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FREE ENERGY OF ACTIVATION OF NONADIABATIC ELECTRON-TRANSFER REACTIONS AND THE PARAMETERS OF SOLVENT REORGANIZATION

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UDC 541.13

The physical significance of the solvent-reorganization parameters contained in the expressions for the probability of the elementary act of electron-transfer reactions is established. It is shown that the exponent of the activation factor in the expression for the transition probability is the free energy required to attain the transition configuration. The concept of a solvent reorganization energy is introduced which depends on the symmetry factor and equals the free-energy change occurring when the medium's inertial polarization changes from the initial equilibrium value to the value corresponding to the transition configuration. It is shown that in the case of a classical spectrum of medium polarization fluctuations, the total solvent-reorganization energy equals the system's free-energy change which occurs when the medium's inertial polarization changes from the initial equilibrium value to the final equilibrium value while the charge distribution in the reactants remains unchanged.

It has been shown in numerous papers (e.g., [1]) that the configuration of a polar solvent's molecules close to the reactants strongly changes during electron transfer in the polar liquid. The parameters characterizing solvent reorganization substantially influence the probability of the electron transition (in the case of the outer-sphere reactions between ions with invariable structure to be examined below, this influence is decisive).

It is the aim of the present work to provide a definition and establish the physical significance (energy, free energy) of the solvent-reorganization parameters contained in the expressions for the probability of the elementary act of electron-transfer reactions while following a rigorous derivation and relying as little as possible on any detailed microscopic description of the liquid.

The most convenient object for this discussion are outer-sphere electron-transfer reactions between large, complex ions with invariable intramolecular structure for which the solvent can be described as a continuous, macroscopic dielectric medium [1].

For the probability of the elementary act of a nonadiabatic reaction with fixed distance between the reactants we have, according to [1],

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 17, No. 1, pp. 84-89, January, 1981. Original article submitted March 20, 1980.

0038-5387/81/1701-0070$07.50

$$W_{if} = \frac{\beta}{i\hbar} |V_{if}|^2 e^{\beta \mathcal{F}_i} \int_{-i\infty+c}^{i\infty+c} d\theta \, \mathrm{Sp}[e^{-\beta(1-\theta)H_i^a} e^{-\beta\theta H_f^a}], \tag{1}$$

where V_{if} is the electronic matrix element of the interaction operator for the interaction leading to the transition, $\mathcal{F}_i$ is the system's free energy in the initial state, $\beta = 1/kT$, and H_i^a and H_f^a are the adiabatic Hamiltonians of the initial and final reaction channel.

The adiabatic Hamiltonians of the initial and final channel are of the form of

$$H_i^a = H_s - \int dr P(r) \mathcal{E}_i(r) + \varepsilon_i, \tag{2}$$

$$H_f^a = H_s - \int dr P(r) \mathcal{E}_f(r) + \varepsilon_f, \tag{3}$$

where H_S is the Hamiltonian describing the state of the inertial part of the medium's polarization $P(r)$, $\varepsilon_i(\varepsilon_f)$ is the energy of the electron in the reactant (product) which includes its interaction with the medium's noninertial polarization, and $\mathcal{E}_i(r)$ and $\mathcal{E}_f(r)$ are the electric fields set up by the charge distribution in the reacting species corresponding to the initial ($\sigma_i(r)$) and final ($\sigma_f(r)$) state, respectively:

$$\mathcal{E}_{i(f)}(r) = -\int \sigma_{i(f)}(r') \nabla \frac{1}{|r - r'|} dr'. \tag{4}$$

Introducing the chronological operator T we can transform relation (1) to [1-4]

$$W_{if} = \frac{\beta}{i\hbar} |V_{if}|^2 \int_{-i\infty+c}^{i\infty+c} d\theta f_m(\theta), \tag{5}$$

where

$$f_m(\theta) = \exp[-\beta F(\theta)] \exp[-\beta\theta E_r - \beta\theta \Delta\mathcal{F}]. \tag{6}$$

