Rate Constants and Activation Parameters for Outer-Sphere Electron-Transfer Reactions and Comparisons with the Predictions of Marcus Theory

Mei Chou, Carol Creutz, and Norman Sutin*

Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973.

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Abstract: Rate constants at 25 °C and activation parameters are reported for several outer-sphere electron-transfer reactions. The oxidants studied include $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5py^{3+}$, $Co(phen)_3^{3+}$, and $Ru(NH_3)_4(bpy)^{3+}$ while the reductants include Eu_{aq}^{2+}, V_{aq}^{2+}, $Ru(NH_3)_6^{2+}$, and $Ru(NH_3)_5py^{2+}$. From Marcus calculations using cross-reaction data, self-exchange rates for the $Eu_{aq}^{2+}/Eu_{aq}^{3+}$ and $Cr(bpy)_3^{2+}/Cr(bpy)_3^{3+}$ couples are estimated as 10^{-5} to 10^{-4} M^{-1} s^{-1} and 10^7 to 10^9 M^{-1} s^{-1}, respectively, at 25 °C and $\mu = 1.0$ M. The data for outer-sphere electron transfer reactions between 2+ and 3+ charged ions with known self-exchange rates are reviewed. Marcus theory is found to be reasonably successful in predicting the rate constants for the cross-reactions. In general, however, observed rate constants are smaller than the calculated values. The assumptions of the Marcus model are reviewed in an effort to determine where the model fails.

The Marcus theory for outer-sphere electron-transfer reactions predicts a simple relationship (eq 1) between the rate constant k_{12} for an electron-transfer reaction, K_{12} the equilibrium constant for the reaction, and k_{11} and k_{22} the self-exchange rate constants for the reductant and oxidant couples.[1] (Here Z is a collision frequency, generally taken as 10^{11} M^{-1} s^{-1}.) The Marcus theory is an adiabatic theory of electron transfer and thus proceeds from the assumption that, within the activated complex for electron transfer, the probability of electron transfer is unity. Some additional assumptions made in deriving eq 1 are that the work terms for the self-exchange and cross-reactions are the same, that the electron-transfer reagents may be treated as spherical, structureless reactants, and that the motions of the inner-coordination shells are harmonic (with the breathing force constant of species i having the reduced value $2f_i f_i^p/(f_i + f_i^p)$ regardless of whether it is in the oxidized or in the reduced state).

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$
$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)} \qquad (1)$$

When f_{12} in eq 1 is ~1 (that is when $(\log K_{12})^2$ and/or log $k_{11}k_{22}$ is sufficiently small), eq 1 may be simplified to give eq 2.

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

Thus if a series of related reactions with $f_{12} \sim 1$ is studied as a function of driving force, a plot of log k_{12} vs. log K_{12} should be linear, with slope 0.5 and an intercept 0.5 log $k_{11}k_{22}$. Since the publication of Marcus theory in 1959 several systems displaying the correct free energy dependence have been reported, for example the Fe_{aq}^{2+} reductions of the polypyridineiron(III) complexes[2] and the cerium(IV) oxidation of polypyridineiron(II) complexes.[3] The predictions of the theory have also been tested in numerous systems by comparing individual observed rate constants with those calculated according to eq 1. Some of these results will be mentioned specifically later. In general, in systems in which the best agreement between theory and experiment has been found, the calculated and observed rate constants agree within a factor of 10, with the observed rate constant almost invariably being smaller than that calculated from the Marcus equations.

In recent years the Marcus relation has been used by bioinorganic chemists and inorganic photochemists in efforts to characterize and understand the electron-transfer properties of metalloproteins[4,5] and the excited states of inorganic complexes.[6] For example, the reactions of the metalloprotein with inorganic oxidants or reductants with known self-exchange rates k_{11} were studied, and the self-exchange rate of the metalloprotein k_{22} was estimated[5] from eq 3.

$$k_{22} = (k_{12,\mathrm{obsd}})^2/k_{11}K_{12}f_{12} \qquad (3)$$

The same kind of analysis has also been applied to the excited state reactions. Obviously, a knowledge of the ability of the theory to predict the results of experiment is critical for the intelligent application of eq 3.

In the present study we have determined rate constants and activation parameters for several reactions between complexes with known self-exchange rates and compared these with the predictions of eq 1. We have also attempted to estimate self-exchange rates for the Eu_{aq}^{2+}-Eu_{aq}^{3+} and $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ couples using eq 3. Finally we have taken this opportunity to review much of the available data on outer-sphere electron-transfer reactions in an effort to assess the general reliability of the results of Marcus calculations.

Experimental Section

Materials. Reducing Agents. Solutions of vanadium(II) in perchloric or trifluoromethylsulfonic acid were prepared by amalgamated zinc reduction of vanadium(V) solutions made from V_2O_5 (Fisher). The reduced solutions were used within 5 h of preparation. Hexaammineruthenium(II) solutions were generated by reduction of $Ru(NH_3)_6^{3+}$ by (a) a slight deficiency of Eu_{aq}^{2+} in 0.1 M H^+ or (b) amalgamated zinc in 10^{-3} M H^+. Europium(II) solutions were prepared from amalgamated zinc reduction of Eu_{aq}^{3+} solutions made by dissolving Eu_2O_3 (Ventron) in perchloric or trifluoromethylsulfonic acid. Pentaamminepyridineruthenium(II) was made according to the procedure of Gaunder and Taube[7] and recrystallized from ~50 °C water.

Oxidizing Agents. Tris(1,10-phenanthroline)cobalt(III) perchlorate and tris(2,2′-bipyridine)cobalt(III) perchlorate were prepared according to the procedure given by Baker, Basolo, and Neumann.[8] Pentaamminepyridineruthenium(III) perchlorate was prepared by Ag(I) oxidation of the ruthenium(II) complex.[7] Tetraammine(2,2′-bipyridine)ruthenium(III) was generated by Ce(IV) oxidation of the ruthenium(II) complex which had been prepared from *cis*-tetraammineruthenium(III chloride according to Gaunder's method.[7] Tris(2,2′-bipyridine)chromium(III) perchlorate was prepared according to the procedure of Baker and Mehta.[9]

Trifluoromethylsulfonic acid was redistilled twice under vacuum (taking the center ~80% fraction) before use. Lithium trifluoromethylsulfonate was prepared from the redistilled acid and lithium carbonate which had been recrystallized from hot water. Argon was used as the blanket gas for all air-sensitive solutions.

Methods. Kinetic measurements were made on a Durrum stopped

Table I. Activation Parameters and Rate Constants at 25 °C for Some Outer-Sphere Electron-Transfer Reactions[a]

Reactants	Conditions	k, $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
V_{aq}^{2+}-$Ru(NH_3)_5py^{3+}$	1.0 M ClO_4^-	3.0×10^5	0.0	−33
V_{aq}^{2+}-$Co(phen)_3^{3+}$	1.0 M ClO_4^-	4.0×10^3	3.8	−29
	1.0 M $CF_3SO_3^-$	6.8×10^3		
V_{aq}^{2+}-$Cr(bpy)_3^{3+}$	1.0 M ClO_4^-	4.2×10^2		
$Ru(NH_3)_6^{2+}$-$Ru(NH_3)_5py^{3+}$	1.0 M $CF_3SO_3^-$	1.4×10^6		
$Ru(NH_3)_6^{2+}$-$Co(phen)_3^{3+}$	0.1 M NaCl (pH 8, 0.005 M Tris)	1.5×10^4	4.2	−25
$Ru(NH_3)_6^{2+}$-$Co(bpy)_3^{3+}$	0.1 M NaCl (pH 8, 0.005 M Tris)	1.1×10^4		
$Ru(NH_3)_5py^{2+}$-$Ru(NH_3)_4bpy^{3+}$	1.0 M ClO_4^-	$(1.1 \pm 0.4) \times 10^8$		
$Ru(NH_3)_5py^{2+}$-$Co(phen)_3^{3+}$	1.0 M $CF_3SO_3^-$	2.0×10^3	8.6	−15.0
$Co(phen)_3^{2+}$-$Ru(bpy)_3^{3+}$	0.33 M Na_2SO_4	$\geq 3 \times 10^7$		
Eu_{aq}^{2+}-$Co(phen)_3^{3+}$	1.0 M $CF_3SO_3^-$	9.0×10^2	1.8	−35
Eu_{aq}^{2+}-$Ru(NH_3)_5py^{3+}$	1.0 M ClO_4^-	5.4×10^4	0.0	−37

[a] 0.1 M H^+, 0.9 M Li^+ unless otherwise stated.

flow spectrophotometer[10] equipped with Teflon-covered drive syringe pistons and a 2-cm cuvette. In most experiments the reducing agent was in at least tenfold excess over the oxidant so that pseudo-first-order kinetics obtained, and the plots of log $(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances at time t and infinity, were linear for greater than 90% of the reaction. However, for the $Ru(NH_3)_5py^{2+}$-$Ru(NH_3)_4bpy^{3+}$ reaction the reactants were at equal ($\sim 10^{-5}$ M) concentrations and the absorbance-time behavior was analyzed from plots of $(A_t - A_\infty)^{-1}$ vs. time. Reactions involving $Ru(NH_3)_5py^{n+}$ were followed at 407 nm for $Co(phen)_3^{3+}$ as oxidant, and at 400, 310, 380, and 407 nm for Eu_{aq}^{2+}, V_{aq}^{2+}, $Ru(NH_3)_6^{2+}$, and $Ru(NH_3)_5py^{2+}$, respectively, as reductants. The $Ru(NH_3)_5py^{2+}$-$Ru(NH_3)_4(bpy)^{3+}$ reaction was followed at 523 nm, and the reduction of $Cr(bpy)_3^{3+}$ by V_{aq}^{2+} was monitored at 562 nm.

