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Further Developments in Electron Transfer

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The inverted region in electron transfer reactions is studied for the reaction of electronically-excited ruthenium(II) tris-bipyridyl ions with various metal(III) tris-bipyridyl complexes. Numerical calculations for the diffusion-reaction equation are summarized for the case where electron transfer occurs over a range of distances. Comparison is made with the experimental data and with a simple approximation. The analysis reveals some of the factors which can cause a flattening of the $\ln k_{obs}$ versus ΔG^o curve in the inverted region. Ways of improving the chance of observing the effect are discussed.

Some time ago it was predicted (1, 2) that, in a series of weak-overlap electron transfer reactions, the rate would first increase when ΔG^o was made more negative, and then, when ΔG^o became very negative, eventually decrease. Evidence for such an 'inverted effect' has been given in a number of papers (3-11), but in many other studies the reaction rate reaches a limiting value, rather than a decreasing value, when $-\Delta G^o$ becomes large (e.g., (12-18)). Possible explanations for the latter result have been suggested: (a) alternate pathways for the reaction when ΔG^o is very negative [such as H-atom transfer (19, 20), electronically-excited product states (11, 20), or, when the reaction was observed via quenching of fluorescense, exciplex formation (21, 22)], (b) quantum mechanical nuclear tunneling (20, 23-27), (c) masking by diffusion, and (d) reduction of the inverted effect [by electron transfer over a distance (19)].

Quantum mechanical tunneling reduces the magnitude of the predicted effect but does not eliminate it in weak-overlap systems, as one sees, for example, in some recent calculations for an actual experimental system (20). Moreover, there is a 1:1 correspondence between the quantum mechanically calculated charge transfer spectrum (emission or absorption vs hν) for a weak overlap redox system and the plot (eq 8 and 9 given later) of k_{act} versus the energy of reaction, ΔE (25), and hence in a series of reactions of given ΔS^o, versus $-\Delta G^o$. Here, k_{act} is the activation-controlled quantum mechanically calculated rate constant. Thus, the well-known existence of a maximum in the charge transfer vs wavelength spectrum implies that there will be a maximum in the ln k_{act} vs $-\Delta G^o$ plot when the electron transfer is a weak-overlap reaction. This correspondence removes any question that nuclear tunneling would eliminate the inversion, since that tunneling occurs to the same extent in both the charge transfer spectrum and the k_{act} vs $-\Delta G^o$ plots, and the former has a well-known maximum. It also removes any argument that large anharmonicities in practice eliminate the effect: the correspondence applies regardless of whether the vibrations are harmonic or anharmonic, as long as the electron transfer is a weak-overlap one. (The effects of having a very strong-overlap electron transfer remain to be investigated.)

In a recent paper, an approximate calculation was made of effects (b) to (d) above (19), using an approximate analytical solution for the diffusion problem, for the case where the reaction occurs readily over a short range of separation distances of the reactants. In the present report, we summarize the results of our recent calculations on a numerical solution of the same problem. A more complete description is given elsewhere (28). One additional modification made here to (19) is to ensure that the current available rate constant data at $\Delta G^o = 0$ (Appendix) are satisfied.

Theory

The diffusion-reaction equation for the pair distribution function g(r,t) of the reactants, which react with a rate constant which at any r is k(r), is given by (29-32)

$$\frac{\partial g(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial (r^2 J_r)}{\partial r} - k(r)g(r,t) \tag{1}$$

where J_r is the inward radial flux density (per unit concentration) due to diffusion and to any forced motion arising from an interaction potential energy, U(r), assumed to depend only on the separation distance r. The magnitude of J_r is given by

$$J_r = D\frac{\partial g}{\partial r} + \frac{Dg}{k_B T}\frac{dU}{dr}$$

$$\equiv De^{-U/k_B T}\frac{\partial}{\partial r}(ge^{U/k_B T}) \qquad (2)$$

where D is the sum of the diffusion constants of the two reactants.

The observed rate constant, k_{obs}, at time t is then given by (31, 33)

$$k_{obs} = \int_0^\infty k(r)g(r,t)4\pi r^2\, dr \qquad (3)$$

The steady-state solution to eq 1 satisfies $\partial g/\partial t = 0$, i.e., it satisfies

$$(1/r^2)d(r^2 J_r)/dr = k(r)g(r) \qquad (4)$$

For the experimental conditions investigated thus far, the steady-state solution is an excellent approximation to the solution of eq 1 and we consider this case. However, in proposing some experiments in the picosecond regime to enhance the chance of observing the inverted effect, we consider the time-dependent equation 1.

The rate constant k(r) is typically assumed to depend exponentially on r, varying as $\exp(-\alpha r)$. Theoretical estimates have been made for α of 1.44 $Å^{-1}$ when there is intervening material between the reactants (34), and 2.6 $Å^{-1}$ when there is not (35). A recent calculation for the hexaaquoiron self-exchange reaction yielded α = 1.8 $Å^{-1}$ (36). Experimentally, the value inferred indirectly for an electron transfer between aromatic systems in rigid media is about 1.1 $Å^{-1}$ (37).