Here, $\Delta\mathcal{E}(r) = \mathcal{E}_f(r) - \mathcal{E}_i(r)$, and $\Delta\mathcal{F}$ is the free energy of the reaction at a given distance between the reactants:

$$E_r = -\frac{1}{2} \int dr\, dr' \sum_{\alpha,\beta} \Delta\mathcal{E}_\alpha(r) \Delta\mathcal{E}_\beta(r') D_{\alpha\beta}^R(r, r', \omega=0), \quad \alpha, \beta = x, y, z, \tag{7}$$

while $\exp[-\beta F(\theta)]$ denotes the quantum-statistical mean over the initial state with the Hamiltonian H_i^a:

$$\exp[-\beta F(\theta)] = \left\langle T_\tau \exp\left[\int_0^{\beta\theta} d\tau \int dr\, \delta P_i(r, \tau) \Delta\mathcal{E}(r)\right]\right\rangle_i =$$

$$= \exp(\beta\mathcal{F}_i) \mathrm{Sp}\left\{\exp[-\beta H_i^a] T_\tau \exp\left[\int_0^{\beta\theta} d\tau \int dr\, \delta P_i(r, \tau) \Delta\mathcal{E}(r)\right]\right\}, \tag{8}$$

where $\delta P_i(r, \tau) = P(r, \tau) - P_{0i}(r, \tau)$ is the operator in the Heisenberg representation which describes the deviation of inertial polarization from the equilibrium value $P_{0i}(r)$, corresponding to the initial state, i.e., to the initial charge distribution in the reactants.

In deriving relations (5) and (6) we have used the relation between $P_{0i}(r)$ and the electric field $\mathcal{E}_i(r)$:

$$P_{0i\alpha}(r) = -\sum_\beta \int D_{\alpha\beta}^R(r, r'; \omega=0) \mathcal{E}_{i\beta}(r') dr', \quad \alpha, \beta = x, y, z, \tag{9}$$

where $D_{\alpha\beta}^R(r, r'; \omega)$ is the Fourier component of the Green's temperature lag function,

$$D_{\alpha\beta}^R(r, r'; t) = -i\theta(t) \langle [P_\alpha(r, t), P_\beta(r', 0)] \rangle = D_{\beta\alpha}^R(r, r'; -t). \tag{10}$$

The mean in relation (8) was calculated in a number of papers in various models [1-4]. They all arrive at the following result:

$$\exp[-\beta F(\theta)] = \exp\left[-\frac{1}{2} \sum_{\alpha,\beta} \int dr\, dr' \Delta\mathcal{E}_\alpha(r) \Delta\mathcal{E}_\beta(r') \int_0^{\beta\theta} d\tau \int_0^{\beta\theta} d\tau' D_{\alpha\beta}(r, r'; \tau, \tau')\right], \tag{11}$$

where $D_{\alpha\beta}(x, x') = -\langle T_\tau \delta P_{i\alpha}(x)\, \delta P_{i\beta}(x')\rangle$ is the Green's causative temperature function of the medium polarization operators, and $\delta \mathbf{P}_i(x) = \exp(\tau H_i^a)\, \delta \mathbf{P}_i(\mathbf{r}) \exp(-\tau H_i^a)$.

Considering the relation between Green's causative and retarding functions we obtain for F(θ) [4],

$$\beta F(\theta) = \psi(\theta) - \beta\theta E_r, \tag{12}$$

where

$$\psi(\theta) = -\frac{1}{\pi\hbar}\int d\mathbf{r}\, d\mathbf{r}' \sum_{\alpha,\beta} \Delta\mathscr{E}_\alpha(\mathbf{r})\, \Delta\mathscr{E}_\beta(\mathbf{r}') \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \operatorname{Im} D_{\alpha\beta}^{R}(\mathbf{r}, \mathbf{r}'; \omega)\, \frac{\operatorname{sh}\frac{\beta\hbar\omega(1-\theta)}{2} \cdot \operatorname{sh}\frac{\beta\hbar\omega\theta}{2}}{\operatorname{sh}\frac{\beta\hbar\omega}{2}}. \tag{13}$$

