MASTER

C ONF-771150--2

Electron Transfer Reactions of Metal Complexes in Solution

Norman Sutin

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

It is impossible in an article such as this to do justice to the many hundreds of electron-transfer reactions that have been studied. Instead I shall select a few representative systems and compare their kinetic parameters with the predictions of activated complex models. Moreover, since Taube has just presented an elegant treatment of intramolecular electron-transfer reactions I shall concentrate on bimolecular reactions. The latter electron-transfer reactions are more complicated to treat theoretically since the geometries of their activated complexes are not as well known as for the intramolecular case. In addition in bimolecular reactions the work required to bring the two reactants together needs to be calculated. Since both reactants generally carry charges this presents a non-trivial problem at the ionic strengths usually used to study bimolecular electron transfer.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ELECTRON EXCHANGE REACTIONS

The simplest class of electron-transfer reactions are the outer-sphere electron exchange reactions. The reactants and products of such reactions are identical and the electron transfer occurs without bond formation or rupture. The electron exchange reactions that we will be discussing are

Since there is no net chemical change in the above reactions they can only be studied by labeling one of the oxidation states. The rate constant for the first exchange was determined by using $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ labelled with a radioactive isotope (1), for the second by using $\text{Ru}(\text{ND}_3)_6^{3+}$ as a reactant (2) and for the last by an NMR line broadening technique (3) and also from measurements on the closely-related $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Ru}(\text{phen})_3^{3+}$ reaction (4). The rate constants determined by these methods are summarized in Table I. It will be seen that although all of the reactions involve reactants of charges +2 and +3 and electron configurations d^5 and d^6 , their rate constants span some 9 orders of magnitude. (Rate constants for exchange reactions span some 20 orders of magnitude if cobalt(II)-cobalt(III) systems are included.) The possible origins of these rate differences will next be discussed.

Free Energies of Activation

Most theories of electron-transfer reactions are based upon the Franck-Condon principle. According to this principle, internuclear distances and nuclear velocities do not change during an electronic transition. Since the equilibrium configuration of the inner coordination shell of an ion as well as the polarization of the surrounding solvent depend upon the charge of the complex, the equilibrium configurations of the two reactants of an electron exchange reaction will, in general, be different. Energy conservation therefore requires that the inner coordination shells of the reactants and the polarization of the surrounding medium arrange to some nonequilibrium configuration before the electron transfer can take place (5-11). In the case of an electron exchange reaction this intermediate (activated complex) configuration is one in which the coordination shells of the two reactants have identical geometries. This is shown in Figure 1, which illustrates the intersection of the potential surface of the reactants with that of the products. If there is interaction between the reactants the degeneracy at the intersection will be removed and two new surfaces will be formed. The separation between these two surfaces is equal to $2H_{AB}$ where H_{AB} is the interaction energy (electronic coupling matrix element).

The intersection region can be reached by a suitable fluctuation in the nuclear configurations of the reactants. If E_a is the energy required to change the nuclear coordinates of the reactants from their equilibrium values to the coordinates appropriate to the intersection region, then the rate constant for electron exchange is given by

$$k = \langle \kappa \rangle \frac{kT}{h} \frac{Q^\ddagger}{\pi_i Q_i} e^{-E_a/RT} \quad (1)$$

$$\langle \kappa \rangle = \int_{-E_a}^{\infty} \kappa(E) e^{-E/RT} dE/RT \quad (2)$$

where $\langle \kappa \rangle$ is a thermally averaged transmission factor which allows for the possibility that nuclear tunneling may occur and that the reaction may be nonadiabatic; the Q_i are partition functions and E is the energy relative to the potential energy of the activated complex.

We assume first that $\langle \kappa \rangle = 1$ (at all temperatures) for the reactions listed in Table I. In other words, we assume for the time being that nuclear tunneling may be neglected and that the reactants remain on the lower potential energy surface on passing through the intersection region. Converting to free energies, the rate constant for electron exchange is given by (6-8)

$$k = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad (3)$$

where

$$\Delta G^\ddagger = w_r + \Delta G_{\text{trans}}^\ddagger + \Delta G_{\text{out}}^\ddagger + \Delta G_{\text{in}}^\ddagger \quad (4)$$

$$\Delta G_{\text{trans},a}^\ddagger = -RT \ln(hZ/kT) \quad (5)$$

$$\Delta G_{\text{out}}^\ddagger = \frac{(\Delta q)^2}{4} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \left(\frac{1}{n^2} - \frac{1}{D_s} \right) \quad (6)$$

$$\Delta G_{\text{in}}^\ddagger = \frac{3f_1 f_2 (a_1 - a_2)^2}{(f_1 + f_2)} \quad (7)$$

In the above expressions w_r is the work required to bring the two reactants together, $\Delta G_{\text{trans}}^\ddagger$ is the free energy of formation of the transition state from two non-interacting reactants, and $\Delta G_{\text{out}}^\ddagger$ and $\Delta G_{\text{in}}^\ddagger$ are the energies required to reorganize the outer- and inner-coordination shells of the reactants, respectively. Z is the collision frequency of two uncharged particles in solution (taken as $10^{11} \text{ M}^{-1} \text{ sec}^{-1}$); q_1 , q_2 , a_1 , and a_2 are the charges and radii of the two reactants, respectively, d is the distance between the centers of the two reactants in the activated complex (usually assumed equal to $a_1 + a_2$), f_1 and f_2 are the breathing force constants of the two reactants, n is the refractive index, and D_s is the static dielectric constant of the medium.