These values of α are sufficiently large that k(r) falls off rapidly with r. When this "reaction distance" is small relative to the distance over which the function $h(r) = g \exp(U/k_B T)$ changes significantly, i.e., over which $(h(r) - h(\sigma))/(h(\infty) - h(\sigma))$ becomes appreciable, one can introduce an approximate analytic solution to eq 4 (28, 38, 39):

$$\frac{1}{k_{obs}} = \frac{1}{k_{act}} + \frac{1}{k_{diff}} \qquad (5)$$

where, in the present case, we have (from eq 3 with $g(r) \equiv 0$ for $r < \sigma$)

$$k_{act} = \int_{\sigma}^{\infty} k(r) e^{-U/k_BT} 4\pi r^2 \, dr \quad (6)$$

and where (40)

$$k_{diff} = 4\pi D / \int_{\sigma}^{\infty} \frac{e^{U/k_BT}}{r^2} dr \quad (7)$$

Equation 5 was actually derived for the case where reaction occurs at some contact distance $r = \sigma$. A derivation of eq 5 for the present case of a volume distributed rate constant $k(r)$ is approximate and is given elsewhere (28).

For $k(r)$ we shall assume at first, as in (19), that the reaction is adiabatic at the distance of closest approach, $r = \sigma$, and that it is joined there to the nonadiabatic solution which varies as $\exp(-\alpha r)$. The adiabatic and nonadiabatic solutions can be joined smoothly. For example, one could try to generalize to the present multi-dimensional potential energy surfaces, a Landau-Zener type treatment (41). For simplicity, however, we will join the adiabatic and nonadiabatic expressions at $r = \sigma$. We subsequently consider another approximation in which the reaction is treated as being nonadiabatic even at $r = \sigma$.

The well-known perturbation theory expression for the non-adiabatic rate constant is given by (25, 42-45)

$$k(r) \cong \frac{2\pi}{\hbar} |V(r)|^2 \text{ (F.C.)} \quad (8)$$

where (F.C.) is the Franck-Condon factor and $V(r)$ is the electronic matrix element for the electron transfer. (F.C.) is given by

$$\text{(F.C.)} = \frac{1}{Q} \sum_{i,f} e^{-E_i/k_BT} |\langle i|f\rangle|^2 \delta(E_f - E_i + \Delta E) \quad (9)$$

where i and f denote initial and final (reactants' and products') nuclear configuration states, including those of the solvent; ΔE is the energy of reaction; and Q is $\Sigma_i \exp(-E_i/k_BT)$. The solvent will be treated classically (1) to avoid the quantum harmonic oscillator treatment of the polar solvent which is sometimes used. (The latter yields a large error for ΔS^o when ΔS^o is large (46)). The contribution of the polar solvent to the Franck-Condon factor is (42, cf. 1)

$$\text{(F.C.)}_{solvent} = (4\pi\lambda_{out}k_BT)^{-\frac{1}{2}} \exp[-(\Delta G^{o''} + \lambda_{out})^2/4\lambda_{out}k_BT] \quad (10)$$

where $\Delta G^{o''} = \Delta G^o + E_f^v - E_i^v$ and the superscript v denotes (inner shell) vibrational energy.

The matching of the adiabatic and nonadiabatic expressions for $k(r)$ at $r = \sigma$ yields a value for $V(\sigma)$ given by (28)

$$\frac{2\pi}{\hbar} |V(\sigma)|^2 (4\pi\lambda k_B T)^{-\frac{1}{2}} \sim 10^{13}\ s^{-1} \tag{11}$$

and, for a reorganization parameter λ of about 70 kJ/mol, yields $|V(\sigma)| \sim 0.023$ eV. This value and

$$|V(r)|^2 = |V(\sigma)|^2 \exp[-\alpha(r - \sigma)] \tag{12}$$

were introduced into eq 8 as our first approximation to $V(r)$.

The series of electron transfer reactions (14) for which we calculated rate constants involve quenching of the lowest excited electronic state of $Ru(bpy)_3^{2+}$. This *Ru(II) state is a metal-to-ligand charge-transfer state (47, 48) in which an excess electron appears to be localized on one of the bipyridyl ligands (49), and this electron may be transferred to a metal-centered orbital on the oxidant, at least when an unexcited oxidant is formed. A calculation of the distance dependence of $V(r)$ for this particular transfer would be desirable, but lacking that the simple exponential form indicated in eq 12 has been used instead.

