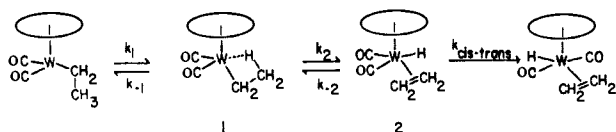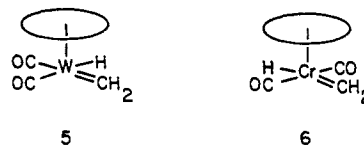**Scheme III**

is present in our solutions in 10^{-3} M. The slow increase in absorbance is the reversible process going to **4** with a forward rate constant k_3. We propose that the rate of this step is not limited by loss of L and thus the rate of the forward reaction should have no dependence on [L]. However, since the reverse step is bimolecular and dependent on the ligand concentration the equilibrium concentrations of **3** and **4** should be dependent on [L]. The rate constant k_3 will be dependent on the donor characteristics of L thus a difference in rate for the solutions containing THF and without THF, where L is water, is seen. That k_3 is an order of magnitude greater for L = H_2O vs. L = THF suggests that THF is a better ligand than water for the tungsten complex.

Discussion

The previously proposed model for the photolysis of CpW-(CO)$_3$Et is represented in Scheme III.[3a] The cis–trans isomerization step is thought to be rate determining and so steps 1 and 2 are at equilibrium. We have measured the rate constant k_1 for formation of the β-hydrogen solvated structure **1** and derived an activation barrier of 10.8 ± 0.4 kcal/mol for that process assuming a preexponential factor of 10^{13} s^{-1}. The second rate constant measured may be either the rate at which the equilibrium between **1** and cis-olefin hydride **2** is set up, i.e., k_2, or if the $1 \rightleftharpoons 2$ equilibrium is fast compared to $k_{cis-trans}$ then the observed rate constant is $k_{cis-trans}$. Thus, from our data we can place an upper bound on the activation energy for the β-elimination process to be 12.3 ± 0.4 kcal/mol.

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In the photolysis of CpW(CO)$_3$Me the identity of **4** is not known; however, we suggest that it is the product arising from α-elimination (**5**). The *trans*-chromium analogue **6** arising from photolysis of CpCr(CO)$_3$Me has been identified in low-temperature matrices.[11] Such processes have precedence and are pro-

posed to participate in many organometallic reactions.[1,12–16] This process may be expected to exhibit a deuterium isotope effect although none was observed when CpW(CO)$_3$CD$_3$ was photolyzed under identical conditions. Of course the lack of an isotope effect does not rule out the α-elimination product as **4** but further studies are required to firmly establish the identity of this product.

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Photochemistry of Compounds in the Constrained Medium Cellulose. 7. The Effect of Temperature on Photoinduced Electron Transfer from Tris(2,2-bipyridine)ruthenium(II) to Methylviologen Solubilized in Cellophane

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Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received March 11, 1985

Abstract: The effect of temperature on photoinduced electron transfer from Ru(bpy)$_3^{2+}$ to MV^{2+} in a cellophane matrix has been studied by steady state and pulsed laser photolysis techniques. The first-order rate constant which depends exponentially on the distance between the reactants shows a non-Arrhenius type of behavior in the temperature interval from 77 to 294 K. This phenomenon, previously found to be of great importance in the biological systems, was quantitatively interpreted in terms of a nonadiabatic multiphonon nonradiative decay process.

The mechanism of electron transfer between reactants, in particular photoinduced electron transfer, is of considerable interest in many avenues of science, both from the point of view of chemists who are concerned with mechanistic features of these reactions

and from a biological point of view when the electron transfer between reactants occurs over some considerable distance.[1–9] In

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simple liquid systems electron transfer can certainly occur on contact of the two reactants. Such reactions are often diffusion controlled and any electron tunnelling process, i.e., when the electron is transferred prior to contact of the reaction, is usually minimized. This is probably due to the fact that electron transfer over distances of some 10 Å usually takes of the order of 10^{-7} s or longer, whereas diffusion over such short distances in media such as water or benzene, i.e., media of viscosity lcp, is much faster than the electron tunnelling reaction. Hence, diffusion takes place to within the contact distance prior to any significant jumping of the electrons between the reactants. If the reactants are organized in some special geometry, e.g., frozen media at low temperatures, so that no motion of the reactants takes place, then it is indeed possible to artifically impose conditions where diffusion is zero, and any electron transfer has to occur via some tunnelling mechanism. This has been observed in several frozen glassy systems.[10,11] These systems usually operate at temperatures which are well below the glass transition and are quite often at liquid nitrogen temperature, 77 K.