We shall limit ourselves to the case where the fluctuation spectrum of the medium's inertial polarization can be regarded as classical [1]. Then,

$$\psi(\theta) = \beta\theta(1-\theta)E_r, \tag{14}$$

$$F(\theta) = -[\theta E_r - \theta(1-\theta)E_r] = -\theta^2 E_r, \tag{15}$$

while evaluation of the integral over θ in (5) yields [1],

$$W_{if} = \frac{|V_{if}|^2}{\hbar(kTE_r/\pi)^{1/2}} \cdot \exp(-\theta^{*2} \cdot E_r/kT) = \frac{|V_{if}|^2}{\hbar(kTE_r/\pi)^{1/2}} \cdot \exp(-\beta|F(\theta^*)|), \tag{16}$$

where F(θ) is determined by relation (15), while

$$\theta^* = \frac{1}{2} + \frac{\Delta\mathscr{F}}{2E_r}. \tag{17}$$

To elucidate the physical significance of the exponent in (16) we shall first consider the case where θ* = 1 (barrierless reaction). Then relation (8) defines the system's free-energy change, F(1), during polarization of the medium by the field $\Delta\mathscr{E} = \mathscr{E}_f - \mathscr{E}_i$ (everywhere we are dealing with the free energy associated only with the medium's inertial polarization). This quantity of course is negative. One can readily see that F(1) in absolute value is equal to the medium's reorganization energy E_r(>0), which defines the physical signifance of E_r as the system's free-energy change which occurs when the inertial polarization changes by an amount

$$\Delta\mathbf{P}(\mathbf{r}) = \mathbf{P}_{0f}(\mathbf{r}) - \mathbf{P}_{0i}(r). \tag{18}$$

Using the relation

$$\Delta P_\alpha(\mathbf{r}) = -\sum_\beta \int D_{\alpha\beta}^{R}(\mathbf{r}, \mathbf{r}'; \omega=0)\, \Delta\mathscr{E}_\beta(\mathbf{r}')\, d\mathbf{r}', \tag{19}$$

we can write down the reorganization energy [see relation (7)] as,

$$E_r = \frac{1}{2}\int d\mathbf{r} \Delta\mathscr{E}(\mathbf{r}) \Delta\mathbf{P}(\mathbf{r}) = \frac{1}{2}\int d\mathbf{r} \Delta\mathscr{E}(\mathbf{r})[\mathbf{P}_{0f}(\mathbf{r}) - \mathbf{P}_{0i}(\mathbf{r})]. \tag{20}$$

For $\theta^* \neq 1$ we note that relation (6) in the classical limit (see (11) to (15)) can be written as

$$\exp[-\beta F(\theta)] = \left\langle T_t \exp\left\{\int_0^\beta dt \int d\mathbf{r}\, \delta\mathbf{P}_i(\mathbf{r}, t)\, [\theta\Delta\mathscr{E}(\mathbf{r})]\right\}\right\rangle_i. \tag{21}$$

Thus, F(θ*) in this case represents the medium's free-energy change which occurs when it is polarized by the field $\theta^*\Delta\mathscr{E}(\mathbf{r}) = \theta^*[\mathscr{E}_f(\mathbf{r}) - \mathscr{E}_i(\mathbf{r})]$. In absolute value F(θ*) coincides with the medium's reorganization energy which is expended when the inertial polarization changes by an amount

$$\Delta P_{\theta^*\alpha}(\mathbf{r}) = \theta^* \Delta P_\alpha(\mathbf{r}) = -\sum_\beta \int D_{\alpha\beta}^{R}(\mathbf{r}, \mathbf{r}'; \omega=0)\, \theta^* \Delta\mathscr{E}_\beta(\mathbf{r}')\, d\mathbf{r}', \tag{22}$$

which corresponds to attainment of the transition configuration [5].

Introducing the reorganization energy required for the medium to attain the transition configuration,

$$E_r(\theta^*) = \frac{1}{2}\int dr\,[\theta^*\Delta\mathscr{E}(r)]\,\Delta P_{\theta^*}(r) = \frac{1}{2}\sum_{\alpha,\beta}\int dr\int dr'\,D^R_{\alpha\beta}(r, r'; \omega = 0)\,[\theta^*\Delta\mathscr{E}_\alpha(r)]\,[\theta^*\Delta\mathscr{E}_\beta(r')], \quad (23,\ 24)$$

we can rewrite relation (16) for the transition probability as,

$$W_{if} = \frac{|V_{if}|^2}{\hbar(kTE_r/\pi)^{1/2}}\exp(-E_r(\theta^*)/kT), \quad (25)$$

which yields the significance of the activation factor as the free energy required to attain the transition configuration.

