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Non-Marcus Energy Gap Dependence of Back Electron Transfer in Contact Ion Pairs

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Abstract: The energy gap dependence of back electron transfer in contact ion pairs, which is not explained by the Marcus theory, has been explained successfully over the whole range of energy gap, by invoking a mechanism based on an interplay between solvent relaxation and electron transfer. It is concluded that in the normal region ($-\Delta G < \lambda$) back electron transfer occurs in the course of solvent relaxation to the equilibrium state, while in the inverted region ($-\Delta G > \lambda$) it occurs after the equilibrium state is established.

1. Introduction

The Marcus theory of electron transfer predicts the bell-shaped dependence of the rate constant on the free energy change. This dependence has been confirmed experimentally for charge shift[1] (CSH). Concerning charge separation (CS) a recent careful analysis[2] has shown that the observed energy gap dependence[3] which appeared to contradict the Marcus theory is also explained within the framework of the Marcus theory, by properly taking into account the distance dependence of the rate constant. For charge recombinant (CR) two cases need be considered: namely, CR in contact ion pairs (CIP) and in solvent-separated ion pairs (SSIP). CIP and SSIP differ primarily by the degree of electronic coupling between the reactants, viz., the magnitude of the transfer integral *J*. CR in SSIP also exhibits the bell-shaped energy gap dependence.[4] However, CR in CIP appears not to be explained by the Marcus theory.[5,6] In this paper we explain the non-Marcus energy gap dependence of CR in CIP over the whole range of energy gap, by invoking a mechanism based on an interplay between solvent relaxation and electron transfer.

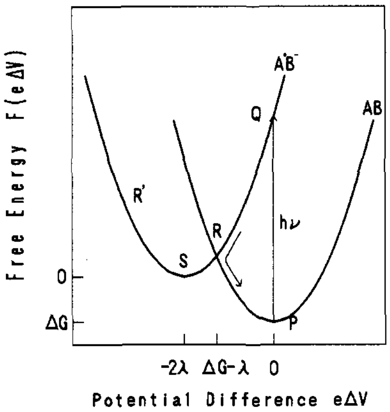

Figure 1. Free energy curves for the ground state (AB) of charge-transfer complex and the ion-pair state (A^+B^-). The abscissa stands for the electrostatic potential difference ΔV between donor and acceptor sites, produced by the surrounding polar solvent. λ stands for the reorganization energy, and ΔG stands for the free energy change between the ground and the ion-pair states. The ion pair state is initially formed at point *Q*. Back electron transfer occurs at point *R*.

2. Theory

In the experiment[5a] of CR in CIP, charge transfer complexes are excited with an ultrashort laser pulse of wavelength lying in the charge transfer absorption band, and CR of produced ion pairs is followed optically. Figure 1 shows the configuration coordinate diagram pertinent to the present problem. The abscissa stands for the solvent configuration. To be more specific, it stands for the electrostatic potential difference ΔV between donor and acceptor sites, produced by the surrounding polar solvent.[7] The ordinate stands for the free energy of the system. Within the framework of the linear solvent polarization, the free energy curves for the ground state (AB) of charge-transfer complex and the ion pair state (A^+B^-) are expressed as[7]

$$F = \frac{1}{4\lambda}(e\Delta V)^2 + \Delta G \qquad \text{for ground state} \tag{1}$$

$$F = \frac{1}{4\lambda}(e\Delta V + 2\lambda)^2 \qquad \text{for ion-pair state} \tag{2}$$

where λ stands for the reorganization energy and ΔG stands for the free energy change between the ground and the ion-pair states.

