SOLVENT REORGANIZATION ENERGY IN ELECTRON-TRANSFER REACTIONS BETWEEN NONSPHERICAL IONS

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The activation energy of charge-transfer reactions in a polar medium depends substantially on the magnitude of the parameter E_S, i.e., the solvent-reorganization energy [1], which is determined both by the distribution of charge in the reagents and by the dielectric properties of the solvent. In [2] it was shown that in the long-wave approximation E_S can be written in the form of the product of two factors, the first of which depends on the dielectric properties of the medium, while the second is the space integral of the square of the difference between the electric induction vectors in the initial and final states of the system

$$E_s = \frac{1}{8\pi}\left[\frac{1}{2\pi}\int_0^{\frac{kT}{\hbar\alpha(1-\alpha)}} \frac{d\omega I_m \varepsilon(\omega)}{\omega|\varepsilon(\omega)|^2}\right]\int (\vec{D}_i-\vec{D}_f)^2 dv = \frac{C}{8\pi}\int (\vec{D}_i-\vec{D}_f)^2 dv, \quad (1)$$

where $\varepsilon(\omega)$ is the complex dielectric constant of the medium, dependent on frequency ω, and the space integral is taken over the whole volume of the solvent after deduction of the volume of the two reacting particles.

In order to compute the space integral contained in Eq. (1) it is necessary to know the electron density distribution in the reagents and reaction products. In the case of ions with spherical form a good approximation can be obtained by the model proposed by Marcus [3], in which it is assumed that the charges in the reagents are distributed uniformly over the surface of the metallic spheres:

$$E_s = \frac{Ce^2}{2}\left(\frac{1}{a_1}+\frac{1}{a_2}-\frac{2}{R}\right), \quad (2)$$

where a_1 and a_2 are the radii of the spheres and R is the distance between their centers.

As was shown in [4], in the production of Eq. (2) the intrinsic volumes of the ions were not taken into account, and Eq. (2) can be used with an accuracy up to terms on the order of $(a/R)^4$. Moreover, with short distance between the reacting particles the effect of the mutual polarizability of the ions can become significant [5], but with fairly large R values the contribution from the intrinsic volume of the ions and the polarizability can be neglected.

As first approximation for calculation of the solvent-reorganization energy in electron transfer between nonspherical reagents it is possible to use a model of the reagents in the form of conducting ellipsoids of rotation, two different variants of the mutual arrangement of which are shown in Figs. 1 and 2. The ellipsoids have semiaxes a_1, a_1, and c_1 and a_2, a_2, and c_2, and the distance between their centers is R. Below we will examine the case where $c_1 < a_1$ and $c_2 < a_2$, which is of the greatest interest since the form of an oblate ellipsoid is most frequently encountered among reacting ions.

The space integral included in Eq. (1) can be transformed in the following way:

$$\int_{\infty-V_1-V_2} (\vec{D}_i-\vec{D}_f)\,dv = \int_{\infty-V_1-V_2} \vec{D}_i^2\,dv + \int_{\infty-V_1-V_2} \vec{D}_f^2\,dv - 2\int_{\infty-V_1-V_2} \vec{D}_i\vec{D}_f\,dv. \quad (3)$$

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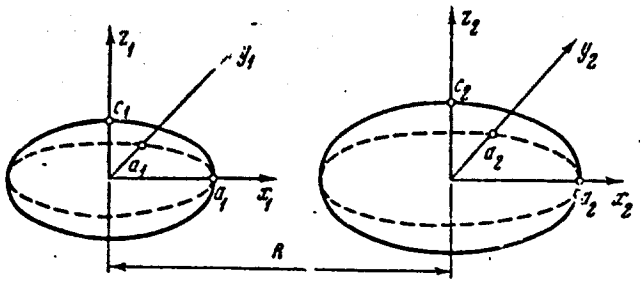


Fig. 1

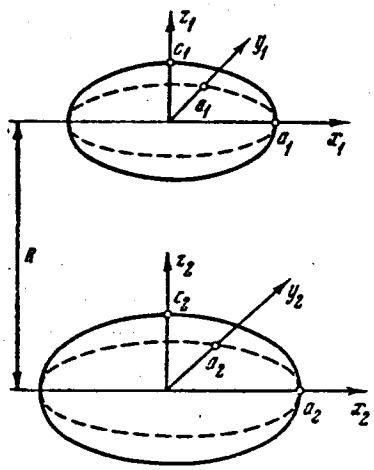


Fig. 2

The induction $\vec{D}_1$ in the initial state is created by the charge e, which is distributed over the surface S_2. If the approximation in [3] is used in the computation of the first two integrals on the right side of Eq. (3), i.e., it is assumed that

$$\int\limits_{\infty-V_1-V_2} \vec{D}_i^2\,dv \simeq \int\limits_{\infty-V_1} \vec{D}_i^2\,dv; \qquad \int\limits_{\infty-V_1-V_2} \vec{D}_f^2\,dv \simeq \int\limits_{\infty-V_2} \vec{D}_f\,dv, \tag{4}$$

then, passing from integration over the volume to integration over the surface, we obtain

$$\int (\vec{D}_i-\vec{D}_f)^2\,dv = \int\limits_{S_1} \varphi_i \nabla\varphi_i\,d\vec{S}_1 + \int\limits_{S_1} \varphi_f \nabla\varphi_f\,d\vec{S}_2 - 2\int\limits_{S_2} \varphi_i \nabla\varphi_f\,d\vec{S}_2$$

$$= 4\pi e\varphi_i(S_1) + 4\pi e\varphi_f(S_2) - 2\int\limits_{S_2} \varphi_i \nabla\varphi_f\,d\vec{S}_2. \tag{5}$$

Here $\vec{D}_{i,f} = -\nabla\varphi_{i,f}$ (where the arrow indicates that the internal normal to the surface is used in the computation of the integral), and $\varphi_i(S_1)$ and $\varphi_f(S_2)$ are the potentials at the surfaces of the ellipsoids S_1 and S_2. The use of the approximation (4) means that we omit terms in $(a/R)^4$.