The reorganization energy E_r defined by relation (7) contains the Green's function $D^R_{\alpha\beta}$ and the electrical field $\Delta\mathscr{E}$, which is calculated as the field set up by the difference in charge distributions between reactants and reaction products, $\Delta\sigma = \sigma_f(r) - \sigma_i(r)$, in vacuum. Because of the polarizability of ions and molecules, the charge distributions in reactants ($\sigma_i(r)$) and reaction products ($\sigma_f(r)$) basically can differ from those in the gas phase. It follows from relation (20), which is equivalent to relation (7), that integration in these expressions is performed only over the region of space taken up by the medium, since outside the medium P = 0.

Using relation (20) one can express E_r in terms of the dielectric properties of the medium. To this end we write down relation (20) as,

$$E_r = \frac{1}{2}\int dr\,\Delta P(r)\,\Delta\mathscr{E}(r) = \int dr\int_0^{\Delta\mathscr{E}(r)}\Delta P_\delta(r)\,\delta\Delta\mathscr{E}(r). \quad (26)$$

The free-energy change described by relation (26) can be found — when allowing for the fact that it only contains inertial polarization — as the free-energy change occurring when the following two processes are carried out: (i) slowly turning up the field from zero to $\Delta\mathscr{E}(r)$, and (ii) rapidly turning off the field from $\Delta\mathscr{E}(r)$ to zero:

$$E_r = -\Big[\int dr\int_{0\,(\text{slow})}^{\Delta\mathscr{E}(r)}\Delta P_t(r)\,\delta\Delta\mathscr{E}(r) + \int dr\int_{\Delta\mathscr{E}(r)\,(\text{fast})}^{0}\Delta P_t(r)\,\delta\Delta\mathscr{E}(r)\Big] =$$

$$= -\Big[\int dr\,\Big\{\frac{1}{2}\Delta P(r)\,\Delta\mathscr{E}(r) + \frac{1}{2}\Delta P_{\text{n.i.}}(r)\,\Delta\mathscr{E}(r) - \frac{1}{2}\Delta P(r)\,\Delta\mathscr{E}(r) - \frac{1}{2}\Delta P_{\text{n.i.}}(r)\,\Delta\mathscr{E}(r)\Big\}\Big], \quad (27)$$

where P_t is the total polarization per unit volume of the medium.

In the right-hand part of the first equality of relation (27), the first term can be transformed as follows [6]:

$$\int dr\int_0^{\Delta\mathscr{E}(r)}\Delta P_t(r)\,\delta\Delta\mathscr{E}(r) = \frac{1}{4\pi}\int dr\int_0^{\Delta\mathscr{E}(r)}(\Delta D - \Delta E)\,\delta\Delta\mathscr{E} -$$

$$-\frac{1}{4\pi}\int dr\int_0^{\Delta\mathscr{E}(r)}(\Delta D - \Delta\mathscr{E})\,\delta\Delta\mathscr{E} - \frac{1}{4\pi}\int dr\int\Delta E\,(\delta\Delta D - \delta\Delta\mathscr{E}). \quad (28)$$

Here the first term has been obtained from the definition of total polarization, $D = E + 4\pi P_t$, of the medium, where E is the electrical field in the medium, Formally, the integration in it can be extended over all space. The second and third term on the right-hand side of (28) are zero. In fact, let us examine the first of them, as an example, and replace $\delta\Delta\mathscr{E}$ in it by $-\text{grad}\,\delta\varphi_0$ (where φ_0 is the potential of field $\Delta\mathscr{E}$):

$$\frac{1}{4\pi}\int dr\int(\Delta D - \Delta\mathscr{E})\;\delta\Delta\mathscr{E} = \frac{1}{4\pi}\int df\int\delta\varphi_0(\Delta D - \Delta\mathscr{E}) - \frac{1}{4\pi}\int dr\int\delta\varphi_0\,\text{div}\,(\Delta D - \Delta\mathscr{E}). \quad (29)$$

