

Temperature Effects on Intramolecular Electron Transfer Kinetics under “Normal”, “Inverted”, and “Nearly Optimal” Conditions

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The temperature dependence of electron transfer over a wide range of driving forces extending from far in the “normal” to deep into the “inverted” region is studied with the aid of a limited number of closely related and fully rigid bridged donor–acceptor systems. The interpretation of temperature-dependent electron-transfer kinetics is shown to be complicated by the relatively large influence of the temperature dependence of the solvent dielectric properties. This problem becomes especially evident if the barrier is small, when it may lead to an overall nullification or even inversion of the temperature effect on the experimental rate. Upon correction for the temperature dependence of the solvent properties, the rate of electron transfer is found to be independent of temperature in the inverted region, where nuclear tunneling becomes dominant, in contradiction to expectations based on the classical Marcus treatment which, however, is shown to be capable of giving a qualitative description of the temperature dependence in the normal region, even under close to “optimal” conditions.

Introduction

Over the past decade an increasing number of rigidly bridged donor–acceptor (D–bridge–A) systems has become available in which thermal or photoinduced electron transfer can be studied between donor and acceptor sites that are held at a narrowly defined distance and relative orientation not influenced by external factors such as solvent and temperature. This development has boosted the investigation of electron transfer processes.¹ Thus much has been learned about such aspects as the influence of distance, the nature of the intervening medium (including the bridge), solvent polarity, and orbital symmetry. Another point of current interest is whether electron transfer can be described as a thermally activated process as suggested by the classical Marcus description^{2,3} which leads to the well-known expression (1) for the Gibbs activation energy of an electron transfer where the overall change in Gibbs energy is ΔG and the total reorganization energy is λ .

$$\Delta G^\ddagger = (\Delta G + \lambda)^2 / 4\lambda \quad (1)$$

From this description the rate of electron transfer is then given by eq 2, where h and k_B are the Planck and Boltzmann constants and H_{rp} is the electronic matrix element coupling the reactant and product states:

$$k_{et} = \frac{2\pi^{3/2}}{h(\lambda k_B T)^{1/2}} H_{rp}^2 \exp\left[\frac{-(\lambda + \Delta G)^2}{4\lambda k_B T}\right] = \frac{2\pi^{3/2}}{h(\lambda k_B T)^{1/2}} H_{rp}^2 \exp\left[\frac{-\Delta G^\ddagger}{k_B T}\right] \quad (2)$$

Both theoretical considerations⁴ and recent experimental results^{5–7} indicate that this attractively simple description may be adequate in the “normal” region where $-\Delta G < \lambda$, but tends to fail in the “inverted” region where $-\Delta G > \lambda$. This failure became primarily evident from the fact that in the inverted region the isothermal rate does not decrease when $-\Delta G$ is increased or

at least not nearly as sharply as predicted by eq 2. Perhaps more revealing, however, are the recent observations by Smit et al.⁸ and by Miller et al.⁹ that in the inverted region the electron transfer rate is almost temperature independent, whereas according to eq 1 a high barrier and therefore a strong temperature dependence should occur.

In the present paper we extend earlier studies on temperature dependence of electron transfer in rigid D–bridge–A systems to cover both a large temperature and a large ΔG range, the latter extending from the “normal” to deep into the “inverted” region.

Results and Discussion

Photoinduced Charge Separation in the “Normal” Region. In order to achieve “normal” region conditions while maintaining a sufficient driving force to prevent significant back reaction, it is advantageous to work under conditions where the total reorganization energy is high. The latter can be achieved readily by employing a polar solvent medium since the solvent reorganization energy for a charge separation is given by¹⁰

$$\lambda_s = e^2(1/r - 1/R_c)(1/n^2 - 1/\epsilon_s) \quad (3)$$

In eq 3 R_c denotes the center-to-center charge separation distance and r the average ionic radius of the created D^+ and A^- species while ϵ_s and n are the static dielectric constant and the refractive index of the solvent medium. Furthermore the driving force for photoinduced charge separation can be calculated via the well-known Weller expression:¹¹

$$\Delta G_{cs} = E_{ox}(D) - E_{red}(A) - E_{00} - e^2/\epsilon_s R_c - (e^2/r)(1/37.5 - 1/\epsilon_s) \quad (4)$$

In eq 4 $E_{ox}(D)$ and $E_{red}(A)$ are the electrochemical oxidation and reduction potentials of D and A as measured in acetonitrile ($\epsilon_s = 37.5$), while E_{00} is the energy of the locally excited state from which the electron transfer occurs.