The free energies of activation calculated from equations 4-7 are compared with experimental values in Table II. In order to calculate the work terms the Debye-Hückel expressions

$$w_r = \frac{q_1 q_2}{D_s d (1 + \beta d \sqrt{\mu})} \quad (8a)$$

$$\beta = \left(\frac{8\pi N_e^2}{1000 D_s RT} \right)^{1/2} \quad (8b)$$

(where N is Avogadro's number and μ the ionic strength) were used.

The calculated and observed free energies of activation for the $\text{Ru}(\text{NH}_3)_6^{2+}$ - $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$ exchanges are seen to be in good agreement. This agreement supports the assumption that

$\kappa = 1$ for these systems. This conclusion is particularly significant for the $\text{Ru}(\text{bpy})_3^{2+} - \text{Ru}(\text{bpy})_3^{3+}$ exchange where the distance between the metal centers (in the outer-sphere approximation) is $14 \text{ \AA}$. Despite this large distance the reaction remains adiabatic presumably as a consequence of the mixing of the metal t_{2g} orbitals with the π^* orbitals of the aromatic ligands (12,13).

The data in Table II show that the relative slowness of the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange derives mainly from its large inner-sphere barrier. The force constants used in calculating this barrier were obtained as follows. The (asymmetric) metal-oxygen stretching frequency of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ determined from infrared measurements is 389 cm^{-1} (14). The metal-oxygen stretching frequency of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ has not been determined and it will be assumed equal to the stretching frequency of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ (490 cm^{-1}) determined by infrared measurements (14). Assuming further that the symmetric breathing frequencies of the complex ions in solution are not too different from the asymmetric stretching frequencies (an assumption supported by the similarity of the infrared and Raman stretching frequencies of hydrated copper(II) and zinc(II) ions (14,15)) and that the motions of the inner coordination shells are harmonic (an assumption made in deriving equation 5) the breathing force constants calculated from $f = 4\pi^2 \omega^2 c^2 \mu / N$ (with μ equal to the mass of a water molecule) are 1.6×10^5 and $2.6 \times 10^5 \text{ dynes cm}^{-1}$ for $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, respectively. These force constants together with $(a_2 - a_3) = 0.14 \text{ \AA}$ were substituted in equation 7 to calculate the inner-sphere barrier for the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange reported in Table II. Although the validity of the harmonic assumption is difficult to assess, recent

calculations show that anharmonicity effects tend largely to cancel (16-18): anharmonicity increases the amount of energy required for compression of a bond and decreases the amount needed for bond stretching. It is, of course, not essential to use a harmonic approximation for the inner-sphere motion. Thus the two-term potential energy expression proposed by Hush (9) may be used. This expression yields a lower inner-sphere barrier (by a few kcal) for the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange. In view of the uncertainty concerning the exact height of the inner-sphere barrier the agreement of the observed and calculated free energies of activation for the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange must also be considered satisfactory.

The expression for $\Delta G_{\text{trans}}^\ddagger$ merits further comment. It can be rationalized as follows: the six translational degrees of freedom of the two reactants have a partition function $(2\pi m_1 kT/h^2)^{3/2} (2\pi m_2 kT/h^2)^{3/2}$ where m_1 and m_2 are the masses of the reactants. These six degrees of freedom become three translations of the transition state with a partition function $[2\pi(m_1 + m_2)kT/h^2]^{3/2}$, two rotational degrees of freedom with a partition function $8\pi^2 d^2 [m_1 m_2 / (m_1 + m_2) kT/h^2]$, and a vibrational degree of freedom associated with the motion of the two reactants with respect to each other in the solvent cage. This vibrational partition function is assumed to be of the order of unity (5). If Z' , the collision number in $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, is taken as $[8\pi kT(m_1 + m_2)/m_1 m_2]^{1/2} d^2$ the equilibrium constant for the formation of the transition state from two non-interacting reactants is equal to hZ'/kT . Converting to a standard state of 1 mole per liter we obtain

$$K_{\text{trans},a} = hZ/kT \quad (9)$$

where $Z = NZ'/1000$. Equations 3, 4 and 9 may now be combined to give equation 10

$$k = \langle \kappa \rangle K_o k_{et} = \langle \kappa \rangle \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad (10)$$

$$K_o = K_{trans,a} e^{-w_r/RT} \quad (11)$$

$$k_{et} = \frac{kT}{h} e^{-(\Delta G_{out}^\ddagger + \Delta G_{in}^\ddagger)/RT} \quad (12)$$

$$\Delta G^\ddagger = w_r + \Delta G_{trans}^o + \Delta G_{out}^\ddagger + \Delta G_{in}^\ddagger \quad (13)$$

Equation 10 shows that the electron-transfer rate constant can be expressed as the product of an equilibrium constant K_o for the formation of a precursor complex and a rate constant k_{et} for electron transfer within the precursor complex. The advantage of this preequilibrium formulation (equations 10-13) over the Marcus reactive-collision formulation (equations 3-5) (19) is that it provides a better description of the reaction coordinate. Moreover, expressions other than equation 9 may be used for the stability constant of the precursor complex. Thus an expression which has been widely used for treating more conventional chemical reactions is

$$K_o' = K_{trans,b} e^{-w_r/RT} = \frac{4\pi Nd^3}{3000} e^{-w_r/RT} \quad (14)$$

