Ultrafast electron transfer rates as influenced by vibrational modes

S. Umapathy

Electron transfer processes are very commonly encountered in biology and chemistry. In recent years, attention has been focused on predicting and experimentally verifying the rates of such reactions. Investigations are also being carried out on the conformational and energetic considerations related to molecules involved in electron transfer processes using ultrafast laser spectroscopy. This report highlights a theoretical development along with supporting experimental evidence published recently[1,2].

The relation between rate of electron transfer and the driving force of a given reaction was first discussed by Marcus[3] in a classical mechanics formalism. Typically the energetics involved in a bimolecular electron transfer reaction can best be described by potential energy curves as shown in figure 1. If the reactants and the product have the same free energy, then the rates depend on the activation energy (Figure 1 a). According to the Arrhenius equation:

$$k \propto \exp(-E_a/RT).$$

This means that smaller the activation barrier the faster the rate of reaction (Figure 1 a). The activation barrier can be related to the driving force (free energy of the reaction) by

$$E_a = (\lambda + \Delta G^0)^2/4\lambda,$$

where λ is the solvent reorganization energy. Further, if the free energy of the products is lower than that of the reactants (an exothermic reaction) as in

Figure 1 b, the reaction is essentially barrierless (case II). However, if the product-free energy is less than that in Figure 1 b, i.e. if the reaction is made more exothermic (ΔG^0 becomes more $-$ve) as in Figure 1 c, then the reaction rate slows down (case III) compared to case II. This region where the reaction rate slows down in spite of the decrease in free energy is called the 'Marcus

Figure 1. Potential energy curves for electron transfer processes (R = reactant; P = product; E_a = activation energy, ΔG^0 = change in free energy).

inverted region', as shown in Figure 2. In the case of barrierless processes as in case II, solvent coordinate motion was shown to be rate-limiting[4]. But for case III, for solvents with very fast relaxation times the theoretically predicted rate constants are close to the experimentally observed value (equivalent to rate of solvation). But for reaction in solvents with slow relaxation times (for example glycerol triacetate) the calculated rate constants differ considerably from the experimental values (rate measured is higher than the solvation rate). In order to explain this difference between the observed and theoretically calculated values, Barbara et al.[1] have developed a hybrid of the available theories. The most important finding of their theory is that in the case of ultrafast electron transfer processes in slowly relaxing solvents, the kinetics is controlled by intramolecular vibrational motion rather than by solvation dynamics.

Theories that help to simulate rate constants for ultrafast electron transfer processes are: (A) the Marcus–Sumi
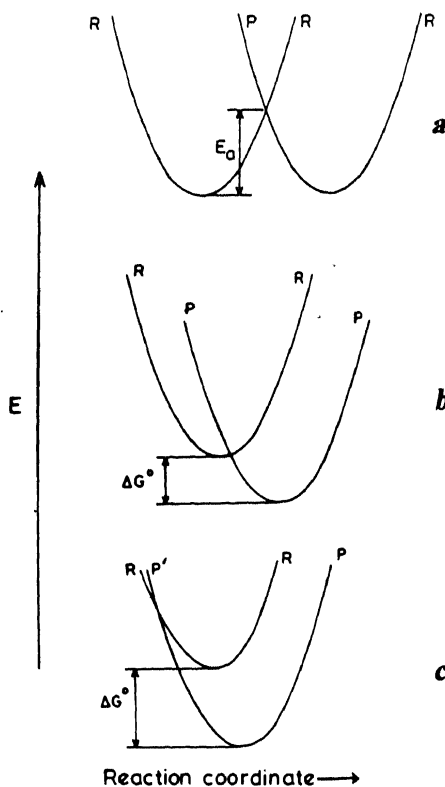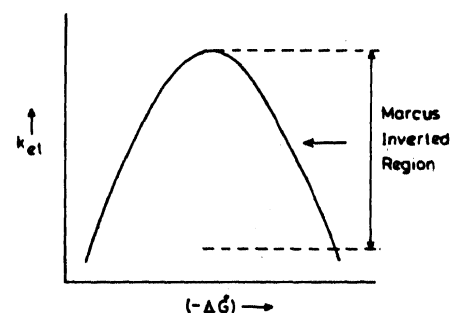

Figure 2. Electron transfer rate dependence on change in free energy.

model[5], which considers classical nuclear degrees of freedom, including low frequency vibrational degrees of freedom and the solvent degrees of freedom; (B) the Jortner–Bixon model[6], which is a quantum mechanical description of high frequency vibrational degrees of freedom along with classical solvent degree of freedom and; (C) the Barbara model[1,2], which is a combination of models A and B, and involves low (classical) and high frequency (quantum mechanical) vibrational degrees of freedom and solvent (classical) degrees of freedom.

