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Quantum Effects for Electron-Transfer Reactions in the "Inverted Region"

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Abstract: Quantum effects in outer-sphere electron transfer reactions in the inverted region are considered. The results of quantum, "semiclassical", and classical calculations on model systems are presented. A series of highly exothermic reactions of tris(bipyridyl) complexes involving electronically excited reactants is discussed with regard to the possible importance of quantum effects and of alternate reaction pathways in understanding the failure of the series of reactions to exhibit pronounced "inverted" behavior. Electronically excited products or alternate atom-transfer mechanisms provide possible explanations for the large discrepancy.

Introduction

In the usual range of standard free energies of reaction $\Delta G°$, outer-sphere homogeneous electron-transfer reactions have rates which increase with increasingly negative $\Delta G°$. However, when $-\Delta G°$ is very large both classical[1,2] and quantum[3,4] theories predict that the electron-transfer rate will ultimately decrease with increasingly negative $\Delta G°$ (inverted region), namely, when $-\Delta G°$ is greater than λ, 4 times the total reorganization energy of the reaction. Experimental studies have shown little or no decrease of the rate constant in this "inverted" region.[5-8] There have been suggestions that quantum effects are responsible,[3,4,9-12] suggestions that electronically excited products may be responsible[5] (they correspond to reactions with a smaller $-\Delta G°$), and suggestions that where the rate of electron transfer is inferred from and, in fact, equated to the rate of fluorescence quenching, the fluorescence quenching in the inverted region may be due instead to a faster alternate nonelectron-transfer initial step, exciplex formation.[13]

In this paper we consider the importance of nuclear tunneling first for a model system and then for an actual system using realistic vibration frequencies and bond length changes for the data of Creutz and Sutin.[6] The discrepancy is found to remain very large, some quantum effects notwithstanding. An alternate pathway of forming an electronically excited product is explored; it reduces the discrepancy considerably. Another possible alternate pathway is an atom transfer. Still another possibility (longer range electron transfer) is also considered.

Theory

Quantum Treatment. An approximate quantum-mechanical rate expression based on the golden-rule transition probability is applicable to electron transfer systems in the nonadiabatic limit.[14] Within the Condon approximation the transition probability involves the product of the square of an electron exchange integral and a thermally weighted sum, G, over Franck–Condon factors

$$G = \frac{1}{Q}\sum_n\sum_m e^{-E_n^{vib}/kT}|(\chi_n|\chi_m)|^2\delta(E_n - E_m) \qquad (1)$$

where Q is the reactants' vibrational partition function and n and m designate initial and final vibronic states, respectively. E_n and E_m are initial- and final-state energies. E_n^{vib} is the initial-state vibrational energy, and $|\chi\rangle$ is treated as a harmonic oscillator eigenfunction assumed equal to a product over the system's degrees of freedom of single-mode haromonic oscillator functions.

The overlap integrals required for evaluating G directly by the sum of eq 1 are well-known (ref 15, for example). The solvent interaction is included in eq 1 via two harmonic modes that have frequencies $\hbar\omega_1 = 1\ cm^{-1}$ and $\hbar\omega_2 = 170\ cm^{-1}$. Details are given in ref 15.

Classical Treatment. When all the degrees of freedom of the system are treated in the classical limit, $\hbar\omega/2kT \to 0$, and when frequency changes are neglected, eq 1 reduces to

$$G = (4\pi kT\lambda)^{-1/2}\exp[-(\Delta E + \lambda)^2/4kT\lambda] \qquad (2)$$

where λ equals $\sum_{j=1}^{N}\lambda_j$, ΔE is the energy of reaction, and λ_j is 4 times the reorganization energy for the jth mode. For a vibrational normal coordinate, $\lambda_j = {}^1/_2F_j(\Delta Q_j)^2$, where F_j is the force constant and ΔQ_j is the equilibrium displacement from reactant state to product state, of the jth normal coordinate. Equation 2 is similar in form to a classical expression[1,2] which allowed for large entropies of reaction when they occurred. However unlike this classical expression it contains energies rather than free energies, since eq 1 does not include any large entropy terms.[15] The other classical expression[1,2] is more general in this respect.[16]