The actual numerical integration of eqs 2 and 4 was performed by converting eq 4 to a pair of ordinary differential equations, then using a standard integration routine (50) for integrating the latter, integrating outward from $r = \sigma$ to large r until $g(r)$ had its correct functional value at large r, $g(r) \sim 1 - c/r$ where c is a constant. (This functional form is the solution of eqs 2 and 4 at r large enough that $k(r) = U(r) = 0$ and for U vanishing more rapidly than $1/r$.) Because $g(\sigma)$ was unknown to a multiplicative constant initially, we actually performed the integration for a function $G(r) = g(r)c_1$, with c_1 unknown and with a preassigned value for $G(r)$ at $r = \sigma$. The terms c_1 and c could be determined from the numerical values of G at large r, and then $g(r) = G(r)/c_1$. The value of k_{obs} was calculated from the total flux at $r = \infty$:

$$k_{obs} = 4\pi D \lim_{r\to\infty} \left(r^2 \frac{dg}{dr}\right) = 4\pi Dc \tag{13}$$

Results

Calculations were performed for the system studied by Creutz and Sutin (9)

$$*Ru(II)bpy_3 + M(III)bpy_3 \rightarrow Ru(III)bpy_3 + M(II)bpy_3 \qquad (14)$$

where the bpy's are various bipyridyls, M is one of several metals, and the asterisk denotes an electronically-excited molecule. The question we address is how, for a model which has the "experimental" rate constant at $\Delta G^o = 0$ ($k_{obs} \sim 4 \times 10^8\ M^{-1}s^{-1}$) (Appendix) and the observed diffusion-limited rate constant ($k_{diff} \sim 3.5 \times 10^9\ M^{-1}s^{-1}$) (9), do the values predicted for k_{obs} at quite negative ΔG^o's compare with those calculated from eq 5 and with the experimental results? Is the effect of electron transfer over a range of distances sufficiently large to explain the observed results (i.e., very little fall-off of rate constant with increasing $-\Delta G^o$'s)?

We use a λ_{in} of 15.5 kJ/mol associated with a frequency of 1300 cm^{-1} (20), and λ_{out} of 54 kJ/mol at $r = \sigma$ (51). All calculations were performed with T = 298K. The dependence of λ_{out} on r (2) is incorporated in the calculation. An equilibrium Debye-Hückel expression for the ion-atmosphere-shielded Coulombic repulsion of the reactants is assumed (52, 53), given by

$$U(r) = \frac{z_1 z_2 e_o^2}{\varepsilon r} \frac{e^{\kappa \underline{a}}}{(1 + \kappa \underline{a})} e^{-\kappa r} \qquad (15)$$

for the case where the two reactants have the same radius. Here, κ is the reciprocal of the Debye-Hückel screening length, ε is the static dielectric constant, the $z_i e_o$ values are the ionic charges of the reactants, and $\underline{a}$ is the distance of closest approach of the ions in the ion atmosphere to a reactant ion. The distance $\underline{a}$ is $r_i + r_a$, where r_i is the radius of a reactant ion and r_a is the radius of the principal ion of opposite sign in the ionic atmosphere. When $r_i \geqq r_a$, $\underline{a}$ lies between $2r_i$ and r_i, being $2r_i$ when $r_i = r_a$ and being r_i when $r_a = 0$. Using the current approximate radii we shall, for concreteness, take $\underline{a} = 3\sigma/4$. (In eq 15 the reactants are assumed to have the same radius. A more general expression than eq 15 is cited in ref. 28). At the prevailing ionic strength of about 0.52 M, κ^{-1} is about 4.2 Å. Because of this large ionic strength, U(r) is quite small, even at $r = \sigma$.

Using $\alpha = 1.5\ Å^{-1}$ and, at first, $V(\sigma) = 0.023$ eV, k_{act} at $\Delta G^o = 0$ is found to be $1.2 \times 10^{10}\ M^{-1}s^{-1}$ which is substantially higher than the current experimental value (Appendix) of ca 4 x 10^8 $M^{-1}s^{-1}$. Assuming the validity of the latter, either $V(\sigma)$ is less than 0.023 eV, i.e., the reaction is not adiabatic at the contact distance $r = \sigma$, or λ is higher than estimated, or eq 15 underestimates $U(r)$. We consider first using a different $V(\sigma)$, namely, 0.0045 eV, which yields the current "experimental" rate constant at $\Delta G^o = 0$. (The same final results for the ln k_{obs} vs ΔG^o plot would be obtained, essentially, if one used instead a different $U(\sigma)$, as long as there is agreement of k_{act} at $\Delta G^o = 0$.)

The numerical solution of eq 4 and the rate constant data of Figure 1 agree at the data's maximum (~3.5 x 10^9 $M^{-1}s^{-1}$) when one chooses 3.0 x 10^{-6} cm^2s^{-1} for the sum of the D's of the two reactants. This D is somewhat near those estimated rather indirectly (electrochemically) for the individual D's of ferric and ferrous phenanthroline complexes (~1.9 x 10^{-6} and 3.7 x 10^{-6} cm^2s^{-1}, respectively) (54).

Since reaction may also yield electronically-excited products when ΔG^o is sufficiently negative, we include this reaction, as we did in (20). The mean excitation energy used for the formation of the electronically-excited Ru(III) product is 1.76 eV (20). As has been explained elsewhere (20, 28), the formation of the other possible electronically excited products is, in most cases at least, less probable. The same $V(r)$ was used for formation of electronically excited $Ru(bpy)_3^{3+}$ as for formation of other products because the detailed information necessary to make a distinct estimate for $V(r)$ was lacking.