Several attempts have been made to arrive at the exact mechanism of electron transfer in assembled systems such a micelles or bilayer systems.[12] These are of direct importance to the biological systems, where electron transfer occurs not in a simple homogeneous medium but in some structured configuration. However, many systems where electron transfer was observed were shown to take place by a contact of the reactants, which takes place via diffusion on the surface of the structure. Any attempt to minimize this diffusion by freezing the systems at 77 K again gives rise to systems where tunnelling is not very efficient. However, an attempt that is of immediate importance is to use media which hold the reactants in some known configuration over a range of temperatures, including room temperature, and to study this effect we have used cellophane. Materials of interest are diffused into cellophane from solutions followed by elimination of the solvent thereby leaving a matrix of cellophane and the chemical system, which can operate from well above room temperature to 77 K or lower. We are able to show that electron transfer takes place in these systems provided the correct reactant configuration is achieved.[13a] Earlier studies were consistently carried out at room temperature, as a convenient experimental condition in our laboratory, and as one of particular interest. There are reports which suggest that there is a pronounced effect of temperature on electron tunnelling reactions.[5] This is due to the coupling of phonon modes of the system with the electronic modes of the reactant molecules.

In the present system we have applied a cellophane matrix[13b] and embodied into it a ruthenium tris(bipyridine), methylviologen [Ru(bpy)$_3$$^{2+}$/MV^{2+}] photosystem, which on excitation of the ruthenium complex gives rise to electron transfer giving reduced methylviologen, which is readily observed spectroscopically due to its two pronounced maxima at 399 and 610 nm. It was shown earlier that at room temperature this mechanism takes place via an electron tunnelling process, and it was possible to describe the data by conventional theories.[14,15] In the present study the effect

of temperature on the Ru(bpy)$_3$$^{2+}$/MV^{2+} system produced data which can be used to investigate the various theories that are being suggested to account for temperature effects for an actual tunnelling process. In particular it is felt that prior data concerned itself with biological systems, which were not particularly well defined, and were quite complicated, whereas the present system is probably as simple a system as could ever be presented, and which could provide sensible data on the effect of temperature on e$^-$ tunnelling processes.

Experimental Section

Materials. Methylviologen chloride salt (Aldrich Chemical Co., Inc.) was recrystallized three times from pure ethanol prior to use. Tris-(2,2'-bipyridine)ruthenium(II) chloride salt (G. Frederick Smith Chemical Co.) was used as received. Cellophane film (type 215 P.D., average thickness = 26 μm) was kindly supplied from DuPont Chemical Co., Polymer Product Department. Samples were prepared as described elsewhere.[16]

Instruments. A short pulse P.R.A. Nitromate laser with a wavelength = 337.1 nm, pulse = 120 ps, and an energy of 30 μJ per pulse was used as an exitation source for *Ru(bpy)$_3$$^{2+}$ emission decay measurements. A Tektronix 7912 AD transient capture device was used to monitor the short-lived species formed. Data analysis was carried out on both a Tektronix 4052A and an IBM 3033 computer.

Steady-state absorption and emission spectra were recorded on a Perkin-Elmer 551 spectrophotometer and a Perkin-Elmer MPF 44B spectrofluorimeter, respectively.

Steady-state and pulsed luminescence quenching studies were performed by positioning the film at a 45° angle to the incident exitation light and the detector. This geometry minimizes scatter off of the film by directing scattering light away from the detector. Since the emission intensity is strongly position dependent the cellophane film was placed between two plates which were made to fit securely into a standard quartz cell always providing the same position of the film.

Low-temperature experiments were carried out by cooling the Dewar flask with N$_2$ gas which has been passed through liquid nitrogen. A desired temperature was achieved by adjusting the N$_2$ flow rate. Temperatures were measured with a calibrated copper-constantan thermocouple.