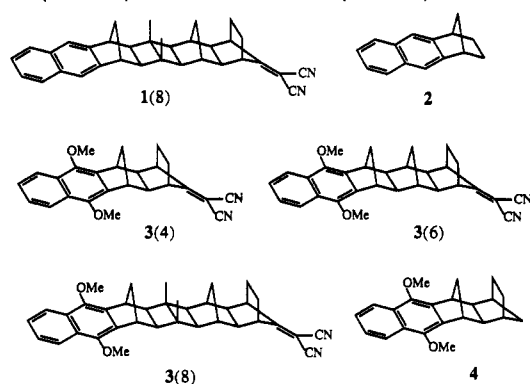
According to eqs 3–4, photoinduced electron transfer in system 1(8) (see Chart I) should have a significant driving force in polar solvents and at the same time fulfill the “normal” region condition that $-\Delta G < \lambda$. As we have reported earlier¹² appropriate

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CHART I: Structure of the Bridged Donor-Acceptor Systems (1 and 3) and Model Donors (2 and 4) Studied^a

^a For the bridged systems the number in parentheses indicates the effective length of the bridge in σ bonds.

TABLE I: Donor Fluorescence Lifetimes and Rates of Charge Separation, As Calculated with Equation 5, for 1(8) in Acetonitrile, Together with the λ , ΔG_{CS} , and ΔG^\ddagger Calculated via Equations 1-4 at Various Temperatures^a

| T (K) | τ (ns) ^b | k_{cs} (10^7 s ⁻¹) | ΔG_{CS} (eV) | λ (eV) | ΔG^\ddagger (eV) |
|---------|--------------------------|-------------------------------------|----------------------|----------------|--------------------------|
| 318 | 5.8 | 15.6 | -0.66 | 1.63 | 0.146 |
| 306 | 6.6 | 13.6 | -0.66 | 1.63 | 0.145 |
| 293 | 7.6 | 11.5 | -0.65 | 1.62 | 0.144 |
| 278 | 12 | 6.5 | -0.65 | 1.61 | 0.143 |
| 271 | 13 | 6.0 | -0.65 | 1.61 | 0.143 |
| 264 | 16 | 4.7 | -0.65 | 1.61 | 0.142 |
| 263 | 15 | 5.2 | -0.65 | 1.61 | 0.142 |
| 252 | 19 | 3.7 | -0.65 | 1.60 | 0.141 |
| 251 | 19 | 3.8 | -0.65 | 1.59 | 0.140 |
| 229 | 22 | 2.9 | -0.65 | 1.59 | 0.140 |

^a The temperature dependence of the refractive index and dielectric constant are expressed as¹³: $n(T) = 1.3441 - 0.00045(T-293)$ and $\epsilon(T) = 37.45 - 0.155(T-293)$. ^b The lifetime (τ_{ref}) of the donor-model 2 was found to increase from 64 ns at 318 K to 68 ns at 229 K.

TABLE II: Donor Fluorescence Lifetimes and Rates of Charge Separation, as Calculated with Equation 5, for 1(8) in Ethyl Acetate, Together with λ , ΔG_{CS} , and ΔG^\ddagger Calculated via Equations 1-4 at Various Temperatures^a

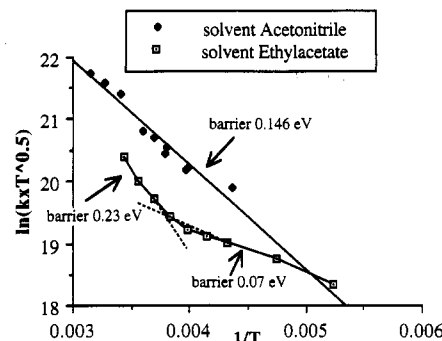
| T (K) | τ (ns) ^b | k_{cs} (10^6 s ⁻¹) | ΔG_{CS} (eV) | λ (eV) | ΔG^\ddagger (eV) |
|---------|--------------------------|-------------------------------------|----------------------|----------------|--------------------------|
| 291 | 17 | 42 | -0.373 | 1.307 | 0.167 |
| 281 | 22 | 29 | -0.388 | 1.314 | 0.163 |
| 271 | 26 | 22 | -0.400 | 1.319 | 0.160 |
| 261 | 30 | 17 | -0.413 | 1.324 | 0.157 |
| 251 | 33 | 14 | -0.424 | 1.328 | 0.154 |
| 241 | 34 | 13 | -0.434 | 1.331 | 0.151 |
| 231 | 35 | 12 | -0.444 | 1.333 | 0.148 |
| 211 | 40 | 9.5 | -0.461 | 1.336 | 0.143 |
| 191 | 46 | 6.6 | -0.476 | 1.338 | 0.139 |