We first compare the present numerical results for the solution of the steady-state eqs 3 and 4 with the approximate solution given by eqs 5, 6 and the experimental value for k_{diff}. The results agreed to about three percent when ΔG^o was varied from +0.6 to -3.0 eV. The experimental value for k_{diff} and eq 7 imply a value of D = 3.5 x 10^{-6} cm^2s^{-1}, compared with the 3.0 x 10^{-6} cm^2s^{-1} found when eqs 3 and 4 were solved. Had the same D been used for both the exact (eqs 3, 4) and the approximate (eq 5) solutions, their agreement for the rate constants would have been about 10% instead of 3%, which is still very close.

The results of solving eqs 3 and 4 are next compared with the experimental data in Figure 1 (9), using $V(\sigma)$ = 0.0045 eV. The solid line refers to the formation of ground state products, and the dotted line to the formation of an electronically-excited Ru(III) product. For further comparison with the solid

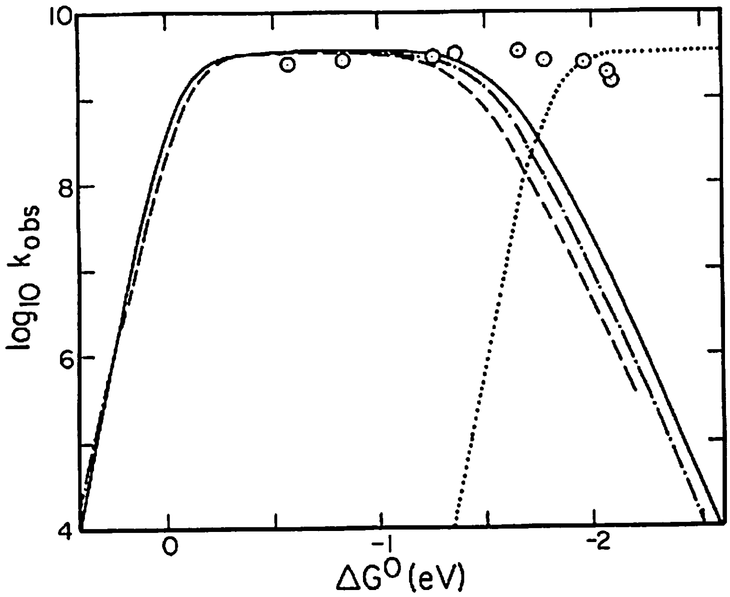

Figure 1. Calculated and experimental rate constants for Reaction 14 vs. ΔG°. Key: ——, r-dependent λ_{out}; — · —, fixed λ_{out}; – – –, from Ref. 1 in which reaction occurred only at r = σ; and · · ·, current result (r-dependent λ_{out}) for formation of an electronically excited product.

line, a calculation was made with λ_{out} held fixed (54 kJ/ mol, the value at $r = \sigma$) and is given by the dash-dot line. In order to obtain agreement with the solid line at $\Delta G^o = 0$, $V(\sigma)$ was reduced to 0.0039 eV in calculating the dash-dot line. The dashed line is the result of a calculation (20) in which reaction was treated as occurring adiabatically, but only at some contact distance σ, and in which eq 5 was used, together with the experimental value for k_{diff}. The λ_{out} value used for this last curve was again 54 kJ/mol, the present $\lambda_{out}(\sigma)$.

In Figure 2 we give a comparison of the solid line of Figure 1 with that obtained using $V(\sigma) = 0.023$ eV and a larger λ ($\lambda_{out}(\sigma) = 83$ kJ/mol). A slightly smaller D (2.7×10^{-6} cm^2s^{-1}) was required to make the latter calculation yield the experimental value of the maximum observed rate constant, 3.5×10^9 $M^{-1}s^{-1}$. Both curves have the same k_{obs} at $\Delta G^o = 0$.

Discussion

The results comparing the exact eqs 3 and 4 with the approximate eqs 5 and 6 show that the latter provide a good approximation for the present conditions, at least. The results in Figure 1 show that, to account for the experimental results at very negative ΔG^o's using the present value of λ_{out} (54 kJ/mol), it is necessary to postulate the formation of electronically-excited products. This was also the case in an earlier result (20). The sum of the two rate constants in Figure 1 yields agreement with the data in Figure 1 to a factor of about 2. If, as for the dashed line in Figure 2, the value of λ were actually appreciably larger, the formation of ground state products alone would suffice to obtain agreement. (Classically, the maximum in the k_{act} versus ΔG^o curve occurs at $\Delta G^o = -\lambda$ and so is shifted to more negative ΔG^o's when λ_{out} is increased.)

Returning to Figure 1, one sees that holding λ_{out} fixed at its value at $r = \sigma$ (dash-dot line) does not cause a large deviation from the more correct result (r-dependent λ_{out}, solid line) in the inverted region. A similar approximation was used, of course, for the dashed line, where a $k(\sigma)$ was used instead of a $k(r)$.