Results and Discussion

Our previous work has shown that the quenching of excited Ru(bpy)$_3$$^{2+}$ by MV^{2+} in a cellophane medium proceeds via an electron tunneling mechanism.[14] The rate constant was found to be dependent on the reacting distance in the following manner: $k(r) = 1.0 \times 10^{10} \exp(-0.46r)$ [s^{-1}], but the parameters obtained are different from those predicted earlier.[17]

Hence, in order to gain further insight into the reaction mechanism, the influence of temperature on the rate constant has been studied by means of a pulsed laser photolysis technique. The rates of decay of excited Ru(bpy)$_3$$^{2+}$ obtained from the cellophane sample which contained 0.01 mol dm^{-3} of Ru(bpy)$_3$$^{2+}$ and 0.1 mol dm^{-3} of MV^{2+} in the temperature interval from 77 to 294 K were interpreted by the same model which has been used in our previous studies at room temperature.

The model, originally proposed by Miller, assumes that the rate constant depends exponentially on the separation of reactants where ν and a are associated with the vibrational frequency and

$$k(r) = \nu \exp(-r/a) \qquad (1)$$

the attenuation length of the wave function, respectively.[18] Later the model was improved from the mathematical aspect by Tachia and Mozumder leading to the following equation which described the emission decay of an excited electron donor in the presence of a randomly distributed acceptor in a rigid medium[19,20]

$$I = I_0 \exp\{-k_0 t - A[\ln^3 (\nu t) + 1.732 \ln^2 (\nu t) + 5.934 \ln (\nu t) + 5.445]\} \quad (2)$$

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Photochemistry of Compounds in Cellulose

J. Am. Chem. Soc., Vol. 108, No. 10, 1986 2515

Table I $Ru(bpy)_3^{2+}$ Luminescence Quenching Parameters Obtained by Fitting Luminescence Decay Data to Eq 8[a]

temp, °C	C_0, mol dm⁻³	R_0, Å	$10^{-8}\nu$, s⁻¹	$1/a$, Å⁻¹	$k_{12A} \times 10^{-5}$, s⁻¹
−195	0.98	794	0.071	0.48	0.24
−190	0.805	7.9	0.091	0.47	0.32
−180	0.605	8.7	0.131	0.46	0.42
−170	0.55	9.0	0.18	0.47	0.60
−160	0.46	9.5	0.26	0.48	0.75
−150	0.39	10.1	0.39	0.48	1.24
−140	0.33	10.6	0.57	0.49	1.60
−130	0.275	11.3	0.85	0.49	2.37
−120	0.235	11.9	1.28	0.49	3.33
−110	0.197	12.6	1.94	0.49	5.05
−100	0.167	13.3	2.98	0.49	7.75
−90	0.142	14.1	4.54	0.49	12.2
−80	0.125	14.7	6.8	0.49	18.2
−70	0.112	15.2	9.8	0.49	25.1
−60	0.103	15.7	13.7	0.49	35.2
−50	0.092	16.3	19.0	0.49	51.2
−40	0.084	16.8	25	0.49	68.8
−30	0.077	17.3	34	0.49	95.0
−20	0.065	18.3	45	0.47	151
−10	0.063	18.5	59	0.48	184
0	0.058	19.0	74	0.47	244
+10	0.054	19.4	91	0.47	308
+21	0.0515	19.7	106	0.47	367

[a] Experimental conditions: cellophane matrix, $[Ru(bpy)_3^{2+}] = 0.01$ mol dm⁻³, $[MV^{2+}] = 0.1$ mol dm⁻³, $\lambda_{ex} = 337.1$ nm, and $\lambda_{em} = 610$ nm.

where k_0 is the rate constant for the inherent unmolecular decay of the excited state and A is a factor which depends linearly on the quencher concentration, where R_0 is "a critical transfer

$$A = \frac{1}{(R_0/a)^3 C_0}[Q] \qquad (3)$$

distance" in the sense that, for an isolated donor–acceptor pair separated by R_0, the electron transfer occurs with the same rate as the spontaneous deactivation in the donor.

The parameters obtained by fitting the experimental data to eq 2 are presented in Table I.

It can be noted that our values are significantly smaller than the values reported earlier for the same donor–acceptor pair studied in glycerol medium.[21,22] There are a number of reasons which could be responsible for the difference observed.

