ROLE OF BRIDGE IONS IN ELECTRON TRANSFER REACTIONS

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In [1] a quasiclassical calculation was carried out of the probability of electron transfer via a virtual intermediate state serving as a possible model for an electron transfer mechanism with activated outer sphere involving a bridge ion. The polar solvent surrounding the ions was described by linear terms.

In the present work the method of calculation of the transition probability through the virtual state is developed for the case of parabolic terms (Fig. 1) which more accurately describe the fluctuations of solvent polarization

$$U_i = I_i + \frac{1}{2}\hbar\omega_i (q - q_i^0)^2. \tag{1}$$

Here I_i is the equilibrium value of the solvent's potential energy in state i, where $i = 1, 2, 3$ correspond to the initial, intermediate, and final state, respectively; q is a dimensionless coordinate describing the solvent's polarization, with q_i^0 as its equilibrium value; and ω_i is the characteristic fluctuation frequency of solvent polarization.

The transition probability per unit time from the initial to the final state is described by a second-order expression of perturbation theory, which in the case of a quasicontinuous solvent energy spectrum being considered here, and with the use of the Frank-Condon approximation, assumes the form [1]:

$$W_{31} = \frac{2\pi}{\hbar} | V_1^{2,1} |^2 | V_2^{3,2} |^2 \frac{\beta\hbar\omega_1}{\hbar\omega_3} e^{\beta I_1} \int\limits_{\max\{I_3, I_1\}}^{\infty} dE_1 e^{-\beta E_1} | M^{3,1}(E_1) |^2. \tag{2}$$

Here $V_2^{3,2}$ and $V_1^{2,1}$ are the electronic exchange integrals from perturbations leading to transitions from the initial to the intermediate and from the intermediate to the final state, respectively;

$$M^{3,1}(E_1) = \frac{1}{\hbar\omega_2} \int\limits_{I_2}^{\infty} dE_2 \frac{\langle\Psi_3 | \Psi_2\rangle \langle\Psi_2 | \Psi_1\rangle}{E_1 - E_2 + ir} \qquad (r \to +0), \tag{3}$$

where the $\Psi_i(E_i)$ are wave functions describing the solvent's state. For classically accessible regions of motion, these functions can be written down in the form

$$\Psi_i = \left[\pi P_i (q) \right]^{-1/2} \cos \left\{ \int\limits_{z_i}^{a} P_i (s)\, ds - \frac{\pi}{4} \right\}, \tag{4}$$

where $P_i(q) = [2(E_i - I_i)/\hbar\omega_i - (q - q_i^0)^2]^{1/2}$; z_i is the left-hand turning point of the classical motion for the state i.

In calculating the overlap integrals one can neglect the small contributions from classically inaccessible regions of motion. In the classically accessible regions the overlap integrals are calculated by the method of the stationary phase [2].

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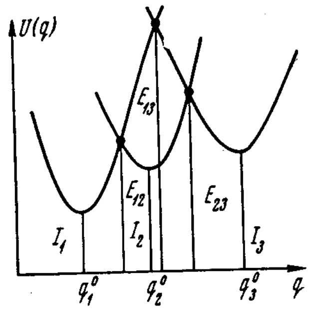

Fig. 1

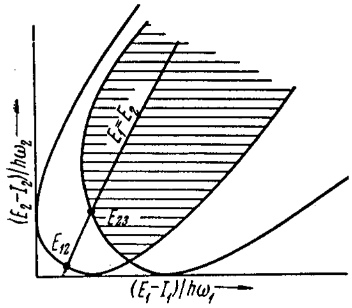

Fig. 2

$$\langle \Psi_i | \Psi_j \rangle = \left[\frac{\pi}{2} | q_i^0 - q_j^0 | P_j(q_{ij}^*)\right]^{-1/2} \cos\left\{ \int\limits_{z_i}^{q_{ij}^*} P_i(s)\,ds - \int\limits_{z_j}^{q_{ij}^*} P_j(s)\,ds - \frac{\pi}{4} \right\}, \tag{5}$$

where q_{ij}^* is a point of the stationary phase satisfying the condition

$$\begin{gathered} P_i(q_{ij}^*) = P_j(q_{ij}^*), \\ q_{ij}^* = \{(E_i - I_i)/\hbar\omega_i - (E_j - I_j)/\hbar\omega_j + [(q_j^0)^2 - (q_i^0)^2]/2\}/(q_j^0 - q_i^0). \end{gathered} \tag{6}$$