We also have explored the solution of the time-dependent eq 1 to study the plot corresponding to Figure 1 when the observation of fluorescence quenching in reaction 14 is made at short times. In these short-time calculations we have assumed, for simplicity, that reaction occurs only at $r = \sigma$. (Calculations are planned for the case in which electron transfer occurs over a range of distance.) Results for $k_{obs}(t)$ are given for several times in Figure 3, and curves are also given for the formation of electronically-excited products. The value of $k_{obs}(t)$ is obtained as the slope at time t of a plot of $[M(III)bpy_3^{+2}]^{-1}$ $\ln[*Ru(II)bpy_3]$ vs t. The results show the enhancement of the predicted inversion effect at small times, and an experimental study of this or related systems at such times would be desirable, and may, in fact, distinguish between the possibilities cited earlier that $V(\sigma) < 0.023$ eV or that $\lambda > (15.5 + 54)$ kJ/mol; at short times there would be a double maximum in the total rate constant versus ΔG^o plot in the first case and a single maximum in the second.

The details of these short-time calculations, made for the case that $U(r) \cong 0$, are given elsewhere (28). Searching for the inverted effect in unimolecular systems (reactants linked to each other) would also be very desirable since their rates would not be diffusion limited.

Appendix. 'Experimental' Rate Constant at $\Delta G^o = 0$

The self-exchange rate constant for reaction 14, when M is Ru and when an excited Ru(II) product is formed, has been estimated (55) to be about $10^8\ M^{-1}s^{-1}$. The self-exchange rate constant for reaction 14, when M is Ru and when the products and reactants are in their ground electronic states, has been estimated (56) to be $1.2 \times 10^9\ M^{-1}s^{-1}$, which is the observed rate constant for the oxidation of $Ru(bpy)_3^{2+}$ by $Ru(phen)_3^{3+}$, for which $\Delta G^o \sim 0.01$ eV. Corrected for diffusion (eq 5), the k_{act} for the latter is $2 \times 10^9\ M^{-1}s^{-1}$. Sutin (57) has noted that the cross-relation (1, 2) should be applicable to a nonadiabatic electron transfer if the electronic matrix element, V(r), for the cross-reaction is equal to the geometric mean of the matrix elements for the self-exchange reactions. Assuming that that condition is approximately satisfied, the exchange rate constant for reaction 14 when $\Delta G^o = 0$ is estimated to be the geometric mean, $(20 \times 1)^{1/2} \times 10^8\ M^{-1}s^{-1}$, i.e., $4.5 \times 10^8\ M^{-1}s^{-1}$. Corrected for diffusion using eq 5, this becomes $4 \times 10^8\ M^{-1}s^{-1}$, the value given in the text.

Interestingly enough, the rate constant at $\Delta G^o = 0$ for reaction 14 when *Ru(II) and M(III) are replaced by *Cr(III) and Ru(II), respectively, is $\sim 2 \times 10^8\ M^{-1}s^{-1}$ in 1 M H_2SO_4 (10).

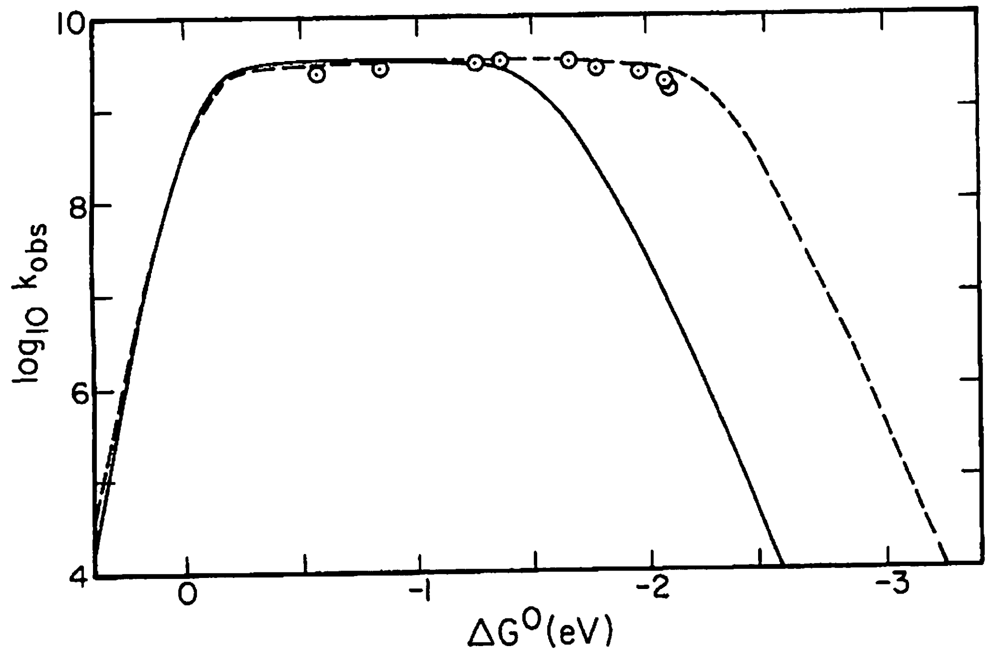

Figure 2. Calculated rate constants for Reaction 14 vs. $\Delta G°$. Key: ——, taken from solid line in Figure 1, $V(\sigma) = 0.0045$ eV, $\lambda_{out}(\sigma) = 54$ kJ/mol; and – – –, $V(\sigma) = 0.023$ eV and $\lambda_{out}(\sigma) = 83$ kJ/mol.