^a The temperature dependence of the refractive index and dielectric constant are expressed as¹³: $n(T) = 1.3724 - 0.00048(T-293)$ and $\epsilon(T) = 6.002 - 0.027(T-293)$. ^b The lifetime (τ_{ref}) of the donor-model 2 was found to increase from 60 ns at 291 K to 66 ns at 191 K.

parameters for 1(8) are $R_c = 11.4$ Å, $r = 4.4$ Å, $E_{00} = 3.87$ eV, $E_{ox}(D) = 1.55$ V, and $E_{red}(A) = -1.7$ V, while the internal reorganization energy for this type of system has been estimated to amount to $\lambda_i = 0.6$ eV. As we have reported earlier¹² 1(8) undergoes photoinduced charge separation upon excitation of the naphthalene donor chromophore in solvents of high and medium polarity. The rate of this process (k_{cs}) is readily determined via eq 5 by comparison of the lifetime, τ , of the residual fluorescence of this chromophore with that of the model system 2.

$$k_{cs} = 1/\tau - 1/\tau_{ref} \quad (5)$$

In Tables I and II we have compiled fluorescence lifetimes of 1(8) as measured in acetonitrile and in ethyl acetate over a wide

**Figure 1.** Modified Arrhenius plots for photoinduced charge separation of 1(8) in acetonitrile and in ethyl acetate.

temperature range as well as the k_{cs} values calculated therefrom. Included in Table I are the ΔG , λ , and ΔG^\ddagger calculated via eqs 1, 3, and 4 employing an internal reorganization energy $\lambda_i = 0.6$ eV ($\lambda = \lambda_i + \lambda_s$) and taking into account the temperature dependence of the solvent dielectric properties. The latter is predicted to exert only a minor influence in the case of acetonitrile, but for ethyl acetate (see last column of Table II) the temperature dependence of the solvent dielectric properties is predicted to induce a very significant temperature dependence of the barrier! In Figure 1 modified Arrhenius plots of $\ln(kT^{0.5})$ versus $1/T$ are presented. According to eq 2 this should provide a linear relation assuming that both the barrier and λ are temperature independent. As predicted by the calculations this requirement is fulfilled quite well in acetonitrile and also the barrier deduced from the regression line through the data points (0.146 eV) matches that predicted by application of the Marcus model extremely well. In ethyl acetate the experimental data support the prediction that the barrier decreases considerably with decreasing temperature. From the difference in slope of the regression in the "high" and the "low" temperature limits (see Figure 1), it appears that this temperature dependence is even more pronounced than predicted, but the average value of 0.15 eV is again (perhaps fortuitously) very close to that predicted from the Marcus model (see last column of Table II).

In conclusion it is thus found that the classical Marcus model provides a good estimate of the barrier for photoinduced charge separation in 1(8) in solvents of medium and high polarity, a process which occurs into the normal region far from the optimal conditions because $\lambda + \Delta G_{cs}$ is estimated to be in the order of +1 eV (see Tables I and II). Furthermore the results obtained demonstrate that because the barrier for long-range electron transfer processes is very sensitive to the, temperature dependent, dielectric properties of the solvent medium, its magnitude may also be considerably temperature dependent. As is evident from the curvature of the modified Arrhenius plot obtained in, e.g., ethyl acetate (see Figure 1) such temperature dependence of ΔG^\ddagger cannot simply be accounted for in terms of activation entropy.