The q_{ij}^* values fall into the classically accessible region of motion at energy values E_i and E_j which lie in a certain region on the plane of E_i and E_j which is defined by the mutual disposition of the terms. These regions are defined by the inequalities

$$\left[\left(\frac{E_i - I_i}{\hbar\omega_i}\right)^{1/2} - \frac{|q_i^0 - q_j^0|}{\sqrt{2}}\right]^2 \leqslant \frac{E_j - I_j}{\hbar\omega_j} \leqslant \left[\left(\frac{E_i - I_i}{\hbar\omega_i}\right)^{1/2} + \frac{|q_i^0 - q_j^0|}{\sqrt{2}}\right]^2. \tag{7}$$

Regions of accessible E_1 and E_2 values are shown in Fig. 2 for the overlap integrals $\langle \Psi_1 | \Psi_2 \rangle$ and $\langle \Psi_2 | \Psi_3 \rangle$.

The hatched region corresponds to those E_1 and E_2 values where neither of the overlap integrals is small.

The Calculation of $M^{3,1}(E_1)$. In evaluating the integrals over E_2 at fixed values of the energy E_1 there can be cases where E_1 is within the limits of integration over E_2, and others where E_1 is outside the integration limits. In the first case the integral over E_2 can be split into a real and an imaginary part:

$$M^{3,1}(E_1) = -i\pi D(E) \cos\Phi_1 \cos\Phi_2 |_{E_2=E_1} + \oint D(E) \frac{\cos\Phi_1 \cos\Phi_2}{E_1 - E_2} dE_2, \tag{8}$$

where Φ_1 and Φ_2 are the phases of the cosines of the overlap integrals $\langle \Psi_1 | \Psi_2 \rangle$ and $\langle \Psi_2 | \Psi_3 \rangle$; $D(E)$ is the slowly changing function of the energy E_2 in the region which provides the chief contribution to the value of the integral.

$$D(E) = [(\pi\hbar\omega_2)/2)^2 | q_1^0 - q_2^0 | \times | q_2^0 - q_3^0 | P_2(q_{12}^*) P_2(q_{23}^*)]^{-1/2}. \tag{9}$$

The real part of the integral can be represented as the bound of the integrals over the contours C_ρ and C [1] shown in Fig. 3.

$$\operatorname{Re} M^{3,1}(E_1) = \lim_{\rho\to 0} \operatorname{Re} \int\limits_{C_\rho} \frac{D}{2} \frac{e^{i(\Phi_1+\Phi_2)} + e^{i(\Phi_1-\Phi_2)}}{E_1 - E_2} dE_2 + \operatorname{Re} \int\limits_{C} \frac{D}{2} \frac{e^{i(\Phi_1+\Phi_2)} + e^{i(\Phi_1-\Phi_2)}}{E_1 - E_2} dE_2. \tag{10}$$

The integral over contour C_ρ is

$$-\pi D(E) \sin\Phi_1 \cos\Phi_2 |_{E_2=E_1}. \tag{11}$$

The remaining integral, over contour C, is evaluated by the cross-over method. In order to determine the cross-over points $E_2 = E_2^*$ we solve the following equations:

$$\frac{d}{dE_2}(\Phi_1 \pm \Phi_2) = 0. \tag{12}$$

It can be shown that after simple transformations, (12) are reduced to

$$\int\limits_{z_2}^{q_{12}^*} \frac{\partial}{\partial E_2} P_2(E, s)\,ds \pm \int\limits_{z_2}^{q_{23}^*} \frac{\partial}{\partial E_2} P_2(E, s)\,ds = 0. \tag{13}$$