Equation 14 has been derived from both diffusion (20) and free-volume considerations (21). The ratio of the two expressions for the stability constant is

$$\begin{aligned} \frac{K_{trans,a}}{K_{trans,b}} &= \frac{(\pi MRT)^{1/2} d}{3 Nh} \\ &= 0.24 M^{1/2} d \end{aligned} \quad (15)$$

where $m_1 = m_2 = m$, $M = Nm$, and d is in Angstroms. Evidently equations 11 and 13 yield the same value for the stability constant of the precursor complex if $M^{1/2}d = 4.2$, which is perhaps the case for electron transfer between H_2 and H_2^+ . The effect is not very large for small reactants: for the $Fe(H_2O)_6^{2+} - Fe(H_2O)_6^{3+}$ exchange use of equation 13 lowers the activation free energy reported in Table II by $1.6 \text{ kcal mol}^{-1}$. For the $Ru(bpy)_3^{2+} - Ru(bpy)_3^{3+}$ exchange, however, the barrier reduction is $2.8 \text{ kcal mol}^{-1}$. This aspect of the problem is discussed further in connection with the entropies of activation for the reactions.

Activation Entropies and Enthalpies

We turn next to a consideration of the activation entropies and enthalpies. The value of $\Delta S^\ddagger$ can be obtained by differentiating equations 4-7 with respect to temperature [$\Delta S = -\partial(\Delta G)/\partial T$].

$$\Delta S^\ddagger = -\frac{\partial w_r}{\partial T} + \Delta S_{\text{trans}}^\ddagger + \Delta S_{\text{out}}^\ddagger + \Delta S_{\text{in}}^\ddagger \quad (16)$$

$$\frac{\partial w_r}{\partial T} = \frac{w_r}{2T(i + \beta d\sqrt{\mu})} \left[\frac{2\beta \ln D_s}{\partial \ln T} + \beta d\sqrt{\mu} \left(\frac{\partial \ln D_s}{\partial T} \right) + \beta d\sqrt{\mu} \right] \quad (17)$$

$$\Delta S_{\text{trans}}^\ddagger = R \ln(hZ/kT) - R/2 \quad (18)$$

where the Debye-Hückel expression (equation 8) for the electrostatic work term has been used. The value of $\Delta H^\ddagger$ can similarly be obtained from $\Delta H = \partial(\Delta G/T)/\partial T$.

$$\Delta H^\ddagger = (w_r - T \frac{\partial w_r}{\partial T}) + \Delta H_{\text{trans}}^\ddagger + \Delta H_{\text{out}}^\ddagger + \Delta H_{\text{in}}^\ddagger \quad (19)$$

$$\Delta H_{\text{trans}}^\ddagger = -RT/2 \quad (20)$$

There is good evidence that $\Delta S_{\text{out}}^\ddagger$ and $\Delta S_{\text{in}}^\ddagger$ are not much different from zero (19). We will assume that these terms may be neglected and thus that $\Delta G_{\text{out}}^\ddagger = \Delta H_{\text{out}}^\ddagger$ and $\Delta G_{\text{in}}^\ddagger = \Delta H_{\text{in}}^\ddagger$.

The above equations predict that both the entropies and enthalpies of activation should increase with increasing ionic strength. In Figure 2 the predicted ionic strength dependence of the entropy of activation is compared with experimental data for electron-transfer reactions for which $\Delta S^0 \approx 0$. The data include several aquo-ion systems (22) and the exchange reaction of a ruthenium amine couple (23). It will be seen that the entropies do not increase with ionic strength as predicted--instead they are essentially independent of ionic strength. Contrary to expectation, the rate increase with increasing ionic strength is reflected almost entirely in a decreased enthalpy of activation. This conclusion has previously been reached on the basis of studies of the aquo-ion systems alone (22). However the aquo-ion exchanges cannot be studied at low ionic strengths since ~ 0.1 M acid is required to suppress the hydrolysis of the +3 ions. The ruthenium amine system extends the measurements to ionic strengths of 2×10^{-3} M. Although a smaller ionic strength dependence of the entropies of activation is predicted by the Guggenheim modification of the Debye-Hückel equation and by the equations derived by Waisman, Worley and Marcus (19), the predicted ionic strength dependence is still larger than is observed. Evidently the ionic strength dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ is not adequately described by the above models, perhaps because of ion pairing or some other type of specific anion effects on the reaction rate.

In view of the uncertainty in the ionic strength corrections for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, the experimental rate constants determined at various ionic strengths will be extrapolated to zero ionic strength and from the temperature dependence of the extrapolated values the infinite dilution $\Delta H_o^\ddagger$ and $\Delta S_o^\ddagger$ will be obtained and compared with theory. At zero ionic strength, equations 16-19 (retaining the assumption that $\Delta S_{out}^\ddagger$ and $\Delta S_{in}^\ddagger = 0$) become

$$\Delta S_{o,a}^\ddagger = \frac{w_r}{T} \left(\frac{\partial \ln D_s}{\partial \ln T} \right) + R \ln \left(\frac{hZ}{kT} \right) - \frac{R}{2} \quad (20a)$$

$$\Delta S_{o,a}^\ddagger = w_r \left(1 + \frac{\partial \ln D_s}{\partial \ln T} \right) - \frac{RT}{2} + \Delta G_{out}^\ddagger + \Delta G_{in}^\ddagger \quad (21a)$$