However, one of them could be that the rise time of our laser photolysis detection (≤1 ns) is long compared to early events, thus resulting in an inaccurate detection of the initial luminescence intensity following the laser pulse. (If the first part of the decay had been omitted, the ν parameter would have been smaller than that given.)

Hence, before the discussion of the results was undertaken, the steady-state experiment was performed in order to prove both that our experimental data are correct and that the quenching is well described by eq 2.

The emission intensities of samples containing various quencher concentrations are presented in Figure 1. If the model accurately describes the quenching and our pulse photolysis data are accurate, then the I/I_0 ratios calculated from Figure 1 should fit the integrated form of eq 2 i.e.

$$I/I_0 = 0\int{}^{\infty}I(t)\,dt \qquad (4)$$

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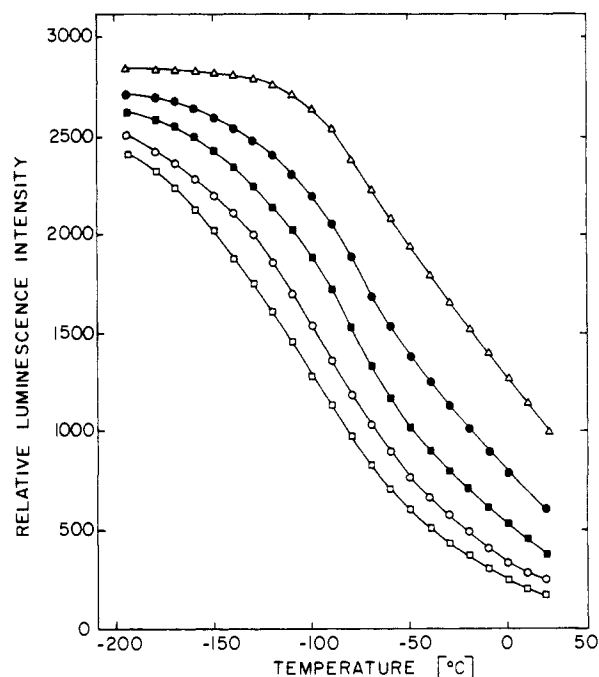
Figure 1. The temperature dependence of $Ru(bpy)_3^{2+}$ luminescence intensities in the cellophane sample with various MV^{2+} concentrations [mol dm⁻³]: (△) 0, (●) 0.25, (■) 0.05, (○) 0.075, (□) 0.1. All intensities are normalized with respect to the sample at 21 °C with no MV^{2+}, the luminescence intensity of which is arbitrarily taken as 1000.
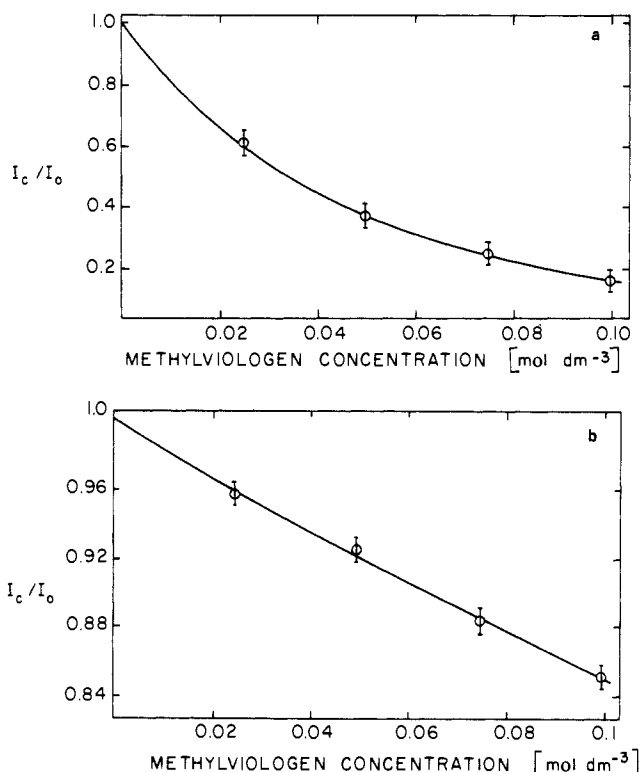

Figure 2. The relative yields of $Ru(bpy)_3^{2+}$ luminescence intensity computed from the pulsed laser photolysis data with eq 4 (solid line) and from the steady-state quenching data of Figure 1. Part a corresponds to 295 K while part b corresponds to the liquid nitrogen temperature.