Table II. Estimates of the Eu_{aq}^{2+}-Eu_{aq}^{3+} and $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ Self-Exchange Rates (k_{11}) at 25 °C from Cross-Reaction Rate Constants

Reactants	k_{12}, $M^{-1}\,s^{-1}$	k_{11},[a] $M^{-1}\,s^{-1}$
Eu_{aq}^{2+}-$Co(en)_3^{3+}$	$\sim 5 \times 10^{-3}$ [b]	9.2×10^{-4}
Eu_{aq}^{2+}-$Ru(NH_3)_6^{3+}$	2.3×10^3 [c]	8.6×10^{-6}
Eu_{aq}^{2+}-$Ru(NH_3)_5py^{3+}$	5.4×10^4	5.0×10^{-8}
Eu_{aq}^{2+}-$Co(phen)_3^{3+}$	9.0×10^2	1.6×10^{-8}
Eu_{aq}^{2+}-Fe_{aq}^{3+}	9.5×10^3 [d]	1×10^{-10}
$Cr(bpy)_3^{2+}$-$Co(en)_3^{3+}$	1.8×10^2 [b]	1.1×10^9
V_{aq}^{2+}-$Cr(bpy)_3^{3+}$	4.2×10^2	1.4×10^7
$Cr(bpy)_3^{2+}$-$Co(NH_3)_6^{3+}$	6.9×10^2 [b]	$1\text{-}3 \times 10^8$ [e]

[a] These values are calculated from eq 3 using the potential and self-exchange data in Table III. The values −0.43 V (W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, Englewood Cliffs, N.J., 1952) and −0.25 V[9] were used for the Eu_{aq}^{3+}-Eu_{aq}^{2+} and $Cr(bpy)_3^{3+}$-$Cr(bpy)_3^{2+}$ potentials, respectively. [b] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964). [c] M. Faraggi and A. Feder, *Inorg. Chem.*, **12**, 236 (1973), value for 1.0 M $NaClO_4$. [d] D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968). [e] C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).

Results

For all the oxidation-reduction reactions studied the reaction rate is given by

$$-\frac{d[Ox]}{dt} = k_{12}[Ox][Red] \qquad (4)$$

The values of k_{12} at 25 °C and $\Delta H_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ data for some of the systems are summarized in Table I. Except where noted the reactions were studied in 1 M perchlorate or trifluoromethylsulfonate with 0.1 M H^+ and 0.9 M Li^+.

Where comparison is possible, the present results are in good agreement with results obtained by other workers. At 25 °C we find $k = 3.0 \times 10^5$ M^{-1} s^{-1} for the V_{aq}^{2+}-$Ru(NH_3)_5py^{3+}$ reaction. Although this is greater than the value 1.2×10^5 M^{-1} s^{-1} reported by Gaunder and Taube,[7] the latter number is based on a limited number of runs with V_{aq}^{2+} in only threefold excess. The rate constant (4.0×10^3 M^{-1} s^{-1}) obtained for the V_{aq}^{2+}-$Co(phen)_3^{3+}$ reaction is in excellent agreement with the value 3.8×10^3 M^{-1} s^{-1} reported by Przystas and Sutin.[11] The rate constant 1.4×10^6 M^{-1} s^{-1} obtained here for the $Ru(NH_3)_6^{2+}$-$Ru(NH_3)_5py^{3+}$ reaction at 1 M ionic strength seems quite consistent with the value $(7.2 \pm 0.4) \times 10^5$ M^{-1} s^{-1} at 0.1 M ionic strength.[12] The $Ru(NH_3)_6^{2+}$-$Co(bpy)_3^{3+}$ reaction ($k = 1.1 \times 10^4$ M^{-1} s^{-1}) is, however, an exception; 2×10^5 M^{-1} s^{-1} has been reported for this reaction at 25 °C and 0.1 M ionic strength.[13]

Although perchlorate has been used as the preferred noncomplexing medium by most workers studying electron-transfer reactions, many systems do not readily lend themselves to this medium. Hexaammineruthenium(II) is both oxidized and precipitated by perchlorate. Tris(1,10-phenanthroline)cobalt(III) is only very slightly soluble in 1 M perchlorate. Thus much of the present work which involves these reagents rather frequently was carried out in a trifluoromethylsulfonate medium. Scott and Taube, in estimating the affinity of $Cr(H_2O)_6^{3+}$ for $Cr_3SO_3^-$, showed that the anion is only slightly more complexing than ClO_4^-.[14] The present results for the V_{aq}^{2+}-$Co(phen)_3^{3+}$ reaction ($k = 4.0 \times 10^3$ M^{-1} s^{-1} in 1 M ClO_4^- and 6.8×10^3 M^{-1} s^{-1} in 1 M $CF_3SO_3^-$) bear out the idea that the two media are nearly interchangeable. Unfortunately analogous data could not be obtained for the other systems.

In the course of our investigations of the reactions of the luminescent excited state of tris(2,2′-bipyridine)ruthenium(II), Eu_{aq}^{3+} and Eu_{aq}^{2+} proved very useful electron-transfer quenchers.[6,15] In order to make full use of the quenching results, the value of the self-exchange rate for the Eu_{aq}^{2+}-Eu_{aq}^{3+} couple was needed. From the work of Meier and Garner the chloride-free self-exchange rate k_{22} must be $\leq 2 \times 10^{-4}$ M^{-1} s^{-1} at 39 °C and 2 M ionic strength.[16] We had hoped to obtain a firmer estimate for the exchange rate at 25 °C and 1 M ionic strength from the rate constants for the reaction of europium(II) with oxidants of known exchange rate (Table II). Trial values of k_{11} were calculated from eq 3 using k_{22} and $E°$ values from Table III, with the values of f_{12} and k_{11} being iterated until the agreement between successive values was within ~10%. The results of this exercise (see Table II) proved quite surprising. The values of k_{11} obtained range from 10^{-3} to 10^{-10} M^{-1} s^{-1} and drop as the strength of the oxidant used increases. In fact the same behavior is observed for V_{aq}^{2+} and

Table III. Reduction Potentials and Self-Exchange Rates

Couples	$E°$, V	k_{ex}, $M^{-1}\,s^{-1}$
V_{aq}^{3+}-V_{aq}^{2+}	-0.255 [a]	3×10^{-3} [b,q] 1×10^{-2}
Cr_{aq}^{3+}-Cr_{aq}^{2+}	-0.40 [a]	$\leqslant 10^{-5}$ [r]
Fe_{aq}^{3+}-Fe_{aq}^{2+}	$+0.74$ [c]	4.0 [d]
Co_{aq}^{3+}-Co_{aq}^{2+}	$+1.96$ [a]	~ 5 [s]
$Co(en)_3^{3+}$-$Co(en)_3^{2+}$	-0.24 [k]	2.0×10^{-5} [l]
$Co(phen)_3^{3+}$-$Co(phen)_3^{2+}$	$+0.37$ [m]	4×10^{1} [n]
$Ru(NH_3)_6^{3+}$-$Ru(NH_3)_6^{2+}$	$+0.051$ [e]	4.3×10^{3} [f]
$Ru(NH_3)_5isn^{3+}$-$Ru(NH_3)_5isn^{2+}$	$+0.39$ [h]	4.3×10^{5} [g]
$Ru(NH_3)_5py^{3+}$-$Ru(NH_3)_5py^{2+}$	$+0.31$ [e]	4.3×10^{5} [g]
$Ru(NH_3)_4bpy^{3+}$-$Ru(NH_3)_4bpy^{2+}$	$+0.51$ [h]	2.1×10^{6} [g]
$Ru(bpy)_3^{3+}$-$Ru(bpy)_3^{2+}$	$+1.26$ [i]	2.0×10^{9} [j]
Fe(III)cyt c-Fe(II)cyt c	$+0.26$ [o]	1.2×10^{3} [p,q] 1×10^{4}