It has been shown[17] that frequency changes may be included in an approximate manner by using average force constants to calculate λ rather than using the actual force constants. The average force constant is

$$F_{av} = 2FF'/(F + F') \qquad (3)$$

where F and F' are the force constants in the reactant and product states, respectively. We use F_{av} when evaluating the classical value of the Frank–Condon sum (eq 2). Arguments were given in Appendix IV of ref 17 based on a perturbation expansion, sug-

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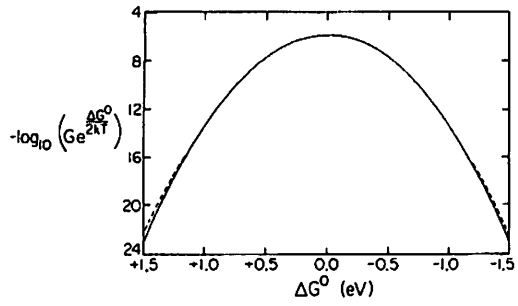

Figure 1. Model $M(bpy)_3^{3+/2+}$: —, classical Franck–Condon sum; ---, quantum Franck–Condon sum (λ_{out} = 54 kJ/mol; λ_{inner} = 0; temp = 300 K).

Table I. Hypothetical System (temp = 300 K)

	$\hbar\omega_{react}$, cm^{-1}	$\hbar\omega_{prod}$, cm^{-1}	λ, kJ/mol
internal modes	494	357	35
	357	494	18
solvent modes	170	170	48
	1	1	25

gesting that the approximation in eq 3 is adequate.

Semiclassical Treatment. A "semiclassical" treatment of electron transfer has been given[18] and discussed in detail elsewhere.[15,16] The semiclassical expression for the thermally weighted Franck–Condon sum is

$$G = (2\pi\lambda\hbar\omega \coth \gamma)^{-1/2} \exp[-(\Delta E + \lambda)^2/(2\lambda\hbar\omega \coth \gamma)] \quad (4)$$

The variables of eq 4 are defined as for eq 2 and $\lambda\hbar\omega \coth \gamma$ is an abbreviation for $\sum_{j=1}^{N}\lambda_j\hbar\omega_j \coth \gamma_j$, where γ_j is $\hbar\omega_j/2kT$. "Semiclassical" has come to denote a variety of different methods in the dynamics literature, one of which yields eq 4.

Comparison of the Three Treatments. Figure 1 is a plot of G, the Franck–Condon sum, calculated classically and quantum mechanically, vs. $\Delta G°$, the standard free energy of reaction for a model system. $\Delta G°$ is the same as ΔE in eq 1 and 2, since eq 1 tacitly assumes zero for $\Delta S°$ when $F_i = F_i'$. The model system represents metal-bipyridyl systems (e.g., $Ru(bpy)_3^{2+}$ + $Os(bpy)_3^{3+}$). The internal reorganization in such systems is negligible (λ_{inner} = 0) and the outer-sphere reorganization energy $^1/_4\lambda_{out}$ is ~13.4 kJ/mol.[19] The ordinate is a plot of log ($Ge^{\Delta G°/2kT}$) vs. $\Delta G°$. As shown in a recent paper,[16] both the classical and quantum values of the ordinate are symmetric in $\Delta G°$, when plotted in this manner.

Figure 2 is a plot similar to Figure 1. The λ's and frequencies used are for the hypothetical system described in Table I. This system differs from that of Figure 1 by including two high-frequency internal modes and having both a larger inner-sphere and a larger outer-sphere reorganization energy. (The frequencies of the internal modes are comparable to those in the cobalt hexaammine system.) In Figure 2 the ordinate is a log plot of the Franck–Condon sum, G, vs. $\Delta G°$, and so Figure 2 unlike Figure 1 is not symmetrical about $\Delta G° = 0$.