When the ground-state charge-transfer complex is excited with a laser pulse of wavelength lying in the charge-transfer absorption band, the ion pair state is formed[5a] initially at point *Q*. It relaxes from *Q* downward to *S* along the free energy curve A^+B^-. This relaxation corresponds to the relaxation of the polar solvent around the newly formed ion pair. This relaxation has in fact been experimentally observed[5a] as the shift of the absorption spectrum of the ion pair state. At the intersection point *R* which is given by $e\Delta V = \Delta G - \lambda$, the energy of the ion-pair state coincides with that of the ground state, and back electron transfer from A^- to B^+ becomes possible. The rate of back electron transfer at *R* depends on the magnitude of the transfer integral *J*. In the case of SSIP the rate of back electron transfer at *R* is rather small, since *J* is small. In this case back electron transfer hardly occurs during relaxation to the equilibrium state, although the ion-pair state passes through *R* in the course of relaxation. It occurs

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almost exclusively after equilibration, when the ion-pair state gets thermally activated to R again. Therefore, back electron transfer in SSIP is in principle described by the Marcus theory.

On the other hand, in the case of CIP the rate of back electron transfer at R is rather large, since J is large. If this rate is much larger compared with the rate of relaxation, back electron transfer occurs with a probability of almost unity when the ion-pair state passes through R in the course of relaxation. In other words, back electron transfer is relaxation-controlled, and the effective rate of back electron transfer may be calculated from the time required for the ion pair state to relax from point Q to R.

The role of solvent relaxation in controlling the electron-transfer kinetics has been discussed extensively.[8] However, in all previous work except Jortner's[8a] the equilibrium distribution centered at point S was assumed as the initial distribution. Our problem here is to consider the role of solvent relaxation in the case where the initial distribution is given by a δ function centered at point Q. It should be pointed out that the same problem was already considered by Jortner[8a] in connection with the primary electron-transfer process in bacterial photosynthesis. Heisel and Miehe[9] also studied a similar problem in a different context.

We introduce a new variable x which is given by

$$x = e\Delta V + 2\lambda \tag{3}$$

Then the free energy curve for the ion-pair state is given by $F = (1/4\lambda)x^2$. The positions of Q and R are given by $x = 2\lambda$ and $x = \Delta G + \lambda$, respectively. The ion-pair state starts at Q. The relaxation of the ion-pair state may be described by a Brownian motion along the free energy curve A^+B^-. When the ion-pair state reaches R, the electron transfer occurs at a rate proportional to $(2\pi/\hbar)J^2$. The probability density $w(x,t;x_0)$ that the ion-pair state produced initially at x_0 will be found at x at time t satisfies the following modified Smoluchowski equation and the associated initial condition.

$$\begin{aligned}\partial w(x,t;x_0)/\partial t = D\partial/\partial x[\partial w(x,t;x_0)/\partial x +\\ (1/k_BT)w(x,t;x_0)\mathrm{d}F(x)/\mathrm{d}x] - (2\pi/\hbar)J^2\delta[x -\\ (\Delta G + \lambda)]w(x,t;x_0)\end{aligned} \tag{4}$$

$$w(x,0;x_0) = \delta(x - x_0) \tag{5}$$

where $F(x) = (1/4\lambda)x^2$ and D stands for the diffusion coefficient. According to the Debye model of dielectric relaxation, the diffusion coefficient is expressed[10] as $D = 2\lambda k_BT/\tau_L$ where τ_L stands for the longitudinal relaxation time. The probability $W(x_0,t)$ that the ion-pair state produced initially at x_0 will be still alive at time t is given by

$$W(x_0,t) = \int_{-\infty}^{\infty} w(x,t;x_0)\mathrm{d}x \tag{6}$$

It can be shown[11] that $W(x_0,t)$ satisfies

$$\begin{aligned}\partial W(x_0,t)/\partial t = D[\partial^2 W(x_0,t)/\partial x_0{}^2 -\\ (1/k_BT)\mathrm{d}F(x_0)/\mathrm{d}x_0\cdot\partial W(x_0,t)/\partial x_0] - (2\pi/\hbar)J^2\delta[x_0 -\\ (\Delta G + \lambda)]W(x_0,t)\end{aligned} \tag{7}$$

$$W(x_0,0) = 1 \tag{8}$$

The mean time $\tau(x_0)$ for the ion-pair state produced initially at x_0 to be converted to the ground state is given by

$$\tau(x_0) = \int_0^{\infty} t[-\partial W(x_0,t)/\partial t]\mathrm{d}t = \int_0^{\infty} W(x_0,t)\mathrm{d}t \tag{9}$$