Figure 3 shows the participation of the vibrational modes in an exothermic electron transfer process. It is known from classical theories that the electron transfer occurs at the curve crossing (point A in Figure 3). However, if one considers the participation of high frequency vibrational modes (that is if quantum mechanical effects are included) then electron transfer can occur via vibrationally excited states (points B in Figure 3) with low activation energies. The rate is then predicted to be faster than the previous case as has been observed by Barbara et al.

Barbara and co-workers have used Betaine-30 as a model system and studied the intramolecular electron transfer kinetics using ultrafast laser spectroscopy. Betaine-30 is a typical example for a system in the Marcus inverted regime. The electron transfer rate measured in rapidly relaxing solvents, such as acetone and acetonitrile, has been shown to be approximately close to the solvation rate. For slowly relaxing solvents like glycerol triacetate the rate measured is much faster than the values calculated using the first two theories but the Barbara model has predicted values close to the experimental result. The
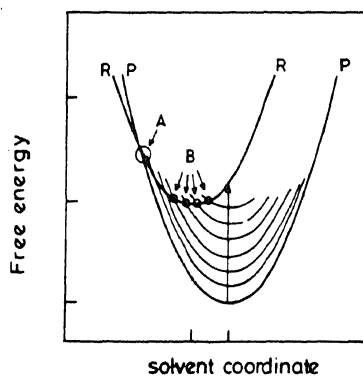
Figure 3. Potential energy curves depicting the participation of vibrational modes with lower activation energies than the activation energy at curve crossing during electron transfer (R = reactant, P = Product; A & B, see text) (adapted from ref. 2).
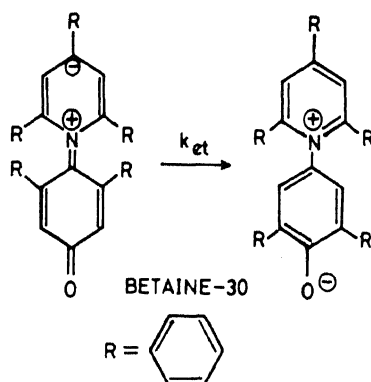
simulated results from the three theories and the experimental results are summarized in Figure 4. As the figure shows the theoretical predictions of model C are in good agreement with the experiment. This model is probably the best starting point for studying any ultrafast electron transfer processes in the inverted regime. However, the reader is cautioned about two points, namely, these theories
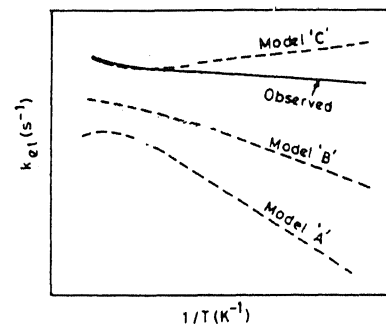
Figure 4. Arrhenius plots for the electron-transfer rate of Betaine-30 in glycerol triacetate. (From ref. 2.)

(a) consider overdamped solvation dynamics with single relaxation time and (b) consider only a small number of effective vibrational modes rather than the complete set of vibrational modes of the reactants. Therefore we look forward to further progress in ultrafast processes in terms of theoretical approximations that corroborate experimental observations.

1. Walker, G. C., Akesson, E., Johnson, A. E., Levinger, N. E. and Barbara, P. F., *J. Phys. Chem.*, 1992, **96**, 3728–3736.
2. Barbara, P. F., Walker, G. C. and Smith, T. P., *Science*, 1992, **256**, 975–981.
3. Marcus, R. A., *J. Chem. Phys.*, 1956, **24**, 966–978; *Ann. Rev. Phys. Chem.*, 1964, **15**, 155–196.
4. Kang, T. J., Jerzeba, W., Barbara, P. F. and Fonseca, T., *Chem. Phys.*, 1990, **149**, 81–95.
5. Sumi, H. and Marcus, R. A., *J. Chem. Phys.*, 1986, **84**, 4894–4914.
6. Jortner, J. and Bixon, M., *J. Chem. Phys.*, 1988, **88**, 167–170.

S. Umapathy is in the Inorganic and Physical Chemistry Department, Indian Institute of Science, Bangalore 560 012, India.