[a] W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Englewood Cliffs, N.J., 1952. [b] K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80,** 5921 (1958). [c] E. H. Swift, "A System of Chemical Analysis", Prentice-Hall, New York, N.Y., 1949, p 542. [d] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56,** 846 (1952). [e] H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11,** 1460 (1972). [f] T. J. Meyer and H. Taube, *Inorg. Chem.*, **7,** 2369 (1968). [g] G. Brown, H. Krentzien, and H. Taube, cited by H. Taube in *Adv. Chem. Ser.*, in press. [h] G. Brown, private communication. [i] Reference 6. [j] R. C. Young, F. R. Keene, and T. J. Meyer, *J. Am. Chem. Soc.*, **99,** 2468 (1977). The value reported (1.2×10^9 $M^{-1}\,s^{-1}$) has been corrected for the effects of diffusion control according to $1/k_{act} = 1/k_{obsd} - 1/k_{diff}$ using $k_{diff} = 3 \times 10^9$ $M^{-1}\,s^{-1}$. [k] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", Haase, Copenhagen, 1941, p 227. [l] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **65,** 1892 (1961) (0.2 M ionic strength). [m] A. Ciana and V. Crescenzi, submitted for publication. [n] H. M. Neumann, quoted in R. Farina and R. G. Wilkins, *Inorg. Chem.*, **7,** 514 (1968). [o] R. Margalit and A. Schejter, *Eur. J. Biochem.*, **32,** 492 (1973). [p] R. K. Gupta, S. H. Koenig, and A. G. Redfield, *J. Magn. Reson.*, **7,** 66 (1972); R. K. Gupta, *Biochim. Biophys. Acta*, **292,** 291 (1973). [q] At 0.1 M and 1 M ionic strength, respectively. [r] A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76,** 3826 (1954). [s] N. A. Bonner and J. P. Hunt, *J. Am. Chem. Soc.*, **82,** 3826 (1960).

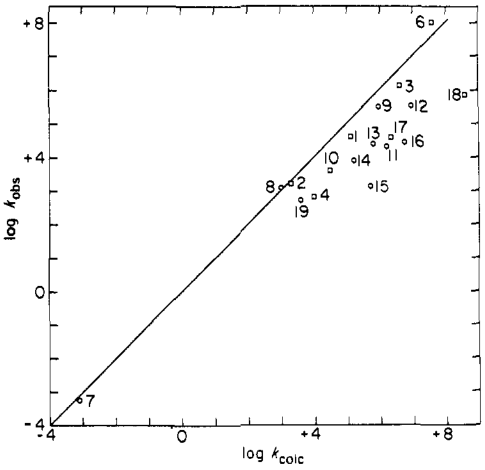

Figure 1. Logarithm of $k_{12,obsd}$ (the observed electron-transfer rate constant) vs. the logarithm $k_{12,calcd}$ (the rate constant calculated from eq 1) for reactions between +2 and +3 ions. The points are taken from and numbered according to Table IV. Squares are for reactions between nonaquo ions.

Cr_{aq}^{2+} reductions of the same oxidants (vide infra). For V_{aq}^{2+} (whose self-exchange rate has been directly measured) the agreement between observed and calculated exchange rates is very good only for the first two oxidants in Table II. Thus based on the $Co(en)_3^{3+}$ and $Ru(NH_3)_6^{3+}$ reactions the self-exchange rate for Eu_{aq}^{2+}-Eu_{aq}^{3+} at 25 °C and $\mu = 1.0$ M should be between 10^{-5} and 10^{-3} $M^{-1}\,s^{-1}$. Since the larger value appears too high based on the results of Meier and Garner, k_{11} 10^{-5} to 10^{-4} $M^{-1}\,s^{-1}$ would appear a more reasonable range. The first five entries in Table II show that eq 3 must be used with extreme caution in some systems. Even after the corrections appropriate at large driving force (the f_{12} term) the estimated k_{11} drops precipitously at large K_{12}; evidently eq 3 is best used when K_{12} is $\sim$1.

Also included in Table II are k_{11} values calculated for the $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ couple. From the $Co(en)_3^{3+}$, V_{aq}^{2+}, and $Co(NH_3)_6^{3+}$ reactions with $Cr(bpy)_3^{n+}$ (all of which have $K_{12} \sim 1$) the self-exchange rate for the $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ couple at 25 °C at $\mu = 1.0$ M is estimated to lie between 1.4×10^7 and 1.1×10^9 $M^{-1}\,s^{-1}$. Thus the exchange process appears to have only a very small activation barrier, as is expected from the electronic configurations ($(t_{2g})^4$-$(t_{2g})^3$) of the exchanging ions.

Comparison of Observed Rate Constants and Activation Parameters with the Predictions of Marcus Theory. In Table IV we have summarized the data available for outer-sphere electron-transfer reactions between +2 and +3 complexes with known self-exchange rates and reduction potentials. The calculated rate constants were obtained from eq 1 using the reduction potentials and exchange rates given in Table III. The same data are presented in Figure 1 in which log $k_{12,obsd}$ is plotted against log $k_{12,calcd}$. There it is apparent that the observed and calculated rate constants are in fair agreement for the 19 systems considered over a rate constant variation of 12 orders of magnitude. On the other hand, it is noteworthy that, with only two exceptions, the observed rate constants are consistently smaller than those calculated from eq 1.

In an effort to detect trends in the data, we have broken the data down into three classes: reactions between nonaquo ions, V_{aq}^{2+} and Eu_{aq}^{2+} reductions, and reactions of Fe_{aq}^{2+} or Fe_{aq}^{3+}. Data for the nonaquo ions are given as the first entries in Table IV and are marked with squares in Figure 1. For these ions, no particular trend is evident in the figure. All of the calculated rate constants lie within a factor of 10 of the observed values, and this must be taken as good agreement between theory and experiment. Unfortunately, with the exception of the diffusion-controlled $Ru(NH_3)_6^{2+}$-$Ru(bpy)_3^{3+}$ reaction (log $K_{12} = 20.5$) for which the agreement between theory and experiment is excellent, the available data for nonaquo ions encompass a rather limited free energy range (log $K_{12} \leqslant 6$). It would be of considerable value to know how other systems in this class behave at larger K_{12}. Since the reactants considered here are characterized by relatively high self-exchange rates (4×10^1 to 4×10^5 $M^{-1}\,s^{-1}$), their k_{12} values are relatively large and at log K_{12} values larger than $\sim$6, the rate constants exceed the limits of the stopped-flow technique. In order to investigate the behavior of the class at larger free energy changes some ingenuity will be required; nevertheless, it would be very useful to know if calculated and observed rate constants continue to agree within a factor of 10 over a wider free energy range.

Equation 1 may alternatively be expressed as eq 5

$$\Delta G_{12}^* = (\Delta G_{11}^* + \Delta G_{22}^*)/2 + \Delta G_{12}°(1 + \alpha)/2 \qquad (5)$$

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

and expressions for ΔS_{12}^* and ΔH_{12}^* may be obtained[17] by differentiating eq 5 with respect to temperature.

$$\Delta S_{12}^* = \left[\frac{\Delta S_{11}^* + \Delta S_{22}^*}{2}\right](1 - 4\alpha^2) + \frac{\Delta S_{12}°}{2}(1 + 2\alpha) \qquad (6)$$