Integrating eq 7 over t from 0 to ∞, one obtains[12] the following equation for $\tau(x_0)$.

$$\begin{aligned}D[\partial^2\tau(x_0)/\partial x_0{}^2 - (1/k_BT)\mathrm{d}F(x_0)/\mathrm{d}x_0\cdot\partial\tau(x_0)/\partial x_0] -\\ (2\pi/\hbar)J^2\,\delta[x_0 - (\Delta G + \lambda)]\tau(x_0) = -1\end{aligned} \tag{10}$$

From the above equation $\tau(x_0)$ is calculated as

$$\begin{aligned}\tau(x_0) = [(4\pi\lambda k_BT)^{1/2}\hbar/2\pi J^2]\exp[(\Delta G + \lambda)^2/4\lambda k_BT] +\\ [(4\pi\lambda k_BT)^{1/2}/2D]\int_{\Delta G+\lambda}^{x_0}\exp(x^2/4\lambda k_BT)\cdot\{1 +\\ \mathrm{erf}[-x/(4\lambda k_BT)^{1/2}]\}\mathrm{d}x \qquad \text{for } x_0 > \Delta G + \lambda\end{aligned} \tag{11}$$

where $\mathrm{erf}(x)$ is the error function. This result has already been derived by Sebastian[13a] using a different method. The mean time for the ion-pair state produced initially at point Q to be converted to the ground state is obtained by putting $x_0 = 2\lambda$ in eq 11. The rate constant of back electron transfer is given by the reciprocal of the mean time. In the limit $J \to 0$, eq 11 reduces to the Marcus equation.

$$\tau(x_0) = [(4\pi\lambda k_BT)^{1/2}\hbar/2\pi J^2]\exp[(\Delta G + \lambda)^2/4\lambda k_BT] \tag{12}$$

This is reasonable since in this limit back electron transfer occurs effectively after relaxation to the equilibrium state. In this case the rate of back electron transfer does not depend on the inital position x_0 of the ion-pair state. In the limit $J \to \infty$, eq 11 reduces to the result of Poornimadevi and Bagchi.[13b]

$$\begin{aligned}\tau(x_0) = [(4\pi\lambda k_BT)^{1/2}/2\mathrm{D}]\int_{\Delta G+\lambda}^{x_0}\exp(x^2/4\lambda k_BT)\cdot\{1 +\\ \mathrm{erf}[-x/(4\lambda k_BT)^{1/2}]\}\mathrm{d}x \qquad \text{for } x_0 > \Delta G + \lambda\end{aligned} \tag{13}$$

3. Results and Discussion

We calculated the rate constant of back electron transfer in CIP in acetonitrile solvent as a function of the free energy change ΔG by using eq 11. The longitudinal relaxation time of acetonitrile is estimated[14] as $\tau_L = 0.3$ ps by using the dielectric relaxation data of Krishnaji and Mansingh[15a] and as $\tau_L = 0.53$ ps by using the dielectric relaxation data of Arnold, Yarwood, and Price.[15b] The results obtained by the former value are reported here. The difference between the two results obtained by the two different values for τ_L is very small. The temperature was taken as 300 K. The reorganization energy was assumed as $\lambda = 1.5$ eV. Figure 2 shows the calculated energy gap dependence of the rate constant for various values of the transfer integral J. In the case of $J = 0.003$ eV the energy gap dependence calculated from eq 11 is essentially the same as that predicted from the Marcus theory (eq 12). Figure 3 compares the calculated energy gap dependence for $J = 0.3$ eV with the experimental data[5a] on back electron transfer in CIP. One can see that the non-Marcus energy gap dependence of back electron transfer in CIP is explained fairly well by the present theory.

