, 18581-79-8; $Co(phen)_3^{2+}$, 16788-34-4; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(bpy)_3^{2+}$, 15878-95-2; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5py^{2+}$, 21360-09-8.

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Solid-State Structure and Electronic Properties of a Mixed-Valence Two-Dimensional Metal, KCu_4S_3

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KCu_4S_3, prepared by the high-temperature reaction of copper, potassium carbonate, and sulfur, crystallizes with a unique layered structure. Double layers of tetrahedrally coordinated (by S) copper ions are separated by layers of potassium ions. Although formally a mixed-valence Cu(I, I, I, II) complex, all copper ions are crystallographically equivalent. Consistent with its Robin and Day class III designation, KCu_4S_3 exhibits electrical conductivity characteristic of a metal. Room-temperature compaction conductivities of ca. 4000 Ω^{-1} cm^{-1} increase to ca. 60 000 Ω^{-1} cm^{-1} at 20 K. The metallic nature of this two-dimensional material is supported by the temperature-independent paramagnetism and the metallic reflectivity through the visible and near-ultraviolet region of the spectrum.

Introduction

In recent years there has been an intensive search for new materials which exhibit high electrical conductivity. Several factors motivate research in this area, including the desire to find new materials with high superconducting transition temperatures. This has been approached by both systematic modifications of known types of superconducting materials and also by the search for new types of superconducting materials, particularly the elusive "excitonic" superconductor.[2] At a more fundamental level, activity in the field has been sustained by the discovery of several new classes of conducting materials, most specifically the one- and two-dimensional conductors which have proven so important in our understanding of the electrical properties of solids.

One class of compounds which have been widely studied are the transition-metal chalcogenides, typified by TaS_2, which crystallize with layer structures.[3] Although most common with the early transition metals, a large number of compounds are known which have certain structural similarities, namely, strong covalent metal–sulfur bonding within a two-dimensional sheet and either weak (van der Waals) or ionic interactions between layers. Many of these materials exhibit either metallic (TaS_2) or semiconducting (MoS_2) electrical behavior, and in each case the properties are highly anisotropic. For example, one crystalline modification of TaS_2 exhibits metallic conductivity in the layers but semimetal or semiconducting behavior perpendicular to the layers, with an anisotropy in the resistivity as high as 500 at low temperatures.[4] Many of these materials exhibit superconductivity at low temperature. Several of these compounds are susceptible to chemical modification. TaS_2, for example, reacts either with organic bases such as pyridine (py) or with alkali metals by intercalation. The lattice expands perpendicular to the planes in order to accommodate the intercalate between the layers. Although the magnitude of the parallel conductivity does not vary greatly in such materials, both the anisotropy in the conductivity and the superconducting transition temperature do change. Thus, the metal sulfides and their ternary intercalates provide a rich area for examining high two-dimensional conductivity.

Although layered structures are relatively common among the sulfides of the early transition metals, the later members of the transition series such as copper tend to form sulfides where three-dimensional interactions prevail. We were intrigued by the report[5] that KCu_4S_3 adopts a layered structure.

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