Plots a (294 K) and b (77 K) in Figure 2 show a comparison of the ratio I/I_0 computed with eq 4 and the pulsed laser photolysis data from Table I (solid line) and the I/I_0 ratios calculated from the steady-state luminescence intensity data in Figure 1.

Good agreement was found over the entire temperature region, proving that our experimental data are accurate and that our equipment faithfully follows the radiation-induced events.
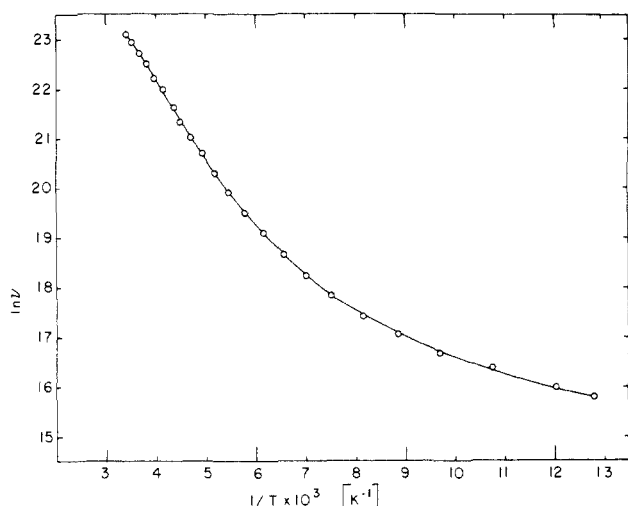
Figure 3. Natural logarithm of the frequency factor vs. reciprocal temperature, obtained by fitting of experimental $Ru(bpy)_3^{2+}$ decay data by eq 2. Experimental conditions: $\lambda_{ex} = 337.1$ nm, $\lambda_{em} = 610$ nm, energy $= 30$ μJ per pulse, $[Ru(bpy)_3^{2+}] = 0.01$ mol dm^{-3}, $[MV^{2+}] = 0.1$ mol dm^{-3}, cellophane matrix.

The data from Table I show several interesting features of the system. The attenuation factor, a, does not change with decreasing temperature. However, the frequency factor, ν, decreases about four orders of magnitude with decreasing temperature down to 77 K, but the Arrhenius plot is not linear, as shown in Figure 3. It is pertinent to note that the shape of the curve is that expected for thermally activated electron tunneling.

Several theoretical approaches have been developed to explain the non-Arrhenius-type dependence of an electron transfer rate constant on temperature,[23-25] and among them Jortner's model seems to be the most consistent and is briefly reviewed below.[26] Electron transfer has been conceptualized in terms of a nonradiative decay process between the vibronic levels $|av\rangle$ and $|bw\rangle$ which correspond to DA and D^+A^-, respectively. The vibronic levels are characterized by the electronic wave functions Ψ_a and Ψ_b and the nuclear wave functions $\chi_{av}(Q)$ and $\chi_{bw}(Q)$, i.e., $|av\rangle \equiv \Psi_a\chi_{av}(Q)$ and $[bw] \equiv \Psi_b\chi_{bw}(Q)$. For the case of displaced harmonic nuclear potential surfaces, characterized by the normal modes $Q = q_1, Q_2, ..., Q_i$ where the frequencies $\{\omega_i\}$ and reduced masses $\{\mu_i\}$ are identical in the initial and the final states, the thermally averaged decay probability for the $\{|av\rangle\} \rightarrow \{|bw\rangle\}$ process can be adequately expressed in terms of the Fermi golden role (i.e., first-order perturbation theory). The general solution of the problem incorporates the effects of both low-frequency phonon modes and high-frequency molecular vibrational modes.