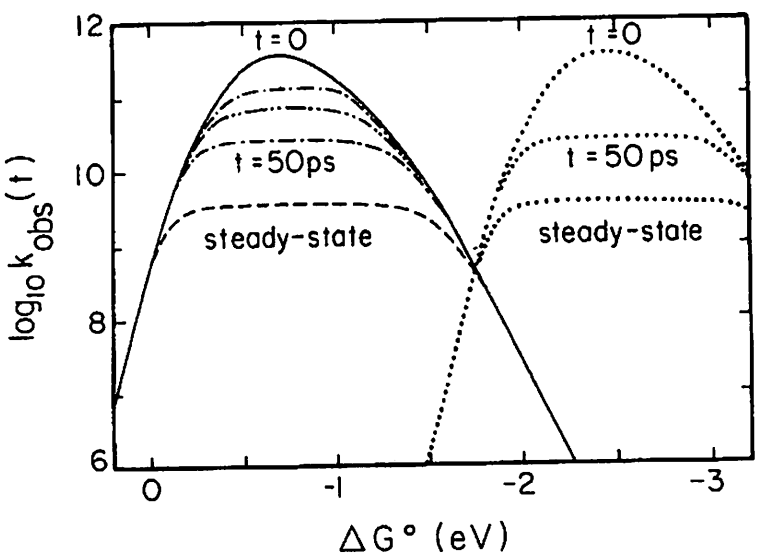

Figure 3. Time-dependent calculations of $k_{obs}(t)$ vs. $\Delta G°$ for various observation times. Key: – · –, 1 ps; – · · · –, 5 ps; and · · ·, $k_{obs}(t)$ for formation of an excited-state Ru(III).

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General Discussion—Further Developments in Electron Transfer
Leader: P. P. Schmidt

DR. THOMAS MEYER (University of North Carolina): One experimentally valid approach to this problem of the inverted region begins with a systematic study of a series of related metal bypyridine charge transfer excited states. In these excited states there are ruthenium(III) or osmium(III) cores bound, if you will, to a ligand radical anion. By making variations in the other four ligands of these six-coordinate complexes it is possible to vary systematically the energy gap (i.e., the spacing between the upper level surfaces) and to measure radiationless decay rates from lifetime and quantum yield measurements. The results show that good linear correlations exist between $\ell n\ k_{nr}$ and ΔE in agreement with the weak vibrational coupling limit expression derived by Englman and Jortner [Englman, R.; Jortner, J. Molec. Phys. 1970, 18, 145; cf., Curtis, J. C.; Bernstein, J. S.; Schmehl, R. H.; Meyer, T. J. Chem. Phys. Lett. 1981, 81, 48].

DR. LESLIE DUTTON (University of Pennsylvania): I am intrigued by the fact that people have not taken Beitz and Miller's data more seriously [Beitz, J. V.; Miller, J. R. J. Chem. Phys. 1979, 71, 4579]. Miller showed that it is possible to find a data set for similar chemicals going two or three orders of magnitude over the hump. Why are those data being ignored?

DR. SIDERS: The data of Beitz and Miller are very interesting but I feel uncertain about their correct interpretation because the measurements were for transfer of an electron from a solvent trap rather than from a molecule. Also, there's lot of scatter in the data, although they do seem to show inversion. Finally, the data were obtained in a 2-methyl-tetrahydrofuran glass at 77°K, which may differ significantly from water at room temperature.

DR. MARSHALL NEWTON (Brookhaven National Laboratory): I'd like to ask a question about Hopfield's numbers. The alpha parameter from his 1974 paper [Hopfield, J. J. Proc. Natl. Acad. Sci., USA 1974, 71, 3640] was based not on the direct metal-metal interaction but rather was based on carbon-carbon overlap because it was two carbons which were closest together in his electron transport system. In contrast, Dr. Sutin gave some different numbers based on metal orbitals. Depending on whether one is interested in carbon-carbon overlap between two organic rings, or in direct metal-metal overlap, one might or might not opt for the Hopfield parameters. However, at the level of fuzziness which we have, it may not make any difference, I realize.

DR. SIDERS: The edge atoms on the rings of the tris-bipyridyl complexes that we considered are a long way out from the central metal ions. For that reason we thought that an estimate such as Hopfield's, based on a carbon-carbon overlap, would be more appropriate than one based on a metal-metal overlap.

DR. EPHRAIM BUHKS (University of Delaware): I would like to mention briefly some recent work which demonstrates that quantum-mechanical calculations really can provide a basis for understanding the mechanism of slow electron exchange in systems such as $Co(NH_3)_6^{3+,2+}$ [Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. Inorg. Chem. 1979, 18, 2014].

The electron transfer rate can be represented in terms of a product of the electron exchange matrix element and Franck-Condon factors; the latter takes into account the contributions of solvent polarization and intramolecular-vibrational modes both of the acceptor and donor ions. These factors, in general, incorporate the contribution of the frequency change. The detailed calculation, considering 30 vibrational modes, demonstrates that the frequency change is not very important for this electron-exchange reaction. It rather provides some small factor of 10^{-1} or so. The most important term, which includes the exponential of the square of the change in metal-ligand bond distances, is responsible for the eight orders of magnitude ratio between Franck-Condon factors for the $Ru(NH_3)_6^{3+,2+}$ and $Co(NH_3)_6^{3+,2+}$ exchange. The other contribution which should be taken into account is the electron exchange matrix element. Electron exchange between the ground states of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_6^{2+}$ is spin forbidden. For this reason, the true electronic states should take into account a combination of the ground state with excited electronic states for both Co(II) and Co(III).