The two plots are qualitatively alike. The classical value for the ordinates in each plot is generally less than the quantum value, as expected since the classical theory does not include vibrational tunneling. In the normal region (i.e., $-\Delta G° < \lambda$) the classical and quantum values agree very well. But as the free energy decreases into the inverted region, the quantum value decays less rapidly than the classical. Because of the high-frequency internal modes included in the second system, the discrepancy between the classical and quantum values only becomes appreciable in Figure 2. Similar results were observed earlier by Jortner et al. using other model systems.[4]

Table II. Comparison of Quantum and Semiclassical Franck–Condon Sums,[a] −log G

system	$\Delta G°$, eV	quantum	semi-classical
model[b] $M(bpy)_3^{3+/2+}$	0.5	12.2	9.4
	0.0	6.3	5.7
	−0.5	3.8	3.9
	−1.0	3.0	4.0
	−1.5	5.6	6.1
	−2.0	8.0	10.1
hypothetical[c]	0.5	13.9	12.7
	0.0	8.8	8.3
	−0.5	5.5	5.4
	−1.0	4.0	3.9
	−1.5	3.9	3.9
	−2.0	4.9	5.4

[a] G is in cm. [b] $\lambda_{inner} = 0$. λ_{out} = 35.3 kJ/mol at $\hbar\omega_1$ = 170 cm^{-1} and 18.2 kJ/mol at $\hbar\omega_2$ = 1 cm^{-1}. temp = 300 K. [c] λ's and ω's used are those in Table I.

Table III. Creutz and Sutin Reactions[a]

$$*RuL_3^{2+} + ML'_3{}^{3+} \xrightarrow{k_{obsd}} RuL_3^{3+} + ML'_3{}^{2+}$$

reaction[a]	M	L	L'	$\Delta G°$, eV	$\Delta G°*$,[b] eV
1	Cr	bpy	bpy	−0.57	1.19
2	Cr	Mebpy	bpy	−0.83	0.93
3	Os	bpy	bpy	−1.66	0.1
4	Os	Mebpy	bpy	−1.78	−0.02
5	Ru	bpy	Mebpy	−1.96	−0.20
6	Ru	Mebpy	Mebpy	−2.07	−0.31
7	Ru	bpy	bpy	−2.09	−0.33

[a] The numbers correspond to the numbered points in Figure 3. [b] $\Delta G°*$ is the $\Delta G°$ to form the electronically excited state of the RuL_3^{3+}.

Table IV. Reduction Potentials

	reduction potential, eV	ref
$Cr(bpy)_3^{3+}$	−0.26	21, 22
$Os(bpy)_3^{3+}$	0.82	8
$Ru(Mebpy)_3^{3+}$	1.10	23
$Ru(bpy)_3^{3+}$	1.26	24, 25, 26

The "semiclassical" values are compared with the quantum for selected values of $\Delta G°$ in Table II. They are smaller when the system is in the inverted region and high otherwise. This effect is due to an approximation to vibrational tunneling inherent in the "semiclassical" method which, as discussed in recent papers,[15,16] is valid only when the slope of the products' potential energy curve is extremely steep near its intersection with the reactants' potential energy curve. (Only then is the semiclassical nuclear tunneling distance *ac* in Figures 3 and 4 of ref 16 or Figure 2 of ref 15 equal to the effective nuclear tunneling distance *ab* there.)

The quantum values plotted in Figures 1 and 2 were calculated both by the direct evaluation of eq 1 and by the saddle-point method described elsewhere.[15,20] The results of the two com-

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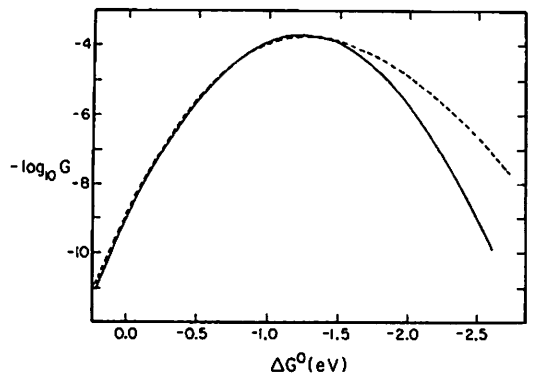

Figure 2. Hypothetical systems (λ's and frequencies in Table I): —, classical Franck–Condon sum (assuming also eq 3); ---, quantum Franck–Condon sum.

putations were found to be superimposable, so that the saddle-point approximation is a very good approximation in these common electron-transfer systems. Another approximation—an equivalent single-mode approximation—is also available (eq 19 of ref 16) and has yielded excellent agreement with the quantum results when used within its region of validity (given in eq 21 of ref 16).