Integration in (29) is performed over all space, so that the surface integral is taken over the infinitely distant surface f, and equals zero. The last term on the right-hand side of (29) is zero since $\Delta D = \text{div}\,\Delta\mathscr{E} = 4\pi\sigma$, where $\Delta\sigma$ is the charge density giving rise to the field $\Delta\mathscr{E}$ and the induction ΔD. Returning to relation (28) we obtain

$$\int dr \int_0^{\Delta\mathscr{E}(r)} \Delta P_i(r)\,\delta\Delta\mathscr{E}(r) = \frac{1}{4\pi}\int dr \int_0^{\Delta\mathscr{E}(r)} \Delta\mathscr{E}\,\delta\Delta\mathscr{E} - \frac{1}{4\pi}\int dr \int_{0\,(\text{slow})}^{\Delta D(r)} \Delta E\delta\Delta D, \tag{30}$$

where ΔD is the electrostatic induction corresponding to the field $\Delta\mathscr{E}$.

In a similar fashion the second term on the right-hand side of relation (27) can be transformed:

$$\int dr \int_{\Delta\mathscr{E}(r)}^{0} \Delta P_i(r)\,\delta\Delta\mathscr{E}(r) = \frac{1}{4\pi}\int dr \int_{\Delta\mathscr{E}(r)}^{0} \Delta\mathscr{E}\delta\Delta\mathscr{E} - \frac{1}{4\pi}\int dr \int_{\Delta D(r)\,(\text{fast})}^{0} \Delta E\delta\Delta D. \tag{31}$$

Substituting (30) and (31) into (27) and taking into account that for a local medium $\Delta E_{(\text{slow})}=\Delta D/\varepsilon_s$ and $\Delta E_{(\text{fast})}=\Delta D/\varepsilon_0$, where ε_S and ε_0 are the static and optic dielectric permittivity of the medium, we finally obtain

$$E_r = \frac{1}{8\pi}\int dr\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_s}\right)[\Delta D]^2 = \frac{1}{8\pi}\int dr\, c[\Delta D(r)]^2. \tag{32}$$

Outside the region occupied by the dielectric we have $\varepsilon_S = \varepsilon_0$, so that the integration in (32) actually is performed over the region occupied by the medium. For a nonlocal medium we similarly obtain

$$E_r = \frac{1}{8\pi}\sum_k c(k)\,|\Delta D_k|^2, \tag{33}$$

where c(k) and ΔD_k are the corresponding Fourier components.

It must be noted that, although the initial expression (20) for the reorganization energy contains the difference of electrical fields $\Delta\mathscr{E}$, relations (32) and (33) contain the difference of electrostatic inductions $\Delta D=D_f-D_i$, set up in the medium by the reaction products and the initial reactants.

Relations of the type of (32) for reorganizaton energy had first been obtained by Marcus [7] with the model of conducting spheres for the reacting species. The derivation given in the present work makes no use of this model, so that the results reported are valid for any model of reactants of arbitrary shape, provided that they have no inertial polarizability. The same result has been obtained independently by German via a calculation based on the methods of nonequilibrium thermodynamics, and similar to the calculation used by Marcus.

It follows from the above discussion that in the classical limit, the expression for the exponent of the activation factor in the relation for the transition probability represents the free energy which must be expended to attain the transition configuration. The solvent's total reorganization energy equals the system's free-energy change which occurs when the inertial polarization changes from the initial equilibrium value to the equilibrium value of the final state while the charge distribution in the reactants remains fixed. It is also possible in the classical limit to introduce the concept of a solvent reorganization energy which depends on the symmetry factor $\alpha = \theta^*$ and equals the system's free-energy change which occurs when the inertial polarization changes from the initial equilibrium value to the value corresponding to the transition configuration.

The author expresses his gratitude to R. R. Dogonadze for discussion of the work and for a number of valuable remarks.

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