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NOTES

What is the solvent longitudinal time scale controlling electron transfer rates?

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Solvent motions play a significant role in controlling the rates and the adiabaticity of electron transfer (ET) processes with small activation barriers.¹⁻⁶ As these motions become slow, a nonadiabatic reaction will turn adiabatic. Kosower and Huppert⁶ have found a correlation between photochemical intramolecular ET rates and τ'_1 , the solvent longitudinal time in alcohols. τ'_1 is precisely defined for the Debye model⁷ in which the solvent has a single dielectric relaxation time, τ_1 , i.e., $\tau'_1 = (\epsilon_\infty/\epsilon_0)\tau_1$. Here ϵ_∞ and ϵ_0 denote the optical and the zero frequency values of the solvent dielectric function $\epsilon(\omega)$, respectively. The precise definition of the solvent time scale relevant for ET rates for an arbitrary (non-Debye) solvent is an open question, which is of considerable current interest. Kosower⁶ and Eisenthal⁵ have emphasized the significance of solvent polarity which affects the activation barriers, and whose role should be distinguished from that of solvent dynamics (viscosity).

We have developed a theory for ET rates in polar solvents⁸ by utilizing the formal analogy of this problem with the calculation of nonlinear optical line shapes.^{9,10} The approach is based on reduced equations of motion for the density matrix in Liouville space. An approximate resummation of the perturbative series for the rate to infinite order in the electronic coupling was performed, based on the assumption of separation of time scales between the off-diagonal density matrix elements (the coherences) and the diagonal elements (populations). The resulting expression interpolates continuously between the nonadiabatic and the adiabatic limits of the rate, satisfies the detailed balance condition, reproduces the entire Kramers turnover curve as a function of the solvent longitudinal time scale, provides a microscopic definition for the reaction free energy, and generalizes Marcus free energy relation to the adiabatic regime. In this note we

focus on the adiabatic limit whereby the ET rate from state $|a\rangle$ (donor) to $|b\rangle$ (acceptor) is

$$K = (1/\tau_s) \exp(-q_a^2/2), \quad (1a)$$

where $\tau_s = \tau(q_a) + \tau(q_b)$ is the relevant solvent time scale and where $\tau(q_n)$ is the solvent time scale function controlling the ET rate,

$$\tau(q_n) = \exp(-q_n^2/2) \int_0^\infty dt \left\{ \frac{1}{\sqrt{1-M^2(t)}} \times \exp\left[\frac{q_n^2 M(t)}{1+M(t)} \right] - 1 \right\}, \quad (1b)$$

with

$$q_n = \frac{E - \delta_n}{\sqrt{k_B T |\delta_a - \delta_b|}}, \quad n = a, b, \quad (1c)$$

$$Q(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \exp(-i\omega t) \left[\frac{1}{\epsilon_0} - \frac{1}{\epsilon(\omega)} \right], \quad (2)$$

and $M(t) = Q(t)/Q(0)$. Here E is the reaction exothermicity and δ_a (δ_b) is the average value of the solvation coordinate when the ET system is in the state $|a\rangle$ ($|b\rangle$). $q_a^2/2 = \Delta G_{ab}^*/(k_B T)$ and $q_b^2/2 = \Delta G_{ba}^*/(k_B T)$, where ΔG_{ab}^* (ΔG_{ba}^*) is the activation free energy for the forward (reverse) reaction. As the solvent is varied, δ_n and consequently q_n and the activation barriers will vary primarily with the solvent polarity. Approximate relations between δ_n and polarity measures such as ET(30) may be derived¹¹ in agreement with the relationships proposed by Eisenthal.⁵ The dynamical effects of the solvent affect the rate via $M(t)$, which is the normalized correlation function for the longitudinal polarization of the solvent.^{8,12} In order to explore the