Charge Recombination in the "Inverted" Region. Practical problems limit the possibility to design rigidly bridged D/A systems in which photoinduced charge separation occurs under inverted region conditions at rates amenable to sufficiently accurate experimental determination. However, as we¹⁴ and others^{15,16} have pointed out before, determination of charge recombination rates allows the study of electron transfer processes occurring deep into the inverted region. For charge recombination following photoinduced charge separation the driving force is given by eq 6

$$\Delta G_{cr} = E_{red}(A) - E_{ox}(D) + e^2/\epsilon_s R_c + (e^2/r)(1/37.5 - 1/\epsilon_s) \quad (6)$$

Evidently this can now be made most negative by working in a nonpolar solvent which at the same time minimizes λ . For the present purpose we therefore studied charge recombination rates

TABLE III: Lifetimes of the Charge Separated State of 3(4) and 3(6) in *n*-Hexane and *trans*-Decalin at Different Temperatures As Determined from Time-Resolved Microwave Conductivity (TRMC) Measurements, Together with the Lifetimes for 3(6) in *n*-Hexane, Methylcyclohexane (MCH), and *trans*-Decalin As Determined from Time-Resolved Charge Transfer Fluorescence Measurements

| TRMC | | | | | | | | | | | | | |
|------------------|-------------|-----------------------|-------------|------------------|-------------|-----------------------|-------------|------------------|-------------|--------------|-------------|-----------------------|-------------|
| 3(4) | | | | 3(6) | | | | fluorescence | | | | | |
| <i>n</i> -hexane | | <i>trans</i> -decalin | | <i>n</i> -hexane | | <i>trans</i> -decalin | | <i>n</i> -hexane | | MCH | | <i>trans</i> -decalin | |
| <i>T</i> (K) | τ (ns) | <i>T</i> (K) | τ (ns) | <i>T</i> (K) | τ (ns) | <i>T</i> (K) | τ (ns) | <i>T</i> (K) | τ (ns) | <i>T</i> (K) | τ (ns) | <i>T</i> (K) | τ (ns) |
| 296 | 8 | 318 | 9 | 292 | 47 | 316 | 45 | 328 | 54 | 328 | 46 | 368 | 50 |
| 280 | 8 | 293 | 8 | 279 | 46 | 295 | 46 | 319 | 55 | 318 | 44 | 357 | 50 |
| 270 | 8 | 280 | 8 | 269 | 48 | 283 | 46 | 308 | 55 | 308 | 41 | 347 | 49 |
| 260 | 8 | 270 | 8 | 259 | 48 | 273 | 44 | 294 | 55 | 292 | 51 | 337 | 48 |
| 250 | 8 | 260 | 8 | 251 | 47 | 261 | 44 | 278 | 54 | 276 | 50 | 292 | 43 |
| | | 250 | 8 | | | 249 | 42 | 260 | 55 | 258 | 51 | 284 | 43 |
| | | | | | | | | 244 | 54 | 240 | 53 | 275 | 45 |
| | | | | | | | | 226 | 54 | 222 | 52 | 276 | 46 |
| | | | | | | | | 209 | 54 | 204 | 59 | 259 | 49 |
| | | | | | | | | 199 | 55 | 186 | 56 | 253 | 50 |
| | | | | | | | | 180 | 55 | 167 | 56 | 249 | 53 |
| | | | | | | | | | | 152 | 56 | 244 | 53 |

in 3(4) and 3(6) (see Chart I) in which photoinduced charge separation is known to occur quantitatively irrespective of solvent and temperature.^{17,18} Furthermore the rate of charge recombination in these systems can be measured accurately from the lifetime of the charge-transfer fluorescence¹⁹ which accompanies it in nonpolar solvents or from time-resolved microwave conductivity (TRMC) measurements.²⁰

Application of eq 6 for 3(4) and 3(6) in saturated hydrocarbon solvents ($\epsilon_s \approx 2$) with $E_{ox}(D) = 1.1$ V and $R_c = 7.0$ Å for 3(4) and $R_c = 9.0$ Å for 3(6) gives $\Delta G_{cr} = -3.32$ eV and -3.54 eV. In such solvents the solvent reorganization energy is considered to be negligible and therefore $\lambda = \lambda_i$, for which a value of 0.6 eV has been estimated. Thus charge recombination for 3(4) and 3(6) in nonpolar media occurs far into the "inverted" region, with $\Delta G + \lambda$ being as negative as -2.7 to -2.9 eV. As a result the classical Marcus model, eq 1, predicts the existence of a very large barrier for such charge recombination ($\Delta G^\ddagger = 3.08$ eV and 3.60 eV for 3(4) and 3(6), respectively). This should result in a very slow and strongly temperature dependent rate.