Previous considerations related to electron-transfer studies in proteins as well as our earlier low-temperature studies indicate that effective coupling between electronic states and molecular-type vibrations dominates the nuclear contribution to electron-transfer probability. In such cases one obtains the simplified relationship

$$k = A \exp[-S(2\bar{\nu} + 1)]I_p\{2S[\bar{\nu}(\bar{\nu} + 1)]^{1/2}\}[(\bar{\nu} + 1)/\bar{\nu}]^{p/2} \quad (5)$$

where I_p denotes the modified Bessel function of the order $p = \Delta E/\hbar\langle\omega\rangle$, $S = \Delta^2/2$ is electron vibration coupling strength, and $A = 2\pi|V_{ab}(R)|^2/\hbar^2\langle\omega\rangle$. The symbols are as follows: $V_{ab}(R)$ is the electron exchange matrix element between D and A separated by the distance R, ΔE corresponds to the energy gap between the minima of the initial and final nuclear potential surfaces, Δ represents the nuclear displacement, while $\bar{\nu}$ denotes the mean
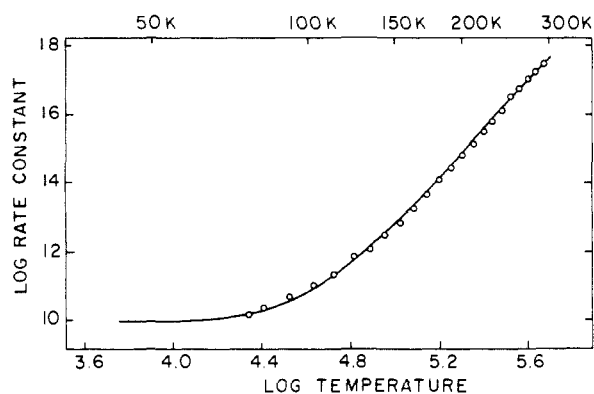
thermal population of the vibrational mode.

Equation 5 was used to fit the experimental data.

It is pertinent to note that the above equation contains four variable parameters. Therefore, before computer fitting of the experimental data was performed, some limitations had to be made in order to avoid "an excellent fit" with parameters which are senseless from the physical point of view. In accord with the thermodynamical analysis of the same reaction in the liquid state,[27] it seems reasonable to assume that e^- transfer from $*Ru(bpy)_3^{2+}$ to MV^{2+} is weakly exothermic in the solid state, thus resulting in an upper limit of 0.5 eV for the energy gap between the minima of the initial and final nuclear potential surfaces. At the present time we have no detailed spectroscopic information concerning the $*Ru(bpy)_3^{2+}/MV^{2+}$ redox couple systems. However, it is possible to obtain some idea about the $\hbar\langle\omega\rangle$ factor by utilizing the detailed analysis of the model[28] which is represented by eq 7. More precisely, the temperature around which the rate constant becomes dependent on temperature is given by

$$t_b = \hbar\langle\omega\rangle/4k \quad (6)$$

It can be noticed in Figure 4 that the onset of the exponential increase of the rate constant with an increase in the temperature occurs somewhere around 100 K which gives $\hbar\langle\omega\rangle \simeq 0.035$ eV. Further, it has previously been estimated that the frequency of the totally symmetrical vibration of the coordination layer for transition-metal complexes is about 0.05 eV.[29] Guided by these two approximations we set the limitation $0.02 < \hbar\langle\omega\rangle < 0.1$ eV. Then, according to eq 5 the p factor should be smaller than 10.

From the high temperature activation energy expression

$$E_a = \frac{(S\hbar\langle\omega\rangle + \Delta E)^2}{4S\hbar\langle\omega\rangle} \quad (7)$$

utilizing the experimental value of $E_a = 0.15$ eV and the parameters estimated above we set the limitation $10 < S < 30$.

Figure 4 shows the temperature dependence of the rate constants at a distance of 12 Å center to center (circles). The solid curve represents the calculation with eq 5 applied to the experimental data (we have chosen to plot log k vs. log T rather than to use a conventional Arrhenius plot since the former demonstrates better the characteristic behavior of the rate constant throughout the temperature range). The best fit was obtained with the following parameters: $\Delta E \approx -0.1$ eV, $A = 1.2 \times 10^{12}$ s^{-1}, $S = 24$, and $\hbar\langle\omega\rangle = 0.044$ eV. From these parameters it is now possible to calculate the electron exchange integral at the known distance of 12 Å (eq 1a from ref 28). The value obtained, $V = 19$ cm^{-1}, is significantly higher than the values estimated by both Jortner and Hopfield. Thus in order to explain the electron transfer mechanism that, it is not necessary to look for other interactions (such as a su-

Figure 4. Natural logarithm of the rate constant of $*Ru(bpy)_3^{2+} + MV^{2+}$ reaction at the center-to-center reaction distance of 12 Å vs. natural logarithm of temperature. The smooth line represents the best fit by eq 5.