Reactions Having Large Negative Free Energies. Both the classical and the quantum theories described earlier predict that the electron-transfer rate will ultimately decrease when ΔG° becomes increasingly negative, i.e., when $-\Delta G^\circ$ exceeds the total λ for the system. The classical theory predicts quadratic dependence in the very negative ΔG° region (cf. ref 3 and 4, and also as seen in Figures 2 and 3). But experimental studies of highly exothermic reactions have shown little or no decrease of the rate constant in the inverted region,[5-8] due to a variety of possible reasons discussed earlier.

We first explore the kinetic effect of formation of products in their lowest electronic state, for reactions of excited $Ru(bpy)_3^{2+}$ with tris(bipyridyl)ruthenium, -osmium, and -chromium quenchers, studied experimentally by Creutz and Sutin.[6] The reactions are listed in Table III. Given there are the standard free energies of reaction calculated from the known reduction potentials in Table IV. The reactions consist of electron-transfer quenching of the lowest luminescent excited state of $Ru(bpy)_3^{2+}$ or $Ru(Mebpy)_3^{2+}$, where bpy = 2,2′-bipyridyl and Mebpy = 4,4′-dimethyl-2,2′-bipyridyl.

The nature of the ruthenium(II) complex excitation—metal to ligand charge transfer[27,28]—contributes a significant internal reorganization energy to the electron-transfer reaction. From vibrational progressions in the low-temperature luminescence and absorption spectra of $Ru(bpy)_3^{2+}$, it appears that a high-frequency mode, $\hbar\omega = 1300$ cm^{-1}, is excited in the luminescing state.[29,30] We have found the associated λ_{inner} to be 1300 ± 100 cm^{-1} (15.5 ± 1 kJ/mol) by fitting the following line-shape function to the emission spectrum

$$\text{intensity} \propto e^{-x}\frac{x^n}{n!} \qquad (5)$$

where n is the vibrational quantum number in the ground electronic state and $x = \lambda/\hbar\omega$; $\hbar\omega$ is the frequency of the vibrational mode ($\hbar\omega = 1300$ cm^{-1} in the present case). Equation 5 gives the square overlap of the lowest single-mode harmonic oscillator state of the electronically excited state with the nth vibrational state of the lowest electronic state of the ruthenium(II) complex, when both states have the same frequency but the equilibrium position of the nth state is displaced relative to that of the zeroth state.[31] Because the vibrational quantum is so large relative to

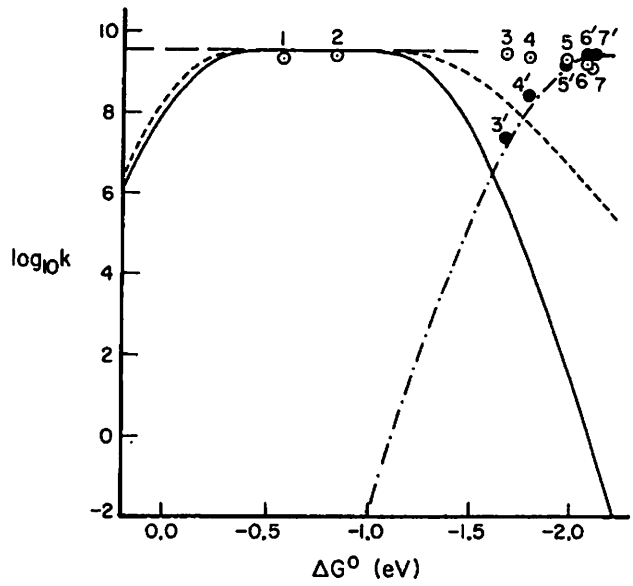

Figure 3. k (calculated and experimental) for bipyridyl systems ($k = (k_{et}^{-1} + k_d^{-1})^{-1}$ with $k_d \simeq 3.5 \times 10^9$ M^{-1} s^{-1}; ΔG° is for formation of ground-state products): —, classical to ground-state products; ---, quantum to ground-state products; ---, calculated classical rate to *Ru(III) products; ●, calculated quantum rate to *Ru(III) products; ⊙, experimental rate constant. The numbers correspond to the numbers in Table III. Primes indicate calculated rates to excited-state products (λ_{out} = 54 kJ/mol; λ_{inner} = 15.5 kJ/mol; temp = 300 K; Ru(III) excitation energy = 1.76 eV).