The results of k_{cr} ($=1/\tau_{cr}$) measurements for 3(4) and 3(6) by the TRMC technique^{8,21} over a limited temperature range have been published before, and in Table III we now repeat these results together with those obtained from CT-fluorescence lifetime measurements for 3(6) over a much larger temperature range in three solvents.^{17,22} The latter data confirm and enhance the conclusion drawn^{8,21} from the TRMC data that not only the charge recombination occurs at a rate much faster than might be expected from eq 2 but k_{cr} is also essentially temperature independent.

As pointed out earlier^{8,9} these results may be interpreted by assuming that under inverted region conditions, where crossing the barrier would become a very slow process, the dominant reaction pathway involves nuclear tunneling through the high, but narrow, classical barrier via one or more high frequency ($\hbar\omega > k_B T$) vibrational modes. It has been found^{8,9} that under these circumstances a satisfactory approximation can in general be provided by expressions,⁴ based on the golden rule, in which the Franck-Condon term is calculated via a quantum mechanical treatment of a limited number of intramolecular high-frequency modes together with a classical treatment of the low frequency (solvent) modes. Equation 2 in fact represents the high temperature limit of such expressions.

Thus, while there is still a kinetic "inverted region effect" in the sense that the rate slows down when one moves deeper into the inverted region, this effect cannot be discussed in terms of an activation barrier. Furthermore (near) temperature independence of the rate of electron transfer does not at all mean that this occurs under the "optimal" conditions as amply demonstrated by extensive studies of Gunner and Dutton²³ revealing that several

steps in the photosynthetic charge separation retain their temperature independence when ΔG is changed over a relatively wide range and that therefore this temperature independence alone is an insufficient criterion to decide that such reactions occur under "optimal" conditions as had been assumed earlier.^{3,24-26}

Electron Transfer under "Nearly Optimal" Conditions. Having established and confirmed that the temperature dependence of electron transfer is rather adequately predicted by the classical Marcus expression in the "normal" region, but not at all in the "inverted" region, where nuclear tunneling involving high-frequency modes becomes dominant, it is of obvious importance to find out what happens in between, i.e. close to the "optimal" situation where $\Delta G + \lambda$ is small and a small barrier is thus predicted by eq 1. This is, however, not a trivial task because under such conditions both a classical, thermally activated, barrier crossing and a tunneling process involving high-frequency modes should lead to an essentially temperature-independent rate. We therefore decided to investigate a situation sufficiently far into the "normal" region to produce a barrier that would be just large enough to detect, but significantly smaller than that found for the "normal region" photoinduced charge separation in 1(8).

As we demonstrated before^{12,18} such a situation can be created by enhancing the electron donor strength of the naphthalene moiety via introduction of two methoxy substituents. Thus for 3(8) (see Chart I) the $E_{ox}(D) = 1.1$ V and the $E_{00} = 3.78$ eV. This structural modification increases the driving force for charge separation in 3(8) as compared to 1(8) sufficiently to make it possible even in saturated hydrocarbon solvents ($\epsilon_s \approx 2$). Under these conditions the driving force is calculated to be in the order of $\Delta G_{cs} \approx -0.1$ eV and thus with $\lambda = \lambda_i = 0.6$ eV the sum of $\Delta G_{cs} + \lambda$ is about 0.5 eV, which is indeed much closer to the optimal conditions than for 1(8) in polar solvents. As a result eq 1 predicts the barrier for photoinduced charge separation in 3(8) to be significantly smaller but still high enough (around 0.1 eV) to produce a measurable temperature dependence of k_{cs} .

The charge separation rate constants were determined,¹⁷ employing the method described for 1(8), in liquid *n*-hexane and *trans*-decalin spanning a temperature range of 253–180 K in *n*-hexane and 290–243 K in *trans*-decalin (see Table IV). These ranges are limited by the boiling and freezing temperature of the solvent and secondly by the detectability of the weak short-lived residual fluorescence, which appears at the same wavelength as a many times stronger much longer lived delayed donor fluorescence component. The latter is the result of thermal repopulation of the D*-state from the CT-state, due to the near degeneracy of both states. Since the quantum yield of delayed donor fluorescence increases strongly at higher temperatures, the residual fluorescence is undetectable beyond a certain