Table IV. Comparison of Observed and Calculated Rate Constants

Reactants	Log K_{12}	$k_{12,\text{obsd}}$, $M^{-1}\,s^{-1}$	$k_{12,\text{calcd}}$, $M^{-1}\,s^{-1}$	$k_{\text{obsd}}/k_{\text{calcd}}$
(1) $Ru(NH_3)_6^{2+}$-Fe(III)cyt c	3.54	3.8×10^{4} [a]	1.2×10^{5}	0.32
(2) Fe(II)cyt c-$Co(phen)_3^{3+}$	1.86	1.5×10^{3} [b]	2.0×10^{3}	0.75
(3) $Ru(NH_3)_6^{2+}$-$Ru(NH_3)_5py^{3+}$	4.40	1.4×10^{6}	4.0×10^{6}	0.35
(4) $Ru(NH_3)_6^{2+}$-$Co(phen)_3^{3+}$	5.42	1.5×10^{4}	1.3×10^{5}	0.12
(5) $Ru(NH_3)_5py^{2+}$-$Co(phen)_3^{3+}$	3.39	2.0×10^{3}	1.1×10^{4}	0.18
(6) $Ru(NH_3)_5py^{2+}$-$Ru(NH_3)_4bpy^{3+}$	0.25	$(1.1 \pm 0.4) \times 10^{8}$	3.9×10^{7}	~2.5
(7) V_{aq}^{2+}-$Co(en)_3^{3+}$	5.19	5.8×10^{-4} [c]	7.2×10^{-4}	1.2
(8) V_{aq}^{2+}-$Ru(NH_3)_6^{3+}$	9.58	1.3×10^{3} [d]	9.9×10^{2}	1.3
(9) V_{aq}^{2+}-$Ru(NH_3)_5py^{3+}$	9.58	3.0×10^{5}	9.5×10^{5}	0.31
(10) V_{aq}^{2+}-$Co(phen)_3^{3+}$	10.59	4.0×10^{3}	3.2×10^{4}	0.13
(11) V_{aq}^{2+}-Fe_{aq}^{3+}	16.90	1.8×10^{4} [e]	1.7×10^{6}	0.011
(12) $Ru(NH_3)_6^{2+}$-Fe_{aq}^{3+}	11.7	3.4×10^{5} [f]	8.8×10^{6}	0.038
(13) $Ru(NH_3)_5isn^{2+}$-Fe_{aq}^{3+}	5.93	2.6×10^{4} [g]	6.3×10^{5}	0.042
(14) $Ru(NH_3)_4bpy^{2+}$-Fe_{aq}^{3+}	3.90	7.2×10^{3} [g]	1.7×10^{5}	0.042
(15) Fe_{aq}^{2+}-$Os(bpy)_3^{3+}$	1.53	1.4×10^{3} [h]	4.9×10^{5} [i]	2.9×10^{-3}
(16) Fe_{aq}^{2+}-$Fe(bpy)_3^{3+}$	3.90	2.7×10^{4} [j]	5.6×10^{6} [k]	4.9×10^{-3}
(17) Fe_{aq}^{2+}-$Fe(phen)_3^{3+}$	5.42	3.7×10^{4} [j]	2.3×10^{7} [k]	1.6×10^{-3}
(18) Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$	8.81	7.2×10^{5} [j]	3.6×10^{8}	2.0×10^{-3}
(19) $Co(phen)_3^{2+}$-Fe_{aq}^{3+}	6.27	5.3×10^{2} [c]	4.2×10^{3}	0.125
(20) $Co(phen)_3^{2+}$-$Ru(bpy)_3^{3+}$	15.08	$\geqslant 3 \times 10^{7}$	2.4×10^{9} [l]	$\geqslant 10^{-3}$
(21) $Ru(NH_3)_6^{2+}$-$Ru(bpy)_3^{3+}$	20.51	$(3.7 \pm 0.6) \times 10^{9}$ [m]	2.9×10^{9} [n]	~1

[a] R. X. Ewall and L. E. Bennett, *J. Am. Chem. Soc.*, **96**, 940 (1974). The oxidant is horse heart ferricytochrome *c*. [b] J. V. McArdle, H. B. Gray, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **96**, 5737 (1974). The reductant is horse heart ferrocytochrome *c*. [c] T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973). [d] C. A. Jacks and L. E. Bennett, *Inorg. Chem.*, **13**, 2035 (1974). [e] B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967). [f] T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968). [g] G. Brown, H. Krentzien, and H. Taube, cited by H. Taube in *Adv. Chem. Ser.*, in press. [h] B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83**, 2061 (1961). [i] Using the potential given in ref *i* and assuming the self-exchange rate to be the same as for $Ru(bpy)_3^{2+}$ (Table III). [j] Reference 2. [k] The potentials used were those summarized in ref 2. The self-exchange rate was taken to be the same as for $Ru(bpy)_3^{2+}$ (Table III). [l] Calculated from $1/k = 1/k_{\text{act}} + 1/k_{\text{diff}}$ with $k_{\text{act}} = 1.3 \times 10^{10}\ M^{-1}\,s^{-1}$ and $k_{\text{diff}} = 3 \times 10^{9}\ M^{-1}\,s^{-1}$. [m] C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974). [n] Calculated from $1/k = 1/k_{\text{act}} + 1/k_{\text{diff}}$ with $k_{\text{act}} = 3.9 \times 10^{10}\ M^{-1}\,s^{-1}$ and $k_{\text{diff}} = 3 \times 10^{9}\ M^{-1}\,s^{-1}$.

$$\Delta H_{12}{}^{*} = \left[\frac{\Delta H_{11}{}^{*} + \Delta H_{22}{}^{*}}{2}\right](1 - 4\alpha^2) + \frac{\Delta H_{12}{}^{\circ}}{2}(1 + 2\alpha) \qquad (7)$$

The relationships between ΔG^*, ΔH^*, and ΔS^* and the usual experimentally derived quantities are

$$\begin{aligned} \Delta G^{\ddagger} &= \Delta G^* - RT \ln (hZ/kT) \\ \Delta S^{\ddagger} &= \Delta S^* + R \ln (hZ/kT) - \tfrac{1}{2}R \\ \Delta H^{\ddagger} &= \Delta H^* - \tfrac{1}{2}RT \end{aligned} \qquad (8)$$

In Table V the observed activation parameters are compared with those calculated according to eq 6 and 7. With the exception of the $Ru(NH_3)_6^{2+}$-Fe_{aq}^{3+} reaction, the agreement between observed and calculated values is acceptable. For the remaining five systems, with the exception of the V_{aq}^{2+}-$Ru(NH_3)_6^{3+}$ reaction, the observed values of $\Delta H_{12}{}^{\ddagger}$ are 2-3 kcal mol^{-1} greater than those calculated from the cross-relations. Interestingly, the agreement between the calculated and observed $\Delta S_{12}{}^{\ddagger}$ values is somewhat better than for the enthalpies; the discrepancies scatter between +3 and −5 eu (with the exception of the V_{aq}^{2+}-$Co(phen)_3^{3+}$ reaction) so that the discrepancy in $T\Delta S^{\ddagger}$ is 0.9-1.5 kcal mol^{-1} at room temperature. The greatest *rate* discrepancies observed in Table IV and the various figures are for the V_{aq}^{2+}-Fe_{aq}^{3+} and Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$ reactions. The activation parameter comparisons in Table V indicate that the low observed rates result almost exclusively from the enthalpies of activation. This will be discussed later.

Discussion

Assumptions of the Marcus Model. The Marcus cross-reaction relation eq 1 is derived from eq 9[18] in which ΔG^* is the free energy barrier to electron transfer in an exchange or cross-reaction.

$$\Delta G^* = w + \frac{\lambda}{4} + \frac{(\Delta G^\circ + w^{p} - w)}{2} + \frac{(\Delta G^\circ + w^{p} - w)^2}{4\lambda} \qquad (9)$$

where

$$\lambda = \lambda_o + \lambda_i$$

$$\lambda_o = (ne)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$

$$\lambda_i = \frac{f_1 f_1{}^{p}}{f_1 + f_1{}^{p}}(\Delta a_1{}^0)^2 + \frac{f_2 f_2{}^{p}}{f_2 + f_2{}^{p}}(\Delta a_2{}^0)^2$$

In the above expressions w is the work required to bring the reactants together and w^p is the corresponding term for the products, ΔG° is the standard free energy change for the reaction, n is the number of electrons transferred, a_1 and a_2 are the radii of the two reactants (assumed spherical), and r, the distance between the centers of the reactants in the activated complex, is equal to $a_1 + a_2$ (in deriving eq 1 from eq 9 it is assumed that $(a_1 + a_2)/2 = (a_1 a_2)^{1/2}$). D_{op} and D_s are the square of the refractive index and dielectric constant of the medium, respectively, f_1 and $f_1{}^p$ are the force constants for the symmetrical breathing vibration of a species when it is a reactant and a product, respectively, $\Delta a_1{}^0$ $(=(a_1 - a_1{}^p))$ is the difference in the radius of species 1 when it is a reactant and a product, and λ_o and λ_i are parameters related to the reorganization of the outer- and inner-coordination shells of the reactants, respectively.