kT ($kT = 208.5$ cm^{-1} = 2.494 kJ/mol at 300 K) transitions from vibrational states higher than the zeroth need not be considered in the emission equation (eq 5).

In the appendix it is shown that when the emission and absorption line shapes are due to a high-frequency vibration ($\hbar\omega \gg kT$) the Stokes shift is approximately twice λ_{inner} for the transition from electronic ground state to electronic excited state. Using the average of the single–triplet absorption maxima at 77 K reported in ref 27, 28, 30, and 32 (18 300 cm^{-1} with some uncertainty) and the average of the emission maxima at 298 K reported in ref 7, 23, and 27 (16 200 cm^{-1} with some uncertainty), one obtains $\lambda_{inner} = {}^1/_2(18\,300 - 16\,200)$ cm^{-1} = 1050 cm^{-1} = 12.5 kJ/mol for the ruthenium charge-transfer transition. This estimate for λ_{inner} is in fair agreement with the value λ_{inner} = 15.5 kJ/mol obtained above by fitting eq 5 to emission spectra. λ_{inner} = 15.5 kJ/mol, inferred for the metal-to-ligand charge transfer, will be assumed for the contribution of the $*Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$ subsystem to the electron-transfer reactions in Table III.

The reactant $Ru(bpy)_3^{2+}$ may be in one of three triplet states, but the splitting of these states is small and may be neglected. (In the ruthenium and osmium complexes the lowest excited states are formed by metal A_{1g} to ligand $^3\pi^*$ excitations.) The triplet states have a total splitting of 0.73 kJ/mol in $Ru(bpy)_3^{2+}$ and 0.77 kJ/mol in $Ru(Mebpy)_3^{2+}$.[33] Both of these splittings are small relative to the ΔG°'s of the electron-transfer reactions being considered, so that each triplet state may be regarded as essentially a single triply degenerate state. The splitting of the $Os(bpy)_3^{2+}$ excited state (needed later) is not known but will be assumed to be negligible when calculating electron-transfer rates to form excited products. It has been postulated to be similar to the splitting in the $Ru(bpy)_3^{2+}$ excited state.[34]

Except for the high-frequency mode discussed above, the bipyridyl systems undergo negligible internal reorganization during electron transfer.[19,22,35] The outer-sphere reorganization energy is roughly constant throughout the series of reactions. λ_{out} has

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been estimated as λ_{out} = 54 kJ/mol.[19,35]

The spacing of the lines in the low-temperature (77 K) emission and absorption spectra of $Ru(Mebpy)_3^{2+}$ [29] indicates that a mode for which $\hbar\omega$ = 1300 cm^{-1} is excited in the luminescing state. Fitting the emission intensities to eq 5 yields λ_{inner} = 15.5 kJ/mol for this ruthenium charge transfer transition.

Using λ_{inner} = 15.5 kJ/mol, λ_{out} = 54 kJ/mol, and the $\Delta G°$'s in Table III, we calculated rate constants for the reactions to form ground-state products. In the adiabatic limit the classical rate constant is given by[17] eq 6 when work terms are negligible

$$k_{et} = Z(4\pi kT\lambda)^{1/2}G \qquad (6)$$

where G is the classical Franck–Condon sum given by eq 2, with ΔE replaced by $\Delta G°$, and $\lambda = \sum_j \lambda_j$ is the sum over inner- and outer-sphere λ's. Z is the collision frequency in solution $\sim 10^{11}$ M^{-1} s^{-1}.[2,17,36] For simplicity, the quantum rate constant was assumed to be given by the same expression (eq 6) but with the quantum Franck–Condon sum (eq 1) used for G. In this way, the quantum expression reduces to the classical in the limit $\hbar \to 0$. Strictly speaking eq 1 and 2 for the G's (classical and quantum) were derived for nonadiabatic electron transfers.