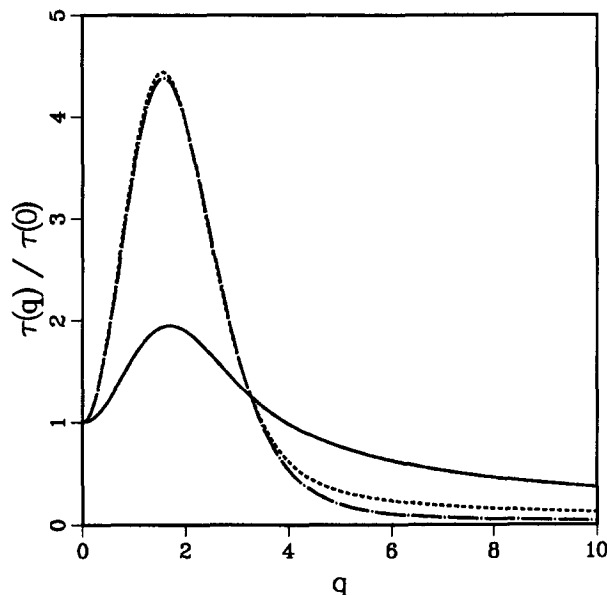


FIG. 1. The solvent time scale function $\tau(q)/\tau(0)$ is plotted for a Debye solvent (solid curve), for propanol (dashed curve), and for decanol (dash-dot curve). For linear alcohols, the $\tau(q)/\tau(0)$ curve is virtually identical. The values of $\tau(0)$ in picoseconds at 23 °C are: 1-propanol (6.9), 1-butanol (12.6), 1-pentanol (21.4), 1-hexanol (29), 1-heptanol (40), 1-octanol (56.4), and 1-decanol (78.4).

significance of solvent dynamics on the ET rate, let us assume that $\epsilon(\omega)$ is characterized by N relaxation times, i.e.,

$$F(t) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \exp(-i\omega t) \frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} \\ = \sum_{j=1}^N c_j \exp(-t/\tau_j). \quad (3)$$

Using Eqs. (2), we then get

$$M(t) = \sum_{j=1}^N c'_j \exp(-t/\tau'_j). \quad (4)$$

Note that $\sum_j c_j = \sum_j c'_j = 1$. Equations (1)–(4) show that the relevant solvent time scales for ET are τ'_j [Eq. (4)] (which are related to the solvent longitudinal correlation function) and not τ_j [Eq. (3)]. For the Debye model ($N=1$), we have $\tau'_1 = (\epsilon_{\infty}/\epsilon_0)\tau_1$. Note, however, that in general we cannot obtain τ'_j from τ_j by simply multiplying with $(\epsilon_{\infty}/\epsilon_0)$. The correct procedure is to use $\epsilon(\omega)$ to get $M(t)$ [Eq. (2)] whose Laplace transform will subsequently yield τ'_j . To illustrate the difference between τ_j and τ'_j , we consider propanol at 23°C which has three relaxation times τ_j , i.e., 408, 21, and 2 ps.¹³ The corresponding relaxation times τ'_j , evaluated using Eqs. (2) and (4), are 80, 15, and 1.4 ps.

In Fig. 1, we display the solvent time scale function $\tau(q)$ for a Debye solvent ($N=1$). Making use of the experimental dielectric function $\epsilon(\omega)$,¹³ we have calculated $\tau(q)$ for linear alcohols (propanol to decanol) and found it to be virtually identical, apart from an overall scaling factor. $\tau(q)$ for propanol and decanol is displayed in Fig. 1 as well. For a Debye solvent $\tau(q)$ is proportional to the longitudinal time scale $\tau'_1 = \tau_1(\epsilon_{\infty}/\epsilon_0)$, and for barrierless reactions $\tau(0) = (\ln 2)\tau'_1$, in agreement with the mean first passage time calculated by Sumi and Marcus¹ for the Debye model in the adiabatic limit. The present expression for $\tau(q_n)$ [Eq. (1b)] generalizes this relation and defines precisely the relevant solvent time scale (τ_s) for any non-Debye solvent with an arbitrary $\epsilon(\omega)$. The correlation $K = 1/\tau'_1$, found by Kosower and Huppert,⁶ may be rationalized since τ_1 is the dominant relaxation time ($c_1 \gg c_2, c_3$) and the linear alcohols are approximately Debye solvents. The present theory separates clearly the solvent polarity effects which affect q_a and q_b and the solvation dynamics which enter via the frequency-dependent dielectric function $\epsilon(\omega)$ and $M(t)$.

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