If equation 13 is used instead of equation 11 for the stability constant of the precursor complex, the activation parameters at zero ionic strength are given by:

$$\Delta S_{o,b}^\ddagger = \frac{w_r}{T} \left(\frac{\partial \ln D_s}{\partial \ln T} \right) + R \ln \left(\frac{4\pi N_d^3}{3000} \right) \quad (20b)$$

$$\Delta H_{o,b}^\ddagger = w_r \left(1 + \frac{\partial \ln D_s}{\partial \ln T} \right) + \Delta G_{out}^\ddagger + \Delta G_{in}^\ddagger \quad (21b)$$

In deriving equation 20 it has been assumed that $\Delta S_{out}^\ddagger$ and $\Delta S_{in}^\ddagger = 0$, that is, that the entropy of activation is equal to the entropy of formation of the precursor complex from the separated reactants. This assumption is consistent with the studies of Fischer, Tom and Taube (24) who found that the activation entropies for (intramolecular) electron transfer within the binuclear

complexes they investigated are close to zero. These authors also suggest that the very negative $\Delta S^\ddagger$ values found for 2+,3+ reactions are largely the result of concentrating charge in the dielectric medium.

Values of $\Delta S^\ddagger_0$ and $\Delta H^\ddagger_0$ calculated from equations 20 and 21 (with $\partial \ln D_s / \partial \ln T = -1.368$ for water at 25°C) are presented in Table III. The agreement of the calculated and "measured" activation enthalpies is satisfactory (the activation enthalpies calculated from equations 21b and 20b differ by only $RT/2$ or 0.3 kcal mol⁻¹). The entropies of activation calculated from equation 20a are also in good agreement with the measured values. On the other hand, the entropies of activation calculated from equation 20b, particularly the activation entropy for the $\text{Ru}(\text{NH}_3)_4\text{bpy}^{2+} - \text{Ru}(\text{NH}_3)_4\text{phen}^{2+}$ reaction, are not sufficiently negative. This could be taken as evidence for nonadiabaticity in the latter reaction (and also perhaps in the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange). However the free energy calculations for the $\text{Ru}(\text{NH}_3)_6^{2+} - \text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+} - \text{Ru}(\text{bpy})_3^{3+}$ exchange reactions summarized in Table II leave very little room for nonadiabaticity. These considerations suggest that equation 20a may provide a better rationalization of the data than does equation 20b (depending upon the sizes of the reactants, the entropies of activation calculated from equation 20b will typically be some 5-15 cal deg⁻¹ mol⁻¹ more positive than those calculated from equation 20a). Additional data are clearly needed before conclusions on this point can be drawn with confidence.

Nonadiabatic Electron Transfer

We shall now explore the possibility that the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange may be nonadiabatic and that nuclear tunneling may be important so far as the motion of the inner coordination shells of the reactants is concerned. Newton (18) has attempted to assess the combined importance of nuclear tunneling and nonadiabaticity in the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange by using an expression which Nikitin (25) has derived for the transmission factor for a nonadiabatic reaction in the weak coupling limit. This expression is

$$\langle \kappa \rangle = \frac{4\pi^2 H_{AB}^2}{h |F_A - F_B|} \left\langle \frac{1}{v} \right\rangle \cdot \exp[(E^*/RT)^3/12] \quad (22)$$

$$\left\langle \frac{1}{v} \right\rangle = \frac{1}{(2RT/\pi\mu)^{1/2}}$$

$$E^* = (h^2 F_{AB}^4 / 8\pi^2 \mu (F_A - F_B)^2)^{1/3}$$

$$F_{AB} = (|F_A F_B|)^{1/2}$$

where H_{AB} is the electronic coupling between the diabatic states, v is the velocity with which the system moves through the intersection region, μ is the tunneling (nuclear) mass, and F_A and F_B are the slopes of the diabatic curves in the intersection region. Typically $\bar{v} = 3 \times 10^4 \text{ cm sec}^{-1}$ and $F_A, F_B = 70 \times 10^8 \text{ kcal mol}^{-1} \text{ cm}^{-1}$. According to equation 22 the transmission factor may be expressed as the product of two factors: the first is the usual Landau-Zener factor and the second is a nuclear tunneling

factor which resembles the expression for tunneling through a triangular barrier. Nikitin identifies the first factor with over-the-barrier transmission and the second with under-the-barrier tunneling. Clearly under-the-barrier tunneling can be influenced by the presence of the upper surface.

The initial and final states for the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange are

The value of the matrix element coupling these two states depends upon the inner-shell coordinates r and the distance between the two metal centers R , and is given by

$$H_{AB}(r^{2+}, r^{3+}, R) = \int_{\text{all space}} \psi_A(r^{2+}, r^{3+}, R, x_i) H(r^{2+}, r^{3+}, R, x_i) \psi_B(r^{2+}, r^{3+}, R, x_i) dx_i$$

where x_i denotes the set of coordinates of all the (valence) electrons and the integration is over all space. Newton used an ab-initio model for the interaction of the two reactants to evaluate H_{AB} (18). The Hamiltonian used by Newton is

$$H(r^{2+}, r^{3+}, R, x_i) = T_e + V_e$$

where T_e is the kinetic energy of all the valence electrons on Fe^{2+} and Fe^{3+} and V_e is the potential energy of all the electrons. V_e consists of six terms:

$$\begin{aligned}
 v_e = & \sum_{11} \frac{Z_a}{r_{ia}} + \sum_{11} \frac{Z_b}{r_{ib}} + \sum_{11} v_a(r_i) + \sum_{11} v_b(r_i) \\
 & + \sum_{i,j}^{11,11} \frac{1}{r_{ij}} + \sum_{i,k}^{11,12} v_{H_2O}(r_i)
 \end{aligned}$$

The first five terms refer to the bare (unhydrated) Fe^{2+} and Fe^{3+} ions.