Thus, in the calculation of the electron exchange matrix element, an additional factor of 10^{-4} appears due to the mixing of the ground states with excited states and their cross terms. Altogether, theoretically, one can account for the 12 orders of magnitude difference in the reactivity of the ruthenium and cobalt couples.

An additional concern arises in regard to any differences which may exist between the classical theory and the quantum-mechanical approach in the calculation of the Franck-Condon factors for symmetrical exchange reactions. In fact, the difference is not very large. For a frequency of 400 cm^{-1} for metal-ligand totally symmetric vibrational modes, one can expect only one order of magnitude difference between rate constants calculated using classical and quantum-mechanical models for systems exhibiting such large changes in metal-ligand distance as exhibited by the $Co(NH_3)_6^{3+,2+}$ couple [Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. J. Phys. Chem. 1981, 85, 3759]. On the other hand, if one considers the variation of activation energy with electronic energy gap, one finds a very large discrepancy between the quantum-mechanical and classical approaches for very exothermic reactions at room temperature (see Figure 1).

A further exploration of the nuclear tunneling phenomena was presented in the study of deuterium isotope effects on electron-exchange reactions [Buhks, E.; Bixon, M.; Jortner, J. J. Phys. Chem. 1981, 85, 3763]. The main cause of the isotope effect on the rate of electron exchange originates from the changes in the metal-ligand vibrational frequencies which are induced by a change of the mass of the ligand. The effect also depends on the changes in the metal-ligand equilibrium configurations accompanying electron transfer and on temperature. For a system characterized by a substantial change in the metal-ligand distance, such as $Co(NH_3)_6^{3+,2+}$, k_H/k_D changes from ~1.3 at room temperature to ~30 at fairly low temperatures, while it is unity in the high temperature classical limit. In the temperature range 0°-70°C it is expected that $\ln(k_H/k_D)$ should decrease as T^{-3}. The deuterium isotope effect, k_H/k_D, exhibits a maximum for the symmetric electron exchange reactions, and decreases for activationless and barrierless reactions (see Figure 2).

These predictions can provide an experimental test of the mechanism for quantum-mechanical tunneling effects on electron transfer processes in solution and in glasses over a wide temperature range.

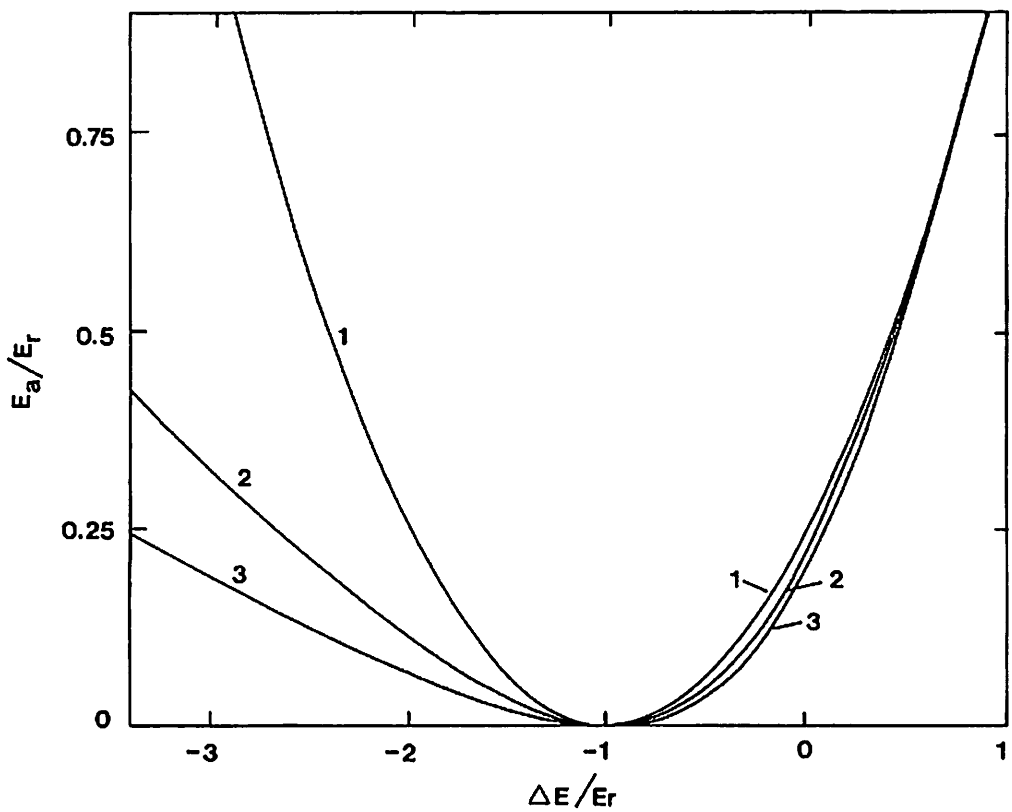

Figure 1. Activation energy of electron-transfer process as a function of electronic energy gap of a reaction. $E_r = E_s + E_c$ is the total reorganization energy where E_s is the classical solvent reorganization energy and E_c is the reorganization energy of an intramolecular mode, $\hbar\omega_c = 2k_BT$, at room temperature. Curve 1 ($E_c = 0$) represents a classical case; curve 3 ($E_s = 0$) represents quantum effects at room temperature; and curve 2 ($E_s = E_c = E_r/2$) represents the interference of the two previous cases.