Newton[19] has examined the consequences of removing some of the assumptions of eq 9 namely (a) the assumption that the reduced force constants for the oxidized and reduced ion are the same (and equal to $2f_i f_i{}^p/(f_i + f_i{}^p)$) and (b) the assumption

Table V. Thermodynamic and Activation Parameters for Electron Transfer Reactions at 25 °C

					Obsd[b]		Calcd[c]	
Reactants	μ, M	$\Delta G°$,[a] kcal mol^{-1}	$\Delta H°$,[a] kcal mol^{-1}	$\Delta S°$,[a] cal deg^{-1} mol^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal deg^{-1} mol^{-1}	$\Delta H_{12}^‡$, kcal mol^{-1}	$\Delta S_{12}^‡$, cal deg^{-1} mol^{-1}
V_{aq}^{3+}-V_{aq}^{2+}	2	+5.87	+13.74	+26.4	12.6	−25		
Fe_{aq}^{3+}-Fe_{aq}^{2+}	0.55	−17.8	−9.6	+27.4	9.3	−25		
$Ru(NH_3)_6^{3+}$-Ru-$(NH_3)_6^{2+}$	0.01	−1.17	−7.24[d]	−17[d]	10.3	−11		
$Co(phen)_3^{3+}$-Co-$(phen)_3^{2+}$	0.01	−9.2	−10.3	−3.6	5.1	−34		
$Co(bpy)_3^{3+}$-$Co(bpy)_3^{2+}$	0.1	−8.5	−8.4	+0.2	7.7	−27		
V_{aq}^{2+}-Fe_{aq}^{3+}	1.0	−23.1	−23.3	+1.0	4.0[f]	−25.5[f]	+2.1	−24.4
V_{aq}^{2+}-$Ru(NH_3)_6^{3+}$	0.1	−7.03	−21.0	−43.4	0.6	−42	+2.1	−36.9
V_{aq}^{2+}-$Co(phen)_3^{3+}$	1.0	−15.1	−24.0	−30.0	3.8	−29	−0.7	−39.5
V_{aq}^{2+}-$Co(bpy)_3^{3+}$	2.0	−14.4	−22.1	−26.2	3.6[g]	−33[g]	+1.1	−36.1
$Ru(NH_3)_6^{2+}$-Co-$(phen)_3^{3+}$	0.1	−8.0	−3.1	+13.4	4.2	−25	2.7	−26
$Ru(NH_3)_6^{2+}$-Fe_{aq}^{3+}	0.1	−16.6	−2.4	44.4	3.2	−22	7.91	−2.1
Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$ [e]	1.0	−13.9	−26.8	−43	−0.3	−33	−2.9	−29

[a] Thermodynamic data taken from the references given in Table III unless otherwise stated. For the exchange reactions, $\Delta H°$ and $\Delta S°$ refer to the reaction $M^{3+} + \frac{1}{2}H_2 = M^{2+} + H^+$, while for the cross-reactions these entries refer to the reaction $M^{2+} + N^{3+} = M^{3+} + N^{2+}$. [b] Kinetic data taken from the references given in Table II. [c] Calculated from eq 5. [d] D. K. Lavallee, C. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **12,** 570 (1973). [e] From Table I in ref 15. [f] A. Ekstrom, A. B. McLaren, and L. E. Smythe, *Inorg. Chem.*, **15,** 2853 (1976). [g] R. Davies, M. Green, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1171 (1972).

of harmonicity. Concerning the force constant assumption, Newton found that the differences in ΔG_{12}^* calculated without assumption a (using eq 9 for the exchange reactions and minimizing the ΔG_{12}^*) and with assumption a (using eq 1) could only amount to ~8% which is much smaller than the observed discrepancies. The differences between the two free energy calculations were found to be greatest for highly exergonic reactions ($\Delta G_{12}° = -30$ kcal mol^{-1}). These comparisons thus suggest that the assumption of equal (reduced) force constants for the oxidized and reduced ions of a redox couple is not the origin of the discrepancies observed in the present data.

With regard to the harmonicity assumption, Newton found that the introduction of anharmonicity (relaxation of assumption b) resulted in corrections of only 1-2% in ΔG_{12}^* (for $\Delta G_{12}° = -15$ kcal mol^{-1}, the only case considered). Recently Søndergaard, Ulstrup, and Jortner have also considered anharmonic effects in a general way.[20] They found that, to the extent that the potentials of the reactants were anharmonic, the reorganization energy was increased for motions involving compression of the complex and decreased for stretching motions. Although the magnitudes of the effects of the anharmonicity on electron-transfer rate constants were found to be difficult to predict without a detailed knowledge of the vibrational potentials of the reactants, the effects were found to cancel to a large extent. Similarly, a detailed calculation of anharmonic effects for a hypothetical Fe_{aq}^{2+}-Fe_{aq}^{3+} exchange with an exothermicity of ~1 V indicates almost complete cancellation of the anharmonic contributions to the activation barrier.[21] Thus depending on the detailed shapes of the reactants' and products' potential energy surfaces, anharmonic effects may be more or less important.

Differences in the stabilities of the precursor and successor complexes for the exchange and cross-reactions (including work terms for bringing the reactants together and separating the products) were neglected in the derivation of eq 1. These are incorporated in eq 10[11]

$$k_{12} = \left[\frac{P_{12}P_{21}k_{11}k_{22}K_{12}f_{12}}{P_{11}P_{22}}\right]^{1/2} \tag{10a}$$

$$\log f_{12} = \frac{[\log (K_{12}P_{21}/P_{12})]^2}{4 \log (k_{11}k_{22}h^2/P_{11}P_{22}k^2T^2)} \tag{10b}$$

where P_{11}, P_{22}, and P_{12} are the stability constants of the precursor complexes for the exchange and cross-reactions and P_{21} is the stability constant of the successor complex for the cross-reaction. Considering eq 10a, there are certainly cases where this equation is not expected to reduce to eq 1 even when f_{12} is ~1 simply because $P_{12}P_{21} \neq P_{11}P_{22}$. For cross-reactions between oppositely charged ions $P_{12}P_{21}$ will be greater than $P_{11}P_{22}$ since the cross-reaction (and not the exchange reactions) benefits from the electrostatic interaction between the ions. For such cross-reactions k_{12} calculated from eq 1 should be less than the observed value. On the other hand, for cross-reactions involving very different kinds of ions, nonelectrostatic contributions to the work terms may give rise to a situation in which $P_{11}P_{22} \gg P_{12}P_{21}$. Under these conditions rate constants calculated from eq 1 for these reactions will be too slow by $(P_{12}P_{21}/P_{11}P_{22})^{1/2}$.

Although eq 10 reduces to eq 1 if $P_{12}P_{21} \approx P_{11}P_{22}$ and $f_{12} \approx 1$, if f_{12} becomes small, deviations from eq 1 may occur even when $P_{12}P_{21} \approx P_{11}P_{22}$. In the not unlikely event that P_{12}/P_{21} ~1, effects from the denominator of the $\log f_{12}$ term (eq 10b) may dominate. Under these conditions, for $P_{11}P_{22} > 1$, rates calculated using eq 1 will be smaller than those from eq 6, while for $P_{11}P_{22} < 1$, the opposite will be true. Thus even for systems in which $P_{12}P_{21} \approx P_{11}P_{22}$ the observed rate constants should be larger than those calculated from eq 1 when the driving force becomes very large (or small) if $P_{11}P_{22} > 1$. Conversely when $P_{11}P_{22} < 1$, rate constants calculated from eq 1 should exceed the observed values at very large (or very small) driving force. For the reactions considered here the reactants are +2 and +3 ions. At 1 M ionic strength (appropriate to most of the cross-reactions and some of the exchange reactions) the ion-pairing constants P_{ii} are likely to be of the order of 10^{-4} to 10^{-2} M^{-1} [22] and certainly do not exceed 1. Thus only the case where $P_{11}P_{22} < 1$ is likely to be relevant and, at least to some extent, the behavior expected for this case is that qualitatively observed—that is, the observed rates are generally smaller than those calculated from eq 1. We shall return to the question of noncancellation of work terms in greater detail when specific systems are discussed in the next section of the paper.

The last assumption of the Marcus treatment we consider is that of adiabaticity. If p_{11} and p_{22} are the electron-transfer probabilities for the self-exchange processes for which k_{11} and k_{22} are the experimentally determined self-exchange rates, the Marcus equations may be modified as follows:[23]

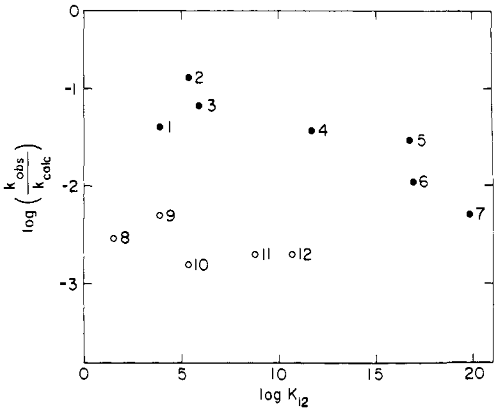

Figure 2. Logarithm of ($k_{12,obsd}/k_{12,calcd}$) (observed and calculated electron-transfer rate constants) vs. the logarithm of K_{12} (the equilibrium constant for the electron transfer) for reactions involving Fe_{aq}^{2+} and Fe_{aq}^{3+}. For the solid circles the reactants are Fe_{aq}^{3+} and 1, $Ru(NH_3)_4bpy^{2+}$; 2, $Co(phen)_3^{2+}$; 3, $Ru(NH_3)_5(isonicotinamide)^{2+}$; 4, $Ru(NH_3)_6^{2+}$; 5, $Cr(bpy)_3^{2+}$; 6, V_{aq}^{2+}; 7, Eu_{aq}^{2+}. For the open circles the reactants are Fe_{aq}^{2+} and 8, $Os(bpy)_3^{3+}$; 9, $Fe(bpy)_3^{3+}$; 10, $Fe(phen)_3^{3+}$; 11, $Ru(bpy)_3^{3+}$; 12, RuL_3^{3+} (L = 5-chloro(1,10-phenanthroline)). For reactions 8-12 the exchange rate was assumed to be that for $Ru(bpy)_3^{n+}$ given in Table III.