The classical and quantum rates and the observed rates are plotted in Figure 3 (solid line for classical, dashed line for quantum). The plotted values are not the electron-transfer rate constants themselves but rather the rate constants corrected for diffusion[36] k_{obsd}

$$k_{obsd} = \left(\frac{1}{k_{et}} + \frac{1}{k_d}\right)^{-1} \qquad (7)$$

where k_d is the diffusion limit: $\sim 3.5 \times 10^9$ M^{-1} s^{-1}.[6]

The difference between the quantum and the classical calculations in the very negative $\Delta G°$ region is again not negligible, because of the high-frequency internal mode involved in the present reactions, $\hbar\omega$ = 1300 cm^{-1}, and the fact that its contribution to λ_{inner} is not negligible. Still, the classical and quantum calculations are in qualitative agreement and *neither* explains the observed rates in the inverted region, as Figure 3 demonstrates. The discrepancy would be even greater if a nonadiabaticity factor[2] κ were introduced.

In order to assess the possibility of the electron-transfer products being formed in excited electronic states, we have calculated quantum mechanically the rates of electron transfer to excited product states. The calculation requires a λ_{inner} for formation of these products. The emission and absorption spectra of $Os(bpy)_3^{2+}$ [37] indicate that a 1300-cm^{-1} mode is involved in the transition to its luminescing state, with λ_{inner} = 9.0 kJ/mol ($\hbar\omega$ was obtained from the spacing of the lines in the emission spectrum, λ_{inner} was obtained by fitting the intensities to eq 5). Quantum mechanical calculations for the reactions involving quenching by $Os(bpy)_3^{3+}$ indicate that formation of electronically excited $Os(bpy)_3^{2+}$ product is less favorable than formation of excited ruthenium(III) products, so formation of electronically excited $Os(bpy)_3^{2+}$ is not considered further. The effect on λ_{inner} of forming electronically excited ruthenium(III) in the reactions of Table III is not known, so λ_{inner} for reactions to form excited-state ruthenium(III) products is taken to be the same as the λ_{inner} for formation of electronic ground-state products; λ_{inner} = 15.5 kJ/mol.

The excitation energies in Table V were used, together with the reduction potentials of Table IV, to yield the $\Delta G°$'s (Table III) for formation of electronically excited ruthenium(III) products. The three reactions involving quenching of excited ruthenium(II) by ruthenium(III) appear to proceed more favorably to an excited ruthenium(III) product than to the ground state. The quantum mechanically calculated rates to excited ruthenium(III) are indicated by solid circles in Figure 3 and are in good agreement with experiment (open circles) for the three reactions involving ruthenium(III) quenchers (points labeled 5, 6, 7 and 5′, 6′, 7′).

Table V. Excitation Energies

	$E_{0\leftarrow 0}$, eV	ref
$Cr(bpy)_3^{2+}$	1.05 ± 0.1[a]	38, 39
$Os(bpy)_3^{2+}$	1.78 ± 0.01	27, 32, 37
$Ru(bpy)_3^{2+}$	2.12 ± 0.02	22, 23, 27, 29, 30, 32, 40
$Ru(Mebpy)_3^{2+}$	2.06 ± 0.02	23, 29
$Ru(bpy)_3^{3+}$	1.76 ± 0.07[b]	6
$Ru(Mebpy)_3^{3+}$	1.76[c]	

[a] The large uncertainty is due to estimating $E_{0\leftarrow 0}$ from the absorption spectrum alone. [b] The large uncertainty is due to estimating $E_{0\leftarrow 0}$ from the absorption spectrum alone (maximum at 1.83 eV[6]), assuming a Stokes shift $\leq$ 2300 cm^{-1} = 0.07 eV. [c] Estimated from $E_{0\leftarrow 0}$ for $Ru(bpy)_3^{3+}$.