The first two terms are the potential energy of interaction of the 11 valence electrons with centers a and b, (Fe^{2+} and Fe^{3+}) respectively, Z_a and Z_b are the effective charges on the centers based upon complete screening ($Z_a = Z_b = (26-18) = 8$). The third and fourth terms are the potential energies of the 11 valence electrons due to incomplete screening by the core electrons. This is represented by an effective core potential on each center. The fifth term is the coulomb and exchange interactions of all the electrons and the last term is the potential energy of interaction with the 12 water molecules in the inner coordination spheres of the reactants. For the coordinated water molecules Newton used the crystal field approximation in which each water molecule is replaced by three point charges which reproduce the water dipole moment.

The orbitals directly involved in the electron transfer in Newton's calculation are shown in Figure 3. These orbitals are directed towards faces of the $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ octahedra and lie along the internuclear axis (the z axis). They are d_{z^2} orbitals formed by taking the symmetric combination of the three conventional t_{2g} orbitals. (As is required for d_{z^2} orbitals, their angular dependence is $(3 \cos^2 \theta - 1)$.) The contours drawn

in Figure 3 enclose 99% of the total electron density; this drawing is to scale for an iron-iron separation of $6.9 \text{ \AA}$. The electron transfer in the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange is assumed to occur by overlap of the d_{z^2} orbitals. This overlap is maximal when the two reactants come together with a pair of octahedral faces in a staggered configuration (Figure 3).

Newton's calculation shows that, as expected, H_{AB} decreases rapidly with the separation between the two reactants and that H_{AB} is not particularly insensitive to variations in the inner-sphere coordinates. At $R = 6.9 \text{ \AA}$, $H_{AB} = 12 \text{ cm}^{-1}$ and $\langle \kappa \rangle = (1 \times 10^{-3})(5) = 5 \times 10^{-3}$. (The numbers in the parentheses are the values of the first and second factor, respectively, in equation 22.) The temperature dependence of κ results in contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of $-2.4 \text{ kcal mol}^{-1}$ and $-21 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively. At $R = 6.4 \text{ \AA}$, $H_{AB} = 33 \text{ cm}^{-1}$ and $\langle \kappa \rangle = (8 \times 10^{-3})(5) = 4 \times 10^{-2}$ with contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of $-2.5 \text{ kcal mol}^{-1}$ and $-18 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The $\Delta H^\ddagger$ arises primarily from the nuclear tunneling factor; $\Delta S^\ddagger$, primarily from the Landau-Zener factor. Nuclear tunneling thus lowers the activation enthalpy and the lowering is of the right magnitude to improve the agreement of the observed and calculated activation enthalpies for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange. However, the contribution of nonadiabaticity to $\Delta S^\ddagger$ results in an activation entropy which is far too negative. These considerations suggest that adiabatic tunneling is needed, that is, the Landau-Zener factor should be ~ 1 (the reaction should be adiabatic) but the nuclear tunneling factor should be larger than unity (the barrier should be permeable). The adiabaticity could be achieved by decreasing the iron-iron distance even further or possibly by including bridging through the coordinated water molecules.

ELECTRON TRANSFERS ACCOMPANIED BY A NET CHEMICAL CHANGE

We now turn to electron-transfer reactions in which the reactants and products are no longer identical. As a prototype reaction we consider the oxidation of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ by $\text{Ru}(\text{bpy})_3^{3+}$ (equation 23). This reaction illustrates many of the features that are important in asymmetric reactions.

The activation entropies and enthalpies for the oxidation of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ by $\text{Ru}(\text{bpy})_3^{3+}$ are $-33 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and $-0.3 \text{ kcal mol}^{-1}$, respectively (26). Note that the activation entropy is very negative and that the activation enthalpy is slightly negative; because of the latter the rates actually decrease with increasing temperature. At first glance these unusual activation parameters might be taken as evidence for nonadiabaticity, tunneling, or some other unusual feature in this class of reaction. However closer inspection shows this not to be the case.

Instead of attempting to calculate the rate parameters for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$ reaction a priori, as was done for the exchange reactions, we shall use the Marcus cross-relations (6-8,27). These equations relate the kinetic parameters for a cross-reaction such as 23 to the parameters for the component exchange reactions.