According to Figure 1, when $-\Delta G < \lambda$, the free energy curve for the ground state intersects that for the ion-pair state on the right side of the minimum point S. In this case the rate-limiting

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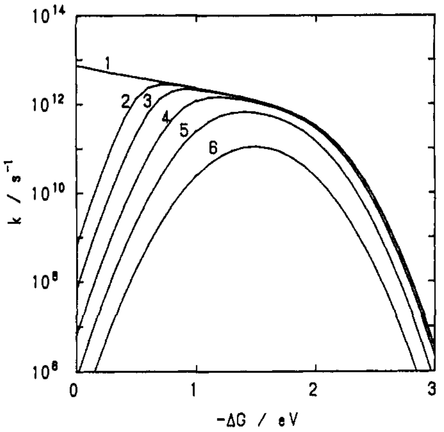

Figure 2. Dependence of the rate constant k of back electron transfer in contact ion pairs on the free energy change ΔG for various values of the transfer integral J: (1) ∞, (2) 0.3 eV, (3) 0.1 eV, (4) 0.03 eV, (5) 0.01 eV, and (6) 0.003 eV.

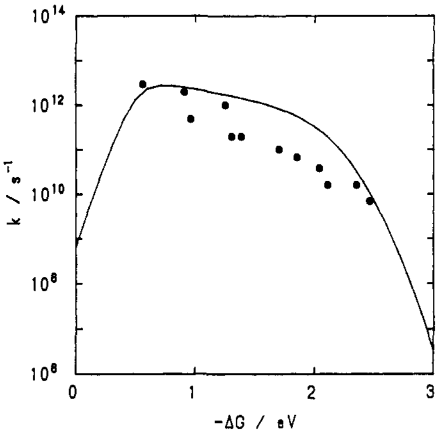

Figure 3. Comparison between theory and experiment on the dependence of the rate constant k of back electron transfer in contact ion pairs on the free energy change ΔG. The full line shows the calculated result for $J = 0.3$ eV. The experimental data (●) were taken from ref 5a.

step for back electron transfer is relaxation from point Q to R. On the other hand, when $-\Delta G > \lambda$, the intersection occurs on the left side of S, say, point R'. In this case the ion-pair state first relaxes to the equilibrium state. Back electron transfer occurs after that, when the ion-pair state gets thermally activated to R'.

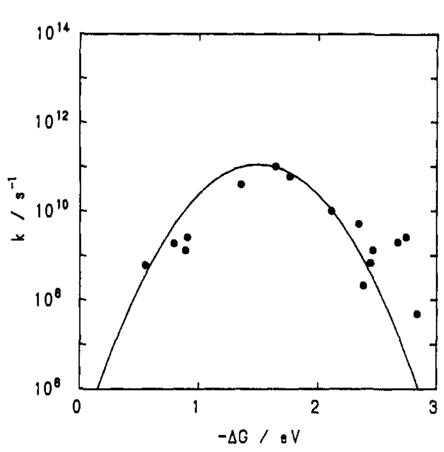

Figure 4. Comparison between theory and experiment on the dependence of the rate constant k of back electron transfer in solvent-separated ion pairs on the free energy change ΔG. The full line shows the calculated result for $J = 0.003$ eV. The experimental data (●) were taken from ref 4a.

This is the reason the predicted energy gap dependence in the inverted region ($-\Delta G > \lambda$) is similar to that of the Marcus theory.

Figure 4 compares the calculated energy gap dependence for $J = 0.003$ eV with the experimental data[4a] on back electron transfer in SSIP. The observed energy gap dependence of back electron transfer in SSIP is also seen to be reproduced by the present theory using a suitable value for J.

We have obtained $J = 0.3$ eV for CIP and $J = 0.003$ eV for SSIP. The transfer integral J depends on the donor–acceptor distance r approximately exponentially.[16]

$$J = J_0 \exp(-\xi r) \tag{14}$$

If we take $\xi = 1$ Å^{-1}, the above results indicate that the donor–acceptor distance in SSIP is 4.6 Å larger than that in CIP. Considering the size of the solvent molecular (acetonitrile), this value seems reasonable.

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