$$k_{12} = p_{12}\left[\frac{k_{11}k_{22}K_{12}f_{12}}{p_{11}p_{22}}\right]^{1/2}$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/p_{11}p_{22}Z^2)} \qquad (11)$$

As has been pointed out previously eq 11 reduces to eq 1 if $p_{12} \approx (p_{11}p_{22})^{1/2}$ and $f_{12} \approx 1$.[23] Thus even if the self-exchange and cross-reactions are nonadiabatic, the simple Marcus cross-relation eq 1 will adequately predict k_{12} values when $p_{12} \sim (p_{11}p_{22})^{1/2}$ provided that the driving force for electron transfer is not so great that the f correction becomes substantial. When, however, K_{12} does become large the simple cross-relation (eq 1) is expected to break down even though $p_{12} \sim (p_{11}p_{22})^{1/2}$. The use of k_{11} and k_{22}, the observed (nonadiabatic) exchange rates, rather than k_{11}/p_{11} and k_{22}/p_{22}, the "intrinsic" adiabatic exchange rates, results in f_{12} values which are too large. Consequently the discrepancy between $k_{12,obsd}$ and $k_{12,calcd}$ is expected to increase as the net free energy change increases if the cross-reaction and one or both of the self-exchange reactions are nonadiabatic. Thus it would appear that deviations from adiabaticity could be responsible for the discrepancies between the calculated and observed rate constants in Table IV. This question will be discussed more fully for specific systems in the next section.

Trends in the Deviations between Theory and Experiment for Specific Systems. In Figures 2 and 3 the logarithm of $k_{12,obsd}/k_{12,calcd}$ (from Table IV) is plotted against the driving force for electron-transfer reactions involving some aquo ions. In general the agreement between theory and experiment is much better for the V_{aq}^{2+} reactions (Figure 3) than for the Fe_{aq}^{n+} reactions (Figure 2). This is true whether common free energy change or common reaction partner is considered: in the log K_{12} range 0-10, the vanadium points lie between log (k_{obsd}/k_{calcd}) = 0 and −0.5 while the iron points fall between −0.9 and −1.4. Comparing common reaction partners, for $Ru(NH_3)_6^{n+}$ the V_{aq}^{2+} rate constant is 1.3 times that calculated while the Fe_{aq}^{3+} rate constant is 25 times too small; for $Ru(NH_3)_5py^{n+}$ the V_{aq}^{2+} rate constant is a factor of 2 smaller than calculated while that for Fe_{aq}^{3+} is again 25 times too small. Interestingly, however, for both aquo ions the $Co(phen)_3^{n+}$ rate constants are about eight times smaller than calculated.

A striking feature of the V_{aq}^{2+} data is the apparent increase in the deviation between theory and experiment as log k_{12} increases. The same pattern is found for Eu_{aq}^{2+} and Cr_{aq}^{2+} reductions of the same oxidants as is required since rate constants for outer-sphere reaction of these reductants are in a constant ratio. In fact, points calculated for europium(II) assuming a self-exchange rate of 1×10^{-4} M^{-1} s^{-1} at 25 °C and μ = 1 M are included in Figure 3 and follow the pattern observed for vanadium(II). The same effect could be present in the Fe_{aq}^{3+} data to a smaller extent if points 1-7 are considered but the Fe^{2+}-$M(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine, M = Fe, Ru, Os) data (points 8-12) are excluded. The latter systems are all too slow by about a factor of 500, evidently independent of driving force, although the range of log K_{12} spanned for these is not large. To summarize, at best the Fe_{aq}^{n+} reactions are a factor of 10 too slow with a possible weak driving force dependence and the Fe^{2+}-$M(bpy)_3^{3+}$ reactions appear to be a separate class where the fit is much poorer. For V_{aq}^{n+} reactions, agreement between theory and experiment is excellent at small driving force and grows poorer with increasing driving force. The data thus suggest the possible operation of two sources of deviation, one of which is important even at small driving force and one of which becomes important only at large driving force. Possible sources for the two kinds of deviation are now considered in turn.

The very poor agreement of the Fe_{aq}^{2+}-$M(bpy)_3^{3+}$ reactions has been previously noted:[2,3,6] for the reaction series Fe_{aq}^{2+}-FeL_3^{3+} [2,3] (L a 2,2′-bipyridine or 1,10-phenanthroline derivative) and Fe_{aq}^{2+}-RuL_3^{3+} [6] plots of log $k_{12,obsd}$ vs. log K_{12} are linear with slope 0.5, the discrepancy between $k_{12,calcd}$ and $k_{12,obsd}$ being entirely in the intercepts of the plots. It has been proposed[2,3] that this discrepancy arises from noncancellation of work terms, i.e. $P_{12}P_{21} \neq P_{11}P_{22}$ in eq 10. This explanation now seems less attractive in light of the fact that the $Co(phen)_3^{2+}$-Fe_{aq}^{3+} reaction is only a factor of 8 (rather than 500) too slow and it does not seem likely that P_{11}, P_{12}, and P_{21} differ greatly for the $Co(phen)_3^{n+}$ and ML_3^{n+} systems. What then is the origin of the slowness of the Fe_{aq}^{2+}-ML_3^{3+} reactions? In light of the $Co(phen)_3^{2+}$-Fe_{aq}^{3+} results, the large discrepancy observed for the iron, osmium, and ruthenium polypyridine complexes cannot result merely from the presence of the polypyridine ligands, but must rather depend on properties of the complex as a whole. We restate the question as "How do $Fe(phen)_3^{3+}$ and its congeners differ from $Co(phen)_3^{3+}$?" The iron, ruthenium, and osmium complexes manifest several unusual properties as a class: in the divalent state there is relatively strong mixing of metal d and ligand π^* orbitals so that significant metal electron density exists on the ligands. Another outstanding (and related) property of this class is their very high self-exchange rates—$\sim 1.2 \times 10^9$ M^{-1} s^{-1} (Table III) which are very nearly diffusion controlled. The first property above is in part responsible for the second one. The back-bonding interaction has the effect of shortening the metal(II)-nitrogen bonds so that the inner-shell reorganization barrier to electron transfer is lowered. In part the introduction of the relatively large pyridine into the coordination shell of the metal helps to lower the outer-shell electron transfer barrier by virtue of the increase in ion size. However, the latter is obviously not the dominant factor since $Co(phen)_3^{3+}$, for which the self-exchange rate is ~40 M^{-1} s^{-1} at 25 °C, is about the same size as $Fe(phen)_3^{3+}$.[24]

There is another possible reason why the presence of pyridine ligands in the iron, osmium, and ruthenium complexes gives rise to such large self-exchange rates. Manipulation of space-filling models of the tris(bipyridine) and -phenanthroline complexes shows that "stacked" overlap of a pyridine ring in one complex with one pyridine in another complex is quite favorable. This contact (in which the metal-metal distance is ~7 Å) may offer an especially facile pathway for the self-exchange reaction. In the divalent complexes appreciable d electron density is found in the ligand π^* orbitals by virtue of the back-bonding interaction. Similarly, in the trivalent complex the acceptor d orbital (which is half-occupied) extends to the pyridine periphery of the molecule. Stacked overlap of the π^* lobes of pyridines in different molecules could thus provide a π^*-π^* electron-transfer pathway. Such a pathway would seem to be highly favorable for the self-exchange reaction in the iron, ruthenium, and osmium polypyridine complexes, especially since the bulk of the ligands is so great that direct d-d overlap is largely prevented. The above geometry for the exchange reactions also has the effect of substantially lowering λ_o (eq 9), the intrinsic outer-sphere barrier to electron transfer. When contact of hard spheres is assumed for the ML_3^{2+}-ML_3^{3+} exchange $\lambda_o/4 \sim 3.2$ kcal mol^{-1} which, even if the inner-sphere barrier is zero and work terms are neglected, imposes an upper limit of 5×10^8 M^{-1} s^{-1} for the exchange rate at 25 °C. However, λ_o will be negligible if interpenetration of the ML_3^{2+} and ML_3^{3+} coordination spheres reduces the metal-metal separation substantially. In fact some special feature of this kind is required to explain the activation-controlled rate constant of 2×10^9 M^{-1} s^{-1}. By contrast, for the $Co(phen)_3^{3+}$-$Co(phen)_3^{2+}$ exchange the absence of back-bonding and therefore of appreciable d electron density on the ligand should preclude the operation of a π^*-π^* pathway.