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (24a)$$

$$\log f_{12} = (\log K_{12})^2/4 \log(k_{11}k_{22}/Z^2) \quad (24b)$$

$$\Delta G_{12}^* = \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{\Delta G_{12}^0}{2} (1 + \alpha) \quad (25)$$

$$\Delta S_{12}^* = \left[\frac{\Delta S_{11}^*}{2} + \frac{\Delta S_{22}^*}{2} \right] (1 - 4\alpha^2) + \frac{\Delta S_{12}^0}{2} (1 + 2\alpha) \quad (26)$$

$$\Delta H_{12}^* = \left[\frac{\Delta H_{11}^*}{2} + \frac{\Delta H_{22}^*}{2} \right] (1 - 4\alpha^2) + \frac{\Delta H_{12}^0}{2} (1 + 2\alpha) \quad (27)$$

$$\alpha = \Delta G_{12}^0 / 4(\Delta G_{11}^* + \Delta G_{22}^*)$$

$$\Delta G^* = \Delta G^\ddagger - \Delta G_{\text{trans}}^\ddagger - w_r \quad (28)$$

$$\Delta S^* = \Delta S^\ddagger - \Delta S_{\text{trans}}^\ddagger + \frac{\partial w_r}{\partial T} \quad (29)$$

$$\Delta H^* = \Delta H^\ddagger - \Delta H_{\text{trans}}^\ddagger - (w_r - T \frac{\partial w_r}{\partial T}) \quad (30)$$

The subscripts 12 refer to the cross-reaction and the subscripts 11 and 22 to the exchange reactions. Some of the assumptions made in deriving the above equations have recently been considered (28). Substitution of the relevant parameters for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$ reaction gives $\Delta S_{12}^\ddagger = -29 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and $\Delta H_{12}^\ddagger = -2.9 \text{ kcal mol}^{-1}$, in good agreement with the observed values (27). This calculation shows that there is nothing special about the oxidation of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ by $\text{Ru}(\text{bpy})_3^{3+}$: the

unusual activation parameters for the electron-transfer reaction derive directly from its atypical thermodynamic parameters ($\Delta S_{12}^{\circ} = -43 \text{ cal deg}^{-1} \text{ mol}^{-1}$, $\Delta H_{12}^{\circ} = -27 \text{ kcal mol}^{-1}$). This example shows the importance of allowing for the thermodynamic changes that accompany the electron transfer before drawing any mechanistic conclusions from the measured activation parameters.

In molecular terms the negative activation enthalpy for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$ electron transfer (and related reactions) arises as follows. The value of $(S_{2+}^{\circ} - S_{3+}^{\circ})$ is essentially zero for the bipyridine complexes since the relatively large bipyridine ligands effectively shield the surrounding medium from the effect of the charge on the central metal ion (29-31). On the other hand $(S_{2+}^{\circ} - S_{3+}^{\circ})$ is large and positive for the $\text{Fe}(\text{H}_2\text{O})_6^{2+,3+}$ couple. As a consequence the standard entropy change for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$ reaction is very negative. Since $S^{\circ} = -k \sum_i W_i \ln W_i$, where W_i the probability of finding the system in some quantum state i , a very negative ΔS_{12}° implies that the quantum states of the products are much more widely spaced than are those of the reactants (27). The mean energy of the reactants is equal to the energy of each quantum state of the system for a given pair of reactants, multiplied by the probability of finding the reactants in that state, summed over all states. The mean energy of the activated complexes is similarly obtained from a Boltzmann-weighted average of the energies of the activated complexes. For the system under consideration, the more energetic states of the activated complex are less reactive than the less energetic ones. This is a direct consequence of the wider spacing of the product (and, therefore, the activated complex) quantum states compared to the spacing of the

reactant states and to the lack of appreciable activation energy for the lowest reactant state. In other words, only the lower energy states of the reactants react readily and the mean energy of the reactants that do react is less than the mean thermal energy of the reactants. The activation energy is therefore negative (27).

The above equations predict the existence of an "inverted region": when $-\Delta G_{12}^0$ becomes larger than $2(\Delta G_{11}^* + \Delta G_{22}^*)$ the observed rate constant should decrease as the standard free energy change becomes more negative. In terms of rate constants the condition for the crossover is

$$\log K_{12} = 2 \log(Z^2/k_{11}k_{22}) \quad (31)$$

Crossover into the inverted region is thus favored when both K_{12} and $k_{11}k_{22}$ are large. Evidence for this kind of behavior has recently been obtained in excited state reactions (32) although the observed rate lowering was many orders of magnitude below that predicted by equation 24. The failure to observe a (large) rate decrease in the inverted region has been ascribed to nuclear tunneling effects (33). Because of nuclear tunneling, the rates may remain constant at the diffusion controlled limit rather than start to decrease as the standard free energy change for the reaction becomes very negative. It may turn out that the best evidence for nuclear tunneling in electron-transfer reactions may come from studies of the crossover region.

CONCLUSIONS

In this article we have considered the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and some Ru(II)-Ru(III) exchange reactions. The kinetic data are consistent with an adiabatic, outer-sphere model in which nuclear tunneling and other quantum effects are small. On the other hand, a calculation of the electronic coupling element for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ - $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange suggests that this reaction is not adiabatic. However, the inclusion of bridging by the coordinated water molecules (34) which was ignored in this calculation might increase the electronic coupling to the adiabatic level ($\sim 200 \text{ cm}^{-1}$).

There is good evidence that the $\text{Eu}_{\text{aq}}^{2+}$ - $\text{Eu}_{\text{aq}}^{3+}$ exchange (35), certain cobalt(II)-cobalt(III) exchanges (36), and a number of spin-equilibrium processes (37) are not adiabatic. In the $\text{Eu}_{\text{aq}}^{2+}$ - $\text{Eu}_{\text{aq}}^{3+}$ exchange the transferred f electron is heavily shielded from the ligands and the acceptor orbital of the oxidant. This could lead to a small electronic coupling element and nonadiabaticity. Similarly, small spin-orbit coupling and, consequently, nonadiabaticity, may obtain in the "spin-forbidden" cobalt(II)-cobalt(III) exchanges and in spin-equilibrium processes.