In the case of quenching of excited ruthenium(II) by the chromium(III) complex there is good agreement between the quantum mechanically calculated values and the experimental values if the electronic ground state of the ruthenium(III) complex is the product (points 1 and 2 in Figure 3). Thus, the alternate pathway of forming an electronically excited ruthenium(III) complex would not be expected to be important and indeed is calculated to be slower than formation of ground-state ruthenium(III) by 22 and 16 orders of magnitude for reactions 1 and 2, respectively.

In the case of the two reactions involving quenching by the osmium(III) complex, the quantum mechanically calculated rate for formation of excited ruthenium(III) products was found to be little or no faster than for the formation of ground-state products (cf. points 3′ and 4′ in Figure 3 with the dashed line). The calculated (quantum) rate constants for formation of ground-state products are 2 and 3 orders of magnitude below the observed rate constants. *In view of the approximations in the* theory, this discrepancy may not be a conclusive one.

Alternatively, unless some not yet known low-lying electronically excited product state exists, quenching by the osmium complex may proceed via another mechanism. For example, H atom transfer followed by proton exchange with the solvent is a possibility. A third possibility is described later in this section.

To allow comparison, we have also calculated classically the rate constants for electron transfer to form electronically excited ruthenium(III) products. The same λ's and $\Delta G°$'s were used as for the quantum calculations discussed above. The classical rates to excited products are shown in Figure 3 by the "dash–dot" line and agree well with the quantum values (solid circles). We note that excited-state formation corresponds to the normal free-energy region, while ground-state product formation lies in the inverted region.

There is a third possible explanation for the large rate constants observed for reactions 3 and 4 in Figure 3 (reaction of two electronically excited ruthenium(II) complexes with the osmium(III) complex). The distance between the centers of the reactants in the activated complex, r, may in this case of an electronically excited reactant, be greater than the distance of closest approach. The distance of closest approach equals $a_1 + a_2$ where a_1 and a_2 are the radii of the two reactants. The value of the outer-sphere reorganization energy used in the rate constant calculations above ($^1/_4\lambda_{out}$ = 13.4 kJ/mol) was calculated by using the classical expression[1] for λ_{out} (eq 8) and assuming $r = a_1 +$

$$\lambda_{out} = (\Delta e)^2\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right) \qquad (8)$$

a_2.[6] In eq 8, Δe is the change in charge of a reactant, ϵ_{op} is the optical dielectric constant, and ϵ_s is the static dielectric constant of the solvent. If r were greater than $a_1 + a_2$, then the outer-sphere reorganization energy would be calculated to be greater than 13.4 kJ/mol, as may be seen from eq 8: the reactions in which $Os(bpy)_3^{3+}$ quenches electronically excited ruthenium(II) complexes

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to form a *ground* electronic-state ruthenium(III) (reactions 3 and 4 of Table III) have large negative free energies, and they lie in the "inverted region". In this case increasing r and hence increasing λ_{out} has, as is seen from eq 2, the effect of increasing the calculated electron-transfer rate. At least, it has this effect of rate enhancement if the reactions do not become too nonadiabatic at the larger r.

Indeed, if $r = 1.3(a_1 + a_2)$ and $a_1 \simeq a_2$, then the quantum mechanically calculated rate constants (corrected for diffusion according to eq 7) for the electron-transfer reaction between $*Ru(bpy)_3^{2+}$ and $*Ru(Mebpy)_3^{2+}$ and $Os(bpy)_3^{3+}$ (reactions 3 and 4 of Table III) are $k_3 = 8 \times 10^8$ M^{-1} s^{-1} and $k_4 = 3 \times 10^8$ M^{-1} s^{-1}, respectively. These values are within 1 order of magnitude of the experimental values obtained by Creutz and Sutin;[6] $k_3 \simeq 3.2 \times 10^9$ M^{-1} s^{-1}, and $k_4 \simeq 2.6 \times 10^9$ M^{-1} s^{-1}. If $r = 2(a_1 + a_2)$ and $a_1 \simeq a_2$, the quantum mechanically calculated values of the rate constants are $k_3 = 2 \times 10^9$ M^{-1} s^{-1} and $k_4 = 1 \times 10^9$ M^{-1} s^{-1}, essentially in agreement with the experimental values. These calculations were performed by using the same numerical values for the quantities other than λ_{out} as were used in the calculations described above that yielded the (dashed line) quantum values in Figure 3. However, electron transfer at too large an r makes the reaction increasingly nonadiabatic and then reduces the reaction rate. The appropriate r is the one which achieves a maximum rate.