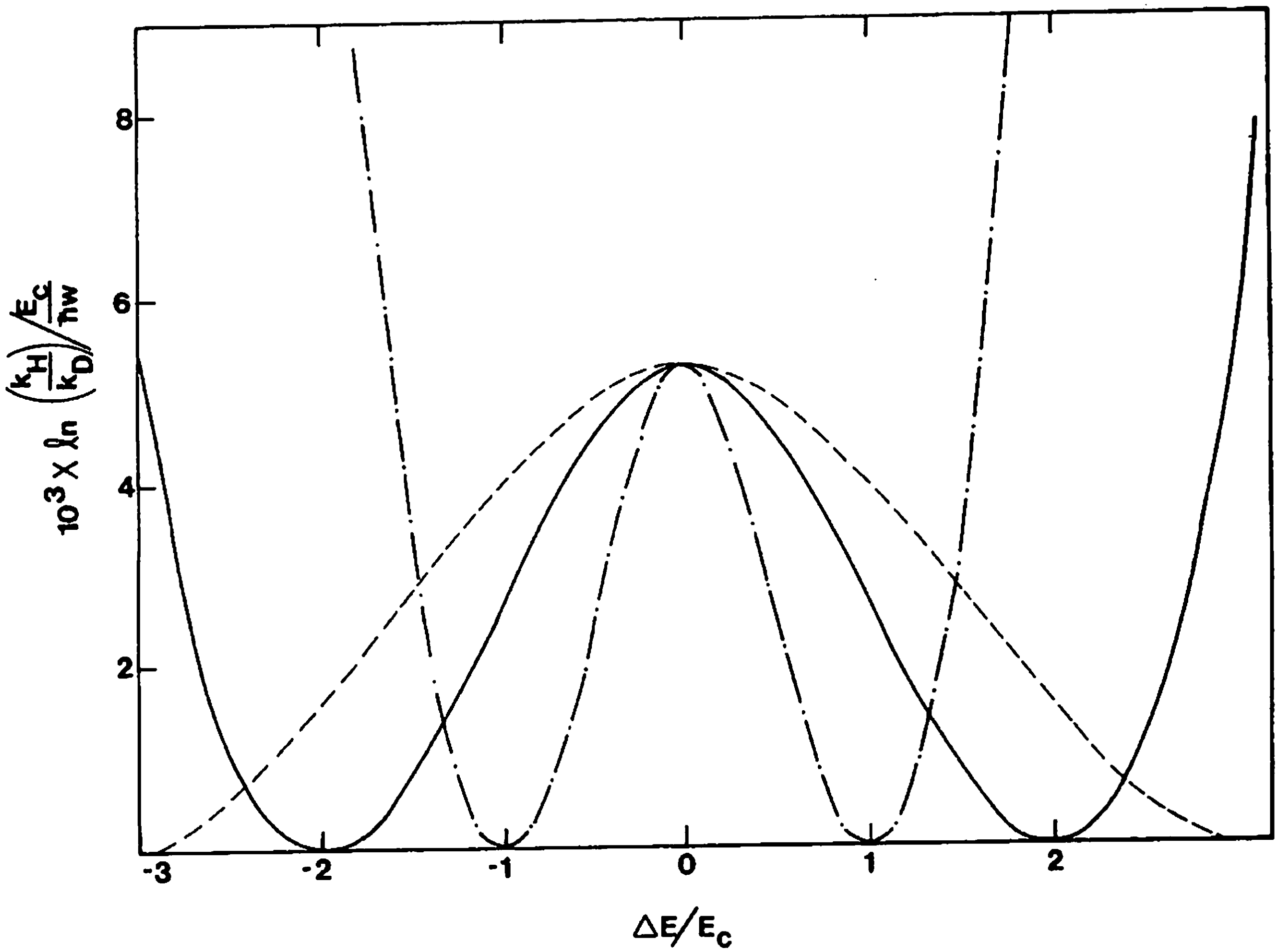

Figure 2. Deuterium isotope effect for electron transfer between ammine complexes as a function of the reduced electronic energy gap $\Delta E/E_c$ *where* E_r *is the total reorganization energy* $E_r = E_s + E_c$. *Key for parameters:* — · —, $h\omega_H/k_BT$ — *2.0 and* $E_s/E_c = 0$; ——, $E_s/E_c = 1$; *and* – – –, $E_s/E_c = 2$.