Finally, the above discussion has shown that the electron-transfer rate constant can be expressed as the product of two factors, a nuclear factor (which depends upon the nuclear configuration and the separation of the reactants) and an electronic factor (which depends upon the electron orbitals of the intervening molecules and on the nuclear coordinates, particularly the separation of the two reactants). Two limiting classes of electron transfer can thus be distinguished. The first corresponds to a large separation of the reactants and a low probability

of electron transfer; the second, to close approach of the reactants (including, perhaps, distortion of their coordination shells) and a high probability of electron transfer (38). The electron transfer in any given system will occur at values of the nuclear coordinates that represent the best compromise between these opposing factors. In reality the entire range from nonadiabatic to adiabatic behavior is to be expected with the former predominating at relatively large separations of non-conjugated donor and acceptor centers. In this connection it is of interest that electron transfer between the relatively large $\text{Ru}(\text{bpy})_3^{2+,3+}$ ions appears to be adiabatic and that the question of nonadiabaticity only arises in regard to the exchange between the comparatively small $\text{Fe}(\text{H}_2\text{O})_6^{2+,3+}$ ions.

Acknowledgments

The author wishes to thank Dr. M. Newton for valuable discussions of the nonadiabaticity problem and for making his calculations available prior to publication. The author also wishes to thank Dr. G. Brown and Dr. B. Brunschwig for important contributions to the ionic strength and related electron transfer problems. This work was performed under the auspices of the U. S. Department of Energy and supported by its Division of Basic Energy Sciences.

References

- (1) J. Silverman and R. W. Dodson, J. Phys. Chem., 56, 846 (1952).
- (2) T. J. Meyer and H. Taube, Inorg. Chem., 7, 2369 (1968).
- (3) R. C. Young, F. R. Keene, and T. J. Meyer, J. Am. Chem. Soc., 99, 2468 (1977).
- (4) M.-S. Chan, Ph.D. dissertation, Washington University, St. Louis, Missouri, 1974.
- (5) R. A. Marcus, J. Chem. Phys., 24, 966 (1956).
- (6) R. A. Marcus, Discussions Faraday Soc., 29, 21 (1960).
- (7) R. A. Marcus, J. Chem. Phys., 43, 679 (1965).
- (8) R. A. Marcus, Annu. Rev. Phys. Chem., 15, 155 (1966).
- (9) N. S. Hush, Trans. Faraday Soc., 57, 557 (1961).
- (10) N. Sutin, Annu. Rev. Nucl. Science, 12, 285 (1962).
- (11) N. Sutin, Accounts Chem. Res., 1, 225 (1968).
- (12) N. Sutin, Advances in Chemistry Series, No. 162, Bioinorganic Chemistry II, K. N. Raymond, Editor, page 156 (1977).
- (13) G. M. Brown, F. R. Hopf, T. J. Meyer, and D. G. Whitten, J. Am. Chem. Soc., 97, 5385 (1975).
- (14) I. Nakagawa and T. Shimanouchi, Spectrochim. Acta, 20, 429 (1964).
- (15) R. E. Hester and R. A. Plane, Inorg. Chem., 3, 768 (1964).
- (16) T. W. Newton, J. Chem. Educ., 45, 571 (1968).
- (17) N. C. Sndergaard, J. Ulstrup, and J. Jortner, Chem. Phys., 17, 417 (1976).
- (18) M. Newton, to be published.
- (19) E. Waisman, G. Worry, and R. A. Marcus, J. Electroanal. Chem., 82, 9 (1977).

- (20) M. Eigen, Z. Physik. Chem., NF1, 176 (1954).
- (21) R. M. Fuoss, J. Am. Chem. Soc., 80, 5059 (1958).
- (22) A. Ekstrom, A. B. McLaren, and L. E. Smythe, Inorg. Chem., 15, 2853 (1976).
- (23) G. M. Brown and N. Sutin, to be published.
- (24) H. Fischer, G. M. Tom, and H. Taube, J. Am. Chem. Soc., 98, 5513 (1976).
- (25) E. E. Nikitin, "Theory of Elementary Atomic and Molecular Processes in Gases," translated by M. J. Kearsley, Clarendon Press, Oxford, 1974, p. 115.
- (26) J. L. Cramer and T. J. Meyer, Inorg. Chem., 13, 1250 (1974).
- (27) R. A. Marcus and N. Sutin, Inorg. Chem., 14, 213 (1975).
- (28) M. Chou, C. Creutz, and N. Sutin, J. Am. Chem. Soc., 99, 5615 (1977).
- (29) J. Lin and W. G. Breck, Can. J. Chem., 43, 766 (1965).
- (30) P. George, G. I. H. Hanania, and D. H. Irvine, J. Chem. Soc., 2548 (1959).
- (31) D. K. Lavalley, C. Lavalley, J. C. Sullivan, and E. Deutsch, Inorg. Chem., 12, 570 (1973).
- (32) C. Creutz and N. Sutin, J. Am. Chem. Soc., 99, 241 (1977).
- (33) S. Efrima and M. Bixon, Chem. Phys. Lett., 25, 34 (1974).
- (34) N. S. Hush, Electrochim. Acta, 13, 1005 (1968).
- (35) H. Taube, Advances in Chemistry Series, No. 163, Bioinorganic Chemistry II, K. N. Raymond, Editor, p. 127 (1977).
- (36) N. Sutin in "Inorganic Chemistry", Vol 2, G. L. Eichhorn, Editor, Elsevier, New York, N. Y., 1973, Chapter 19, p. 611.
- (37) E. V. Dose, M. A. Hoselton, N. Sutin, M. F. Tweedle, and L. J. Wilson, J. Am. Chem. Soc., 100, 000 (1978).
- (38) R. J. Marcus, B. J. Zwolinski, and H. Eyring, J. Phys. Chem., 58, 132 (1954).