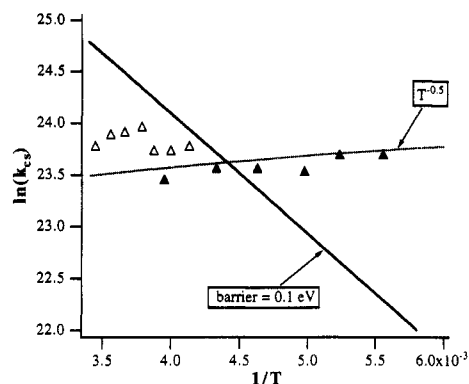


Figure 2. Arrhenius plot of the experimental results (see Table III) for the rate of charge separation in 3(8) in hexane and *trans*-decalin. The solid line indicates the behavior predicted for a reaction with a barrier of 0.1 eV and an Arrhenius type behavior, while the dashed line corresponds to a reaction with $k \sim T^{-0.5}$.

TABLE IV: Charge Separation Rate Constants for 3(8) in *n*-Hexane and *trans*-Decalin at Different Temperatures, As Calculated via Equation 5, Where τ and τ_{ref} Are the Donor Fluorescence Lifetimes of 3(8) and of 4 (i.e. $\tau_{ref} = 10$ ns)

| <i>n</i> -hexane | | | <i>trans</i> -decalin | | |
|------------------|-------------|----------------------------------|-----------------------|-------------|----------------------------------|
| <i>T</i> (K) | τ (ps) | k_{cs} (10^{10} s $^{-1}$) | <i>T</i> (K) | τ (ps) | k_{cs} (10^{10} s $^{-1}$) |
| 253 | 65 | 1.54 | 290 | 47 | 2.13 |
| 231 | 59 | 1.72 | 281 | 42 | 2.38 |
| 216 | 58 | 1.72 | 273 | 41 | 2.44 |
| 201 | 60 | 1.67 | 264 | 39 | 2.56 |
| 191 | 51 | 1.96 | 258 | 49 | 2.04 |
| 180 | 51 | 1.96 | 250 | 49 | 2.04 |
| | | | 242 | 47 | 2.13 |

temperature (253 K in *n*-hexane). Mechanistically the situation for this eight-bond compound in saturated hydrocarbon solvents corresponds to a rapid relaxation in a time τ of approximately 50 ps (see Table IV) following photoexcitation to a dynamic equilibrium between the initially formed locally excited donor state and the CT-state with forward and back electron transfer rates of k_{cs} and k_{-cs} . The initial equilibration period (τ) is on the order of $1/(k_{cs} + k_{-cs})$ and under the experimental conditions mainly determined by k_{cs} .

As indicated by the data in Table IV, k_{cs} was found to show a very minor temperature dependence both in *n*-hexane and in *trans*-decalin over the total temperature range of >100 K. In fact, some tendency toward a negative temperature effect is observed with k_{cs} increasing at lower temperature! As shown in Figure 2 the temperature dependence is thus much smaller than expected for crossing of a barrier of 0.1 eV and can in fact be reconciled reasonably well with the $T^{-0.5}$ dependence that, according to eq 2, should occur under totally barrierless conditions and that has occasionally been used as an indication for such conditions.^{3,24-26}

We wish to stipulate that in the present case this would be a very much unwarranted conclusion. Again it should be realized that the dielectric properties of solvents, including saturated hydrocarbons, change significantly with temperature which makes the barrier a temperature-dependent parameter. For large barriers such as that for charge separation in 1(8) this temperature dependence of ΔG^\ddagger is a relatively minor effect, but in the region close to optimal conditions it may become significant and can even lead to inversion of the expected temperature dependence of the rate. Thus the dielectric constants of the solvents *n*-hexane²⁷ and *trans*-decalin²⁸ are known to increase at lower temperature according to

$$\epsilon_s(\textit{n-hexane}) = 1.89 - 0.00155(T - 293) \quad (7)$$

$$\epsilon_s(\textit{trans-decalin}) = 2.17 - 0.00136(T - 293) \quad (8)$$

This implies that at lower temperature the driving force increases,

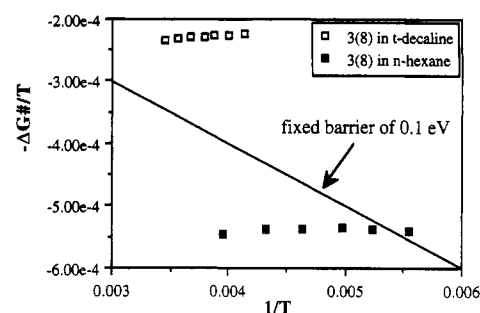


Figure 3. Plots of $-\Delta G^\ddagger/T$ vs $1/T$, as calculated via eqs 1-4 (see Table V) for 3(8) in *n*-hexane and *trans*-decalin. The solid line indicates the behavior for a reaction with a fixed barrier of 0.1 eV.