Next we consider the pathways possible for the reaction of Fe_{aq}^{2+} and Fe_{aq}^{3+} with the polypyridine complexes. In the $Co(phen)_3^{2+}$-Fe_{aq}^{3+} reaction electron transfer probably proceeds via (admittedly) poor d-d orbital overlap. Thus the cross-reaction should, in geometric and energetic requirements, resemble the individual exchange reactions. The iron, ruthenium, and osmium polypyridine reactions with Fe_{aq}^{2+} and Fe_{aq}^{3+} may, on the other hand, be envisaged as proceeding in either of two ways: the model manipulation exercises indicate that an octahedral face of the aquo ion may sit above the channel between the bipyridines enabling direct (and poor) t_{2g}-t_{2g} overlap. Alternatively the octahedral face of the aquo ion may sit above the plane of a pyridine ring so that there is Fe_{aq}^{n+} t_{2g}-bipyridine π^* interaction. Which of these configurations is favored for the electron-transfer reaction depends on steric factors and the relative magnitudes of the two kinds of overlap.

We have now identified a probable difference between the iron, ruthenium, and osmium polypyridine and the $Co(phen)_3^{2+/3+}$ systems. Self-exchange in the latter could involve direct d-d overlap (complicated by the spin multiplicity change), while self-exchange in the former probably involves mediation by the ligands. Further we have ascribed the apparent slowness of the Fe_{aq}^{2+}-ML_3^{3+} (M = Fe, Os, Ru) cross-reactions to the fact that the cross-reactions cannot proceed via a detailed pathway which is common to the exchange processes for both reactants. This mismatch could result in a breakdown of the Marcus model for either of two reasons. The first possibility is that the cross-reaction is nonadiabatic, and that, furthermore, $p_{12} \neq (p_{11}p_{22})^{1/2}$. (That is, even if the exchange reactions are nonadiabatic the simple geometric mean expression is not adequate.) One implication of this hypothesis is that the d-d overlap and/or the Fe_{aq}^{2+} d-ML_3^{3+} π^* overlap in the cross-reaction is much poorer than the geometric mean of the d-d and π^*-π^* overlaps of the exchange reactions. Nonadiabatic effects are expected to be manifested in $\Delta S_{12}^{\ddagger}$. However, as mentioned earlier the calculated and observed values of $\Delta S_{12}^{\ddagger}$ for the Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$ reaction (−29 and −33 cal deg^{-1} mol^{-1}, respectively) are in very good agreement and the bulk of the rate discrepancy appears to arise from $\Delta H_{12}^{\ddagger}$. This does not necessarily rule out a nonadiabatic mechanism since the factors determining the probability of the actual electron transfer are not entirely temperature independent.

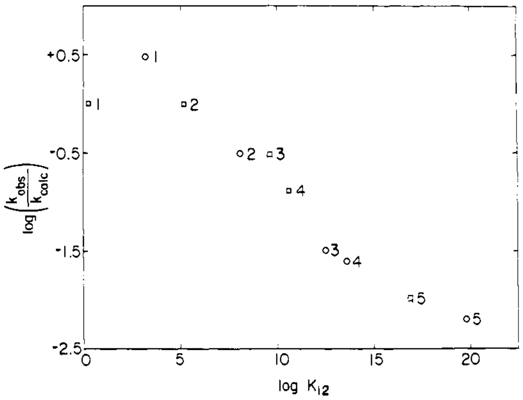

Figure 3. Logarithm of the ratio ($k_{12,\mathrm{obsd}}/k_{12,\mathrm{calcd}}$) (the observed and calculated electron-transfer rate constants) vs. the logarithm of K_{12} (the equilibrium constant for the electron-transfer reaction) for V_{aq}^{2+} (squares) and Eu_{aq}^{2+} (circles) reductions of 1 $Co(en)_3^{3+}$, 2 $Ru(NH_3)_6^{3+}$, 3 $Ru(NH_3)_5py^{3+}$, 4 $Co(phen)_3^{3+}$, and 5 Fe_{aq}^{3+}. The V_{aq}^{2+} data are from Table IV; the Eu_{aq}^{2+} data are from Table II with $k_{11} = 10^{-4}$ M^{-1} s^{-1} used in calculating k_{12}.

There is a second possibility, however. The Marcus treatment assumes that the interaction between reactant and product surfaces is large enough for the probability of crossing to be unity (splitting energy ~0.5 kcal mol^{-1}), but not so large that the height of the barrier is appreciably lowered. It is conceivable that the π^*-π^* interaction proposed above for the ML_3^{2+}-ML_3^{3+} exchange reactions results in a splitting energy too large for the assumptions of the original Marcus treatment to apply. If this is the case the exchange reaction would be effectively too rapid; that is, its rate will not be determined by the zero-interaction barrier but by a barrier lowered by the interaction energy. In cross-reactions where the special π^*-π^* interaction operative in the exchange process is not possible the zero-interaction approximation determines the appropriate intrinsic electron-transfer barrier. As this π^*-π^* interaction should lead to a lowered $\Delta H^{\ddagger}$ for the exchange reaction this interaction could account for the disagreement between the observed and calculated values of $\Delta H_{12}^{\ddagger}$ in the Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$ reaction. A troubling aspect of this model is the magnitude of the splitting energy (~4 kcal mol^{-1}) which would be needed for the observed effects. Conceivably both kinds of effects (nonadiabatic cross-reaction and large-splitting exchange reaction) could be operative.

Returning to Table IV and Figure 2, it is interesting that for the Fe_{aq}^{3+} oxidations of $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5isn^{2+}$ (isn = isonicotinamide), and $Ru(NH_3)_4(bpy)^{2+}$ the rate constants reported are all a factor of 25 lower than those calculated from theory, while the Fe_{aq}^{2+} reduction of $Ru(bpy)_3^{3+}$ is 500 times too slow. This behavior could also be taken to support the idea that the latter cross-reaction is nonadiabatic because of the poor Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$ interaction: in the ruthenium ammine-$iron_{aq}^{n+}$ reaction d-d overlap at octahedral faces of the iron and ruthenium complexes is feasible, but in the Fe_{aq}^{2+}-$Ru(bpy)_3^{3+}$ reaction such overlap would be very poor.

Above we have considered the specific case of the Fe_{aq}^{2+}-ML_3^{3+} reactions where the agreement between theory and experiment is poorest and have sought explanations for the discrepanices in the specific structures and electronic configurations of the reactants. It is, however, worthwhile reiterating that nearly all the Fe_{aq}^{n+} reactions are anomalously slow; we have not suggested any explanations for this general phenomenon.

Returning now to the V_{aq}^{2+} data, we consider factors which may result in a failure of eq 1 at large driving force. If the effects observed in Figure 3 are associated with breakdown in the work term assumptions it could be that, while $P_{12}P_{21} \approx P_{11}P_{22}$ for all the reactions, $P_{11}P_{22}$ is small. As P_{ii} is not likely to be less than 10^{-4} M^{-1} we have calculated k_{12} values from eq 10 assuming $P_{11}P_{22} = 10^{-8}$ M^{-2}. For the V_{aq}^{2+} reduction of $Co(en)_3^{3+}$, $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5py^{3+}$, $Co(phen)_3^{3+}$, and Fe_{aq}^{3+} the k_{12} values obtained in this way from eq 10 were 7.2×10^{-4}, 8.9×10^2, 6.4×10^5, 2.2×10^4, and 0.8×10^6 M^{-1} s^{-1}, respectively. These are to be compared with the values given in the fourth column of Table IV which were computed using eq 1. It is obvious from the comparison that this kind of work term correction gives values which lie within a factor of 2 of the values from eq 1. Thus this effect does not appear to be large enough to account for the observed discrepancies.