Table I. Rate Constants for Electron Exchange Reactions at 25°C

Reaction	Medium	k, M ⁻¹ sec ⁻¹	Reference
$\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{Fe}(\text{H}_2\text{O})_6^{3+}$	0.55 M $\text{HClO}_4/\text{NaClO}_4$	4.2	(1)
$\text{Ru}(\text{NH}_3)_6^{2+} + \text{Ru}(\text{NH}_3)_6^{3+}$	0.10 M HClO_4	4.3×10^3	(2)
$\text{Ru}(\text{bpy})_3^{2+} + \text{Ru}(\text{bpy})_3^{3+}$	1.0 M HClO_4	$2 \times 10^{9^a}$	(4)

^aThe value reported in reference 3 ($1.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$) has been corrected for the effects of diffusion control according to $1/k_{\text{act}} = 1/k_{\text{obsd}} - 1/k_{\text{diff}}$ using $k_{\text{diff}} = 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.

Table II. Comparison of Observed and Calculated Free Energies of
Activation for Electron Exchange Reactions at 25°C

	$\text{Fe}(\text{H}_2\text{O})_6^{2+/3+}$	$\text{Ru}(\text{NH}_3)_6^{2+/3+}$	$\text{Ru}(\text{bpy})_3^{2+/3+}$
$k, \text{M}^{-1} \text{sec}^{-1}$	4.2	4.3×10^3	2×10^9
Ionic Strength	0.55 M	0.10 M	1.0 M
$d, \text{\AA}$	7	7	14
$(a_2 - a_3), \text{\AA}$	0.14	0.04	~ 0
w_r	1.3	2.1	0.3
$\Delta G_{\text{trans}}^\ddagger$	2.45	2.45	2.45
$\Delta G_{\text{out}}^\ddagger$	6.4	6.4	3.2
$\Delta G_{\text{in}}^\ddagger$	$\sim 8.4^a$	0.7	~ 0
$\Delta G^\ddagger(\text{calc})$	~ 18.5	11.7	5.9
$\Delta G^\ddagger(\text{obsd})$	16.6	12.5	4.8

^aThe inner-sphere barrier, corrected for zero point energy, is
7.8 kcal mol⁻¹.

Table III. Comparison of Observed and Calculated Entropies and Enthalpies of Activation at Zero Ionic Strength at 25°C

	$\text{Fe}(\text{H}_2\text{O})_6^{2+} +$ $\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$\text{Ru}(\text{NH}_3)_4\text{phen}^{2+} +$ $\text{Ru}(\text{NH}_3)_4\text{bpy}^{3+}$
$\Delta S_o^\ddagger(\text{obsd})^a$	-22 ± 3^c	-24 ± 3^c
$\Delta S_o^\ddagger(\text{calcd, eq 20a})^a$	-25	-22
$\Delta S_o^\ddagger(\text{calcd, eq 20b})^a$	-16	-12
$\Delta H_o^\ddagger(\text{obsd})^b$	$\sim 11^c$	4.0 ± 0.5^c
$\Delta H_o^\ddagger(\text{calcd, eq 21a})^b$	~ 13	3.8
$\Delta H_o^\ddagger(\text{calcd, eq 21b})^b$	~ 13	4.1

^aIn cal deg⁻¹ mol⁻¹

^bIn kcal mol⁻¹

^cExtrapolated to zero ionic strength

Figure Captions

Figure 1. Profile of the potential energy surfaces of the reactants and products of an exchange reaction as a function of nuclear configuration. (After Marcus (8)).

Figure 2. Entropy of activation as a function of ionic strength for electron-transfer reactions for which $\Delta S^\circ \approx 0$. Circles, reactions between aquo ions (22); triangles, reactions of a ruthenium amine couple (23): 1, $\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{Fe}(\text{H}_2\text{O})_6^{3+}$; 2, $\text{V}(\text{H}_2\text{O})_6^{2+} + \text{Fe}(\text{H}_2\text{O})_6^{3+}$; 3, $\text{V}(\text{H}_2\text{O})_6^{2+} + \text{V}(\text{H}_2\text{O})_6^{3+}$; 4, $\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{Co}(\text{H}_2\text{O})_6^{3+}$; 5, $\text{Co}(\text{H}_2\text{O})_6^{2+} + \text{Co}(\text{H}_2\text{O})_6^{3+}$; 6, $\text{Ru}(\text{NH}_3)_4\text{phen}^{2+} + \text{Ru}(\text{NH}_3)_4\text{bpy}^{3+}$. The measurements on all the systems were made in a perchlorate medium. The solid lines were calculated from equation 17 with $\partial \ln D_s / \partial \ln T = -1.368$ for water at 25°C.

Figure 3. Model of the transition state for the $\text{Fe}(\text{H}_2\text{O})_6^{2+} - \text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange. The distance between the metal centers is 6.9 Å; the contours enclose 99% of the electron density. (After Newton (18)).

6.9 Å