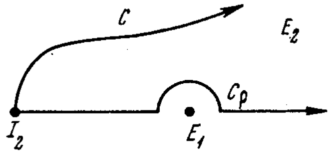

Fig. 3

It is readily seen that solutions of Eqs. (13) only exist when

$$q_{12}^{*}(E_2^{*}) = q_{23}^{*}(E_2^{*}) \equiv q^{*}(E_2^{*}). \tag{14}$$

Taking into account that in the stationary points, the corresponding impulses are equal amongst each other: $P_1(q_{12}{*}) = P_2(q_{12}{*})$ and $P_2(q_{23}{*}) = P_3(q_{23}{*})$, in agreement with the equality (14), one can write down $P_1(q{*}) = P_3(q{*})$, i.e., $U_1(q{*}) = U_3(q{*})$, where $q{*}$ is the point of intersection of the terms U_1 and U_3.

Thus, after simple calculations one can write down the result for the integral over contour C in the form

$$D\sqrt{\frac{\pi(q_2^0 - q_1^0)(q_3^0 - q_0^2)}{(q_3^0 - q_1^0)}}\left[\frac{\hbar\omega_2}{U_2(q^{*}) - U_1(q^{*})}\right]^{3/4}\left[\frac{E_1 - U_1(q^{*})}{U_2(q^{*}) - U_1(q^{*})}\right]^{1/4}\cos(\Phi_1 - \Phi_2)_{q_{12}^{*}=q_{23}^{*}=q^{*}}. \tag{15}$$

Since $\hbar\omega_2/[U_1(q{*}) - U_2(q{*})] \ll 1$, one can neglect this contribution from the cross-over point as compared to the integral over contour C_ρ. (At large E_1 the relative contribution from the cross-over point may be not small, but because of the Gibbsian homogenization, large E_1 in the following do not give rise to a contribution in the final expression.) For the same reason $M^{3,1}(E_1)$ is small when $E_1 = E_2$ is not within the limits of integration over E_2.

From (8) and (11) one can write

$$|M^{3,1}(E_1)|^2 = \pi^2 D^2(E_1)\cos^2\Phi_2(E_1). \tag{16}$$

Thus, the chief contribution to $M^{3,1}(E_1)$ is made by the region $E_2 \approx E_1$, which is shown in Fig. 2, and for this reason the integration over E_1 is begun at the values E_{23} where the straight line $E_2 = E_1$ intersects with the hatched region of Fig. 2. This value E_{23} corresponds to the point of intersection of the second and third term, which in the case being considered lies higher than the point of intersection of the first and second term.

Neglecting the rapidly oscillating term one can replace the square of the cosine by its average value 1/2 when integrating over E_1. After simple computations and taking into account that $(E_{23} - E_{12})\beta \gg 1$, we obtain the final result

$$W_{13} = \frac{2\pi^{3/2}|V_1^{1,2}|^2 |V_2^{2,3}|^2 [(E_{23} - E_{12})kT]^{-1/2}}{\hbar^3\omega_3\omega_2(q_2^0 - q_1^0)(q_3^0 - q_2^0)}\exp\left[-\frac{(E_{23} - I_1)}{kT}\right]. \tag{17}$$

It follows from this expression that when solvent behavior is described by harmonic potentials, the virtual mechanism of electron transfer through a bridge ion, just as in the case of linear potentials, can assure low values of activation energy of the reaction $(E_{23} - I_1)$ relative to activation energies for direct electron transfer bypassing the bridge ion, which would be $E_{23} - I_1$. This will only occur when a given term of the intermediate state $U_2(q)$ intersects with $U_1(q)$ and $U_3(q)$ below the point where $U_1(q)$ and $U_3(q)$ intersect. One can show that the result obtained also remains valid for an arbitrary form of the potential energies.

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