As mentioned earlier the deviations could be due to nonadiabatic effects. We first discuss the situation analogous to that just considered for the work terms; that is $p_{12} = (p_{11}p_{22})^{1/2}$ but $p_{12} < 1$ since $p_{22} < 1$. In this model, the cross-relation eq 1 is expected to work well when $f_{12} \sim 1$, but may break down at small f_{12} values. In evaluating the merits of this explanation we first consider whether it is reasonable to assume that the europium, vanadium (and chromium) self-exchanges are nonadiabatic (i.e., that $p_{11} < 1$). Most workers studying outer-sphere electron-transfer processes have assumed that these reactions are adiabatic. However, the possibility that they are not has been considered[23] and it has also been pointed out that many of the lanthanide and actinide electron-transfer reactions may be nonadiabatic.[25] For Eu_{aq}^{2+}–Eu_{aq}^{3+} the transferred 4f electron is heavily shielded from the environment (including solvent, ligands, and the oxidant acceptor orbital) by the $n = 5$ s, p, and d electrons. Thus, in the exchange process the degree of interaction between the 4f donor and acceptor orbital can be only very weak so that it seems very likely that electron exchange occurs in only a small fraction of the activated Eu_{aq}^{2+}–Eu_{aq}^{3+} pairs. By contrast, for the V_{aq}^{2+}–V_{aq}^{3+} and Cr_{aq}^{2+}–Cr_{aq}^{3+} exchanges the 3d electrons involved are not especially shielded and there are no obvious electronic factors to support the idea that these exchange processes are nonadiabatic. The magnitudes of the self-exchange rates observed for Cr_{aq}^{2+}, V_{aq}^{2+}, and other first transition series aquo ions (first four entries in Table III) may have bearing on this question. Based on size considerations, the exchange rates for the aquocobalt and aquoiron systems are expected to be similar, as indeed they are.[26] On the same basis, however, the V_{aq}^{2+}–V_{aq}^{3+} exchange should be faster than either; in reality it is ~400 times slower. Furthermore, even though the Cr_{aq}^{2+}–Cr_{aq}^{3+} exchange is expected to be the slowest of the set, it is at least three orders of magnitude slower than predicted.[26]

Evidently, then, the Eu_{aq}^{2+}, Cr_{aq}^{2+}, and V_{aq}^{2+} self-exchange reactions are slower than expected from eq 9 and this is in accord with the idea that the processes are nonadiabatic (although the possibility that this is an effect of anharmonicity cannot be ruled out at this time). Assuming that the V_{aq}^{2+}–V_{aq}^{3} self-exchange is nonadiabatic with $p_{22} = 10^{-2}$, we have evaluated eq 11 for the reactions considered in Figure 3 and obtain k_{12} values of 7.2×10^{-4}, 1.3×10^3, 6.1×10^5, 2.2×10^4, and 0.65×10^6 M^{-1} s^{-1} for $Co(en)_3^{3+}$, $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5py^{3+}$, $Co(phen)_3^{3+}$, and Fe_{aq}^{3+}, respectively. (For Fe_{aq}^{3+}, p_{11} was also assumed to be 10^{-2}.) As was found for the work term corrections, the modified equation (eq 10 or 11) fits the observed data better at larger free energy changes, but the improvement is really only very small. Here values calculated from eq 11 are only 30–100% smaller than those from eq 1. Thus it seems clear that corrections for nonadiabaticity with the constraint that $p_{12} \sim (p_{11}p_{22})^{1/2}$ do not give a large enough free energy dependence to account for the trend in Figure 3. Several possible explanations for the behavior remain: one is that the V_{aq}^{2+} and Eu_{aq}^{2+} reductions are nonadiabatic and that the nonadiabaticity is a function of driving force, that is, p_{12} decreases as $\Delta G_{12}°$ decreases. The other possibility is that anharmonic effects become increasingly important as the driving force increases and result in slower observed rate constants. Nonadiabatic effects should be manifested in the $\Delta S^{\ddagger}$ values and anharmonic effects in the $\Delta H^{\ddagger}$ values. As mentioned earlier the rate discrepancy for the V_{aq}^{2+}–Fe_{aq}^{3+} appears to result entirely from the $\Delta H^{\ddagger}$ contribution. From this result it seems likely that, even if the reactions are nonadiabatic, the cross-relation $p_{12} = (p_{11}p_{22})^{1/2}$ is followed very consistently. Thus the possibility that anharmonic effects can cause deviations in $\Delta H^{\ddagger}$ of ~2 kcal mol^{-1} should be considered. As greater knowledge of the force constants and potential energy curves of these complexes becomes available, it should be possible to investigate this possibility through theoretical calculations.

Summary

From the data set considered here it is evident that Marcus theory is generally successful in predicting outer-sphere electron-transfer rate constants between 2+ and 3+ charged reactants to within a factor of 25. (However, if the Marcus equations are used to estimate unknown self-exchange rates this represents a factor of $(25)^2$ or nearly 10^3.) Exceptions to this generalization are the Fe^{2+}–ML_3^{3+} reactions which are consistently ~500 times too slow and some other reactions cited in the literature (for example, reactions between actinide ions[27] and certain cobalt(III) reactions[28]). There is evidence that the fit between theory and experiment worsens as the driving force for the reaction increases. From trial calculations for V_{aq}^{2+} reductions it appears that the observed discrepancies do not arise simply from the effects of noncancellation of work terms and nonadiabatic terms. The limited available data for $\Delta H_{12}^{\ddagger}$ suggest that anharmonic effects could be the origin of the slow observed rates. This survey has brought to attention several unanswered (and presently unanswerable) questions and suggests many experiments. The need for good activation parameters and thermodynamic data ($\Delta H°$ and $\Delta S°$) for both exchange and cross-reactions is evident. For systems in which poor agreement between theory and experiment is obtained for the rate constant, consideration of calculated and observed $\Delta H_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ values should help locate the point where the theoretical assumptions break down. Finally, the data set on which these conclusions are based should be broadened; self-exchange rates for other couples need to be determined so that the rates of the cross-reactions of these may be compared with the predictions of theory. The reactions studied should encompass a wide free energy range. It is hoped that the results of these efforts will suggest improvements in the theoretical model and provide greater insight into the details of the activation process for outer-sphere electron transfer.

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Evidence for an Oscillating Intramolecular Ligand Exchange Mechanism Due to an Alternation between Two Identically Strong Aliphatic Hydrogen to Palladium Interactions

Michèle Postel,[1a] Michel Pfeffer,[1b] and Jean G. Riess*[1a]

Contribution from the Laboratoire de Chimie Minérale Moléculaire,
Equipe de Recherche Associée au CNRS, Parc Valrose, 06034 Nice-Cedex, France,
and the Laboratoire de Chimie de Coordination, Laboratoire Associée au CNRS,
67008 Strasbourg-Cedex, France.

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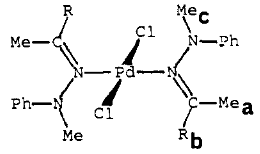
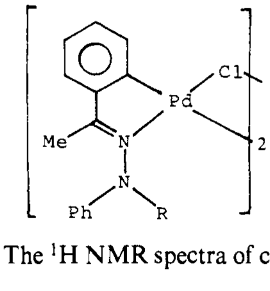
Abstract: The ^1H NMR spectra of compound I reveal: (i) the inequivalence of the two hydrazone ligands at low temperature; (ii) the stereodynamic behavior of the compound; (iii) a remarkably large low-field shift for one of the C–Me groups. This latter fact was traced to the effect of the anisotropy of palladium and affords evidence for a strong Pd···HC interaction with one of the methyl groups, resulting in the nonequivalence of the two ligands. The existence of this interaction was further demonstrated by the study of compounds II and IV. The coalescence of all signals in the NMR above 50 °C showed that the two ligands exchange roles rapidly and that there is an alternation in the Pd···Me interaction. This exchange is intramolecular ($\Delta G^{\ddagger} = 69$ kJ mol^{-1}). The analysis of the variations of the chemical shifts with temperature, in terms of the paramagnetic anisotropy of palladium, enabled us to tentatively propose, as the most probable exchange process, a concerted oscillation, rather than a hindered but complete rotation, of the two ligands about the Pd–N bonds.

Dehand and Pfeffer[2,3] recently pointed out that substituted hydrazines, when coordinated to palladium, react with organic ketones to give hydrazones which remain coordinated to the metal through the condensed nitrogen. Depending on the nature of the ketone, the reaction led to two types of compounds: with aliphatic ketones, σ(N)-coordinated bishydrazone compounds were obtained, as for example compounds I and II, while aromatic ketones led to orthometalated compounds such as III.



I R = Me

II R = CH(Me)$_2$



III R = H, Me, Ph

The ^1H NMR spectra of compound I (Figure 1) reveal three striking features: (i) the inequivalence of the two hydrazone ligands at low temperatures; (ii) the stereodynamic behavior of the compound; (iii) the remarkably large low-field shift for one of the C–Me groups.

This last feature suggested a favored interaction between the metal and one of the methyl groups. Indeed Vrieze et al. have recently shown that such nonbonded metal-alkyl or -aryl interactions exist in platinum(II) azo,[4] imine,[4] and sulfurdiimine[7] compounds. They also isolated orthometalated compounds by reacting aromatic azo and imine ligands with Ir(I) and Rh(I) chlorides,[5] and showed the importance of the basicity of the metal in these C–H bond-breaking reactions.[6]

Compounds I and II appear to be the first examples in which a molecule contains two identical ligands, each likely to give such a metal-alkyl interaction; the two ligands are thus in a situation where they can compete for this interaction with the result that they will become inequivalent in solution. The investigation of such a situation was expected to provide a better knowledge of such metal-alkyl interactions, and is also thought to be relevant to the question of orthometalation.

This paper also describes the dynamic process which causes the hydrazone ligands to become equivalent in the NMR at higher temperatures, and presents evidence for a new intramolecular exchange mechanism based on the concerted oscillation of the two ligands with respect to the coordination plane. Additional data for this investigation were obtained