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perexchange type of electronic coupling) since the large value of *V* itself enables a long-range electron transfer to occur in this system.

Conclusion

The experimental data show the marked effect that temperature imposes on the photoinduced electron transfer from excited tris(2,2'-bipyridine)ruthenium(II) to methylviologen. The unusual kinetics are quantitatively explained by a mechanism whereby the nuclear contribution to the electron transfer probability is dom-

inated by coupling with high-frequency molecular modes. Similar experimental data have been reported earlier for electron transfer in bio systems, while the present data provide the opportunity to check the theoretical consideration in a quantitative fashion.


Ab Initio and Monte Carlo Calculations for a Nucleophilic Addition Reaction in the Gas Phase and in Aqueous Solution

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Abstract: Energy profiles for the nucleophilic addition of hydroxide ion to formaldehyde in the gas phase and in aqueous solution have been determined with quantum and statistical mechanical methods. Ab initio calculations at the 6-31+G* level were utilized to study the gas-phase potential energy surface. In the gas phase, the conversion of reactants to the tetrahedral intermediate is exothermic by 35 kcal/mol and proceeds via an ion–dipole complex. Monte Carlo simulations were then carried out for the reacting system solvated by 269 water molecules at 25 °C and 1 atm with solute–solvent potential functions derived from ab initio calculations in conjunction with the TIP4P model of water. Importance sampling methods were employed to obtain the potential of mean force in solution. A substantial activation barrier is introduced by hydration with the transition state occurring at a C–O separation of ca. 2 Å. The calculated height of the free energy barrier is 24–28 kcal/mol and the tetrahedral intermediate is 10–14 kcal/mol above the reactants. Finally, fixed solute simulations corresponding to the reactants, transition state, and product were carried out to probe the origin of the activation barrier. This established that it is not so much a change in the number of solute–water hydrogen bonds along the reaction path but rather in their strengths that is primarily responsible for the solvent-induced barrier. The charge-localized hydroxide ion participates in six strong hydrogen bonds with water molecules. Upon proceeding to the more charge-delocalized transition state and product, there are still 6–7 water–solute hydrogen bonds; however, they are ca. 40% weaker than for hydroxide ion.

Nucleophilic addition to a carbonyl group is a fundamental process in organic chemistry and biochemistry. Common examples include ester and amide hydrolysis, aldol condensation, and numerous reactions of organometallic reagents and ylides.[1,2] Extensive experimental work has led to general acceptance of the "tetrahedral mechanism" for these processes;[2,3] the key feature is formation of a tetrahedral intermediate that collapses to products (eq 1).
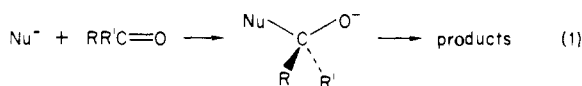
Isolation or spectroscopic detection of the tetrahedral intermediate have been achieved in some cases,[2] while ^{18}O labeling studies have provided additional compelling evidence for its existence.[4] Furthermore, Guthrie's analyses of thermodynamic and kinetic data have provided estimates of the free energy profiles for ester and amide hydrolyses.[5] The formation of the tetrahedral intermediate is normally the rate-determining step.

Still greater knowledge of the mechanism and structure of the intermediate and transition states are important goals. Valuable

information has been obtained from recent gas-phase experiments by several groups.[6] A striking observation is the general tendency of esters to undergo competitive proton transfers, eliminations, and S_N2 reactions in favor of $B_{AC}2$ processes (eq 1) in the absence of solvent. However, reversal of this pattern has been found upon addition of only one solvent molecule.[6d] Asubiojo and Brauman have also found the $B_{AC}2$ mechanism to be operative for gas-phase additions to acyl halides.[6e] Their analysis of the kinetics led to the provocative proposal that the reactions in the gas phase feature a double-well potential surface with the tetrahedral species as a transition state and ion–dipole complexes as minima.

Additional insight on the reaction surface has been provided by Burgi et al.[7a,b] Using crystallographic data for various nucleophilic groups interacting with different carbonyl centers, they were able to suggest likely pathways for approach of the nu-

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