TABLE V: Barrier to Charge Separation in 3(8), As Calculated from the Marcus Theory (Equations 1, 3, and 4)

| solvent <i>n</i> -hexane | | | solvent <i>trans</i> -decalin | | |
|--------------------------|--------------------------|------------------------|-------------------------------|--------------------------|------------------------|
| <i>T</i> (K) | ΔG^\ddagger (eV) | $-\Delta G^\ddagger/T$ | <i>T</i> (K) | ΔG^\ddagger (eV) | $-\Delta G^\ddagger/T$ |
| 253 | 0.138 | 0.000 545 | 290 | 0.068 | 0.000 235 |
| 231 | 0.124 | 0.000 538 | 281 | 0.065 | 0.000 231 |
| 216 | 0.116 | 0.000 537 | 273 | 0.063 | 0.000 23 |
| 201 | 0.108 | 0.000 536 | 264 | 0.06 | 0.000 228 |
| 191 | 0.103 | 0.000 538 | 258 | 0.059 | 0.000 227 |
| 180 | 0.097 | 0.000 541 | 250 | 0.056 | 0.000 225 |
| | | | 242 | 0.054 | 0.000 224 |

while the reorganization energy remains unchanged since $\lambda = \lambda_i$ in saturated hydrocarbons. In a separate study²¹ the temperature dependence of ΔG_{cs} for 3(8) in saturated hydrocarbons was recently determined by studying the equilibration between the charge separated state and the locally excited state. It was found that eq 4 reproduces the temperature dependence of ΔG_{cs} quite well if the temperature dependence of the Coulomb term ($e^2/\epsilon_s R_c$) is neglected and an effective dielectric constant of 2 is used to calculate that term. The latter was argued to account for the fact that in saturated hydrocarbon solvents the Coulomb attraction is mainly mediated via the bridge interconnecting D and A.

In Table V we now compile the temperature-dependent ΔG^\ddagger values for 3(8) calculated by taking into account the temperature dependence of ϵ_s in the last term of eq 4 and maintaining a constant value $\lambda = \lambda_i = 0.6$ eV for the reorganization energy. As a result of the increased dielectric constant the driving force increases and the calculated barrier therefore decreases at lower temperature. Although the latter effect is rather small, it is sufficient to compensate completely the rate decrease that would occur if the barrier were temperature independent. This is demonstrated in Figure 3 where we plot $-\Delta G^\ddagger/T$ for a constant barrier of 0.1 eV as well as for the barriers calculated in Table V.

In conclusion, the classical Marcus description is capable of qualitatively describing the experimentally found temperature dependence of the rate of charge separation in 3(8) if the temperature dependence of the solvent dielectric properties is taken into account.²⁹ The absolute values of ΔG_{cs} in Table V would however predict a factor of approximately 50 lower rate for charge separation in *n*-hexane compared with *trans*-decalin whereas the experimentally determined values are in fact very similar in magnitude.

We like to point out again that a temperature dependence of the barrier can in principle be discussed in terms of the activation enthalpy (ΔH^\ddagger) and the activation entropy (ΔS^\ddagger) involved. In such a description the virtual temperature independence of k_{cs} for 3(8) would imply that ΔH^\ddagger is negligible and that the barrier is totally due to entropy effects. We feel that such a conclusion is unwarranted because in fact the entropy factor is expected to be rather small in the saturated hydrocarbon solvents employed. We therefore prefer the idea that the cancellation of the rate effects resulting from lowering T and the concomitant decrease of ΔG^\ddagger for 3(8) in saturated hydrocarbons is fortuitous. This

is supported by the behavior of 3(8) in more polar solvents where entropy effects are expected to be more dominant but where preliminary measurements¹⁷ indicate the occurrence of strongly curved (modified) Arrhenius plots that—as in the case of 1(8)—clearly cannot be interpreted in terms of a temperature-independent set of ΔS^\ddagger and ΔH^\ddagger values. More data will have to be accumulated to take account of the behavior in dipolar solvents as well as to answer the question how deep one can go into the inverted region before the classical Marcus treatment becomes inadequate.

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