Work terms were neglected. For the $Ru(bpy)_3^{2+} - Ru(bpy)_3^{3+}$ reaction they were estimated[19] to be 1.3 kJ/mol, which would affect the rate by a factor of $\exp(-1.3/2.5) = 0.6$.

At least in the Creutz and Sutin systems, it appears that the lack of significant inverted behavior is indicative either (a) of the third possibility above or (b) of alternate reaction pathways becoming competitive at large negative $\Delta G°$'s rather than (c) of nuclear tunneling. Nuclear tunneling due to the very high-frequency modes involved in transitions from the electronically excited reactants *is* a significant effect at very large negative $\Delta G°$'s but does not explain the lack of inverted behavior, as one sees from the dashed line in Figure 3.

Conclusion

Rate calculations for a hypothetical system and for the bipyridyl systems studied by Creutz and Sutin suggest that quantum effects are expected to be small in the normal region (i.e., for small to moderate $\Delta G°$'s) even for systems having fairly large internal frequencies. At large negative $\Delta G°$'s, quantum effects may frequently be significant. For most of the reactions considered in the "inverted" region, the calculated and experimental results agree within 1 order of magnitude, provided that electronically excited products are formed. An alternate atom-transfer pathway may occur in reactions where the calculated rate constant for an electron transfer is appreciably less than the experimental one in this "inverted" region. A third possibility of electron transfer at a larger distance is also considered.

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Appendix. Relation between λ and the Stokes Shift

We consider the case where excitation of a single harmonic vibrational mode is responsible for the emission and absorption line shapes. We define $X \equiv \lambda/h\nu$, where $^1/_4\lambda$ is the inner-sphere reorganization energy for transition from the electronic ground state to the luminescing state and ν is the frequency of the mode. (ν is assumed to be the same in both electronic states.)

We assume for brevity that $h\nu \gg kT$, and then luminescence will occur from essentially only the lowest vibrational level in the electronically excited state. Equation 5 gives the emission line shape as

$$I_e(l) \propto e^{-X}X^l/l! \tag{A1}$$

where l is the quantum number of the vibrational level in the ground electronic state to which luminescence occurs. The energy of the corresponding quantum emitted is $E_{0\leftarrow 0} - lh\nu$, where $E_{0\leftarrow 0}$ is the electronic excitation energy of the luminescing state relative to the ground state. The energy E_e of this quantum at the emission maximum is

$$E_e = E_{0\leftarrow 0} - l^*h\nu \tag{A2}$$

where l^* is the value of l which maximizes (A1), $l^* = X$.

Similarly, since $h\nu \gg kT$, absorption occurs essentially only from the lowest vibrational level in the electronic ground state, so the absorption intensity is

$$I_a(m) \propto e^{-X}X^m/m! \tag{A3}$$

where m is the vibrational quantum number of an electronically excited vibronic level to which absorption occurs. $I_a(m)$ is maximized with respect to m, and the energy E_a of the absorption maximum is

$$E_a = E_{0\leftarrow 0} + m^*h\nu \tag{A4}$$

where m^* is found by maximization of (A3) to equal X.

The Stokes shift is $E_s = E_a - E_e$.[41] From eq A2 and A4 we have

$$E_s = (m^* + l^*)h\nu = 2Xh\nu \tag{A5}$$

But $X = \lambda/h\nu$, so

$$E_s = 2\lambda \tag{A6}$$

Equation A6 is a well-known approximate formula (e.g., ref 4b). A simple classical derivation is given in ref 42. Equation A6 can also be obtained from the quantum mechanical theory of optical spectra in solids given in ref 43.

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(44) **Note Added in Proof**: The effect on the quantum calculations in Figure 3 of allowing electron transfer to occur over a range of distances is described by R. A. Marcus (*Int. J. Chem. Kinet.*, in press).