For further calculation it is useful to employ oblate spheroidal coordinates ξ, η, the relation of which to the Cartesian coordinates x, y, z is defined by the equation [6]

$$\frac{\rho^2}{a^2+u} + \frac{z^2}{c^2+u} = 1; \qquad \rho^2 = x^2+y^2. \tag{6}$$

This equation has two roots $u_1 = \xi$, $u_2 = \eta$, lying in the ranges where $\xi \geq -c^2$ and $-c^2 \geq \eta \geq -a^2$. The inverse relation between the Cartesian coordinates and the coordinates ξ, η is given by the equations

$$z = \pm\left[\frac{(\xi+c^2)(\eta+c^2)}{c^2-a^2}\right]^{1/2}, \qquad \rho = \left[\frac{(\xi+a^2)(\eta+a^2)}{a^2-c^2}\right]^{1/2}. \tag{7}$$

The distribution of potential outside the charged oblate ellipsoid has the following form [6]:

$$\varphi = \frac{e}{\sqrt{a^2-c^2}}\operatorname{arctg}\sqrt{\frac{a^2-c^2}{\xi+c^2}}. \tag{8}$$

The surface of the ellipsoid corresponds to $\xi = 0$, and thus,

$$\varphi_i(S_1) = \frac{e}{\sqrt{a_1^2-c_1^2}}\operatorname{arctg}\sqrt{\frac{a_1^2-c_1^2}{c_1^2}}, \qquad \varphi_f(S_2) = \frac{e}{\sqrt{a_2^2-c_2^2}}\operatorname{arctg}\sqrt{\frac{a_2^2-c_2^2}{c_2^2}}. \tag{9}$$

To calculate the integral $\int\varphi_i\nabla\varphi_f d\vec{S}_2$ it is convenient first to express $\nabla\varphi_f d\vec{S}_2$ in the oblate spheroidal coordinates:

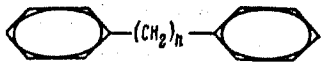


Fig. 3

$$\nabla\varphi_i\, d\vec{S}_2 = -\left(\frac{\partial\varphi}{\partial n}\right)_{s_2} dS_2 = \frac{e\,dS_2}{\sqrt{-a^2\eta}}. \tag{10}$$

Then, from Eqs. (8) and (10) we obtain

$$\int_{s_2}\varphi_i\,\nabla\varphi_j\,d\vec{S}_2 = \int_{s_2}\frac{e^2}{\sqrt{a_1^2-c_1^2}}\operatorname{arctg}\sqrt{\frac{a_1^2-c_1^2}{\xi_1+c_1^2}}\frac{dS_2}{\sqrt{a_2^2\eta_2}}. \tag{11}$$

Taking account of the fact that $\xi_1 \gg c_1^2$ and $\xi_1 \gg a_1^2$ at the surface of the ellipsoid S_2, we calculate the integral (11) approximately with accuracy up to terms in the order of $(a/R)^4$. Here it is necessary to examine the arrangements I and II of the ellipsoids shown in Figs. 1 and 2 separately. It is possible to write φ_1 approximately in the following form:

$$\varphi_i = \frac{e}{\sqrt{a_1^2-c_1^2}}\sqrt{\frac{a_1^2-c_1^2}{\xi+c_1^2}}\left[1-\frac{a_1^2-c_1^2}{3(\xi+c_1^2)}\right]. \tag{12}$$

Changing to Cartesian coordinates and to integration in the x_2, y_2 plane of the section of ellipsoid S_2 and expressing ξ in Cartesian coordinates related to ellipsoid S_2 by means of the approximate solution of Eq. (6), we obtain for case I

$$\int\varphi_i\,\nabla\varphi_j\,d\vec{S}_2 = \frac{2e^2}{a_2}\int_0^{2\pi}\int_0^{a_2}\frac{\rho_2\,d\rho_2\,d\varphi_2\left(1-\dfrac{a_1^2-c_1^2}{3R^2}\right)}{[R^2+2R\rho_2\cos\varphi_2+\rho_2^2+c_1^2-a_1^2+c_2(1-\rho_2^2/a_2^2)]^{1/2}(a_2^2-\rho_2^2)^{1/2}} =$$

$$= \frac{4\pi e^2}{R}\left(1+\frac{a_1^2-c_1^2}{6R^2}+\frac{a_2^2-c_2^2}{6R^2}+0\left(\frac{a^4}{R^4}\right)\right). \tag{13}$$

Thus, from Eqs. (5), (9), and (13), E_S^I for case I takes the following form:

$$E_s^I = \frac{Ce^2}{2}\left[\frac{1}{\sqrt{a_1^2-c_1^2}}\operatorname{arctg}\frac{\sqrt{a_1^2-c_1^2}}{c_1}+\frac{1}{\sqrt{a_2^2-c_2^2}}\operatorname{arctg}\frac{\sqrt{a_2^2-c_2^2}}{c_2}-\frac{2}{R}-\frac{a_1^2-c_1^2}{3R^3}-\frac{a_2^2-c_2^2}{3R^3}\right]. \tag{14}$$

In case II, using the expansion of Eq. (12) and the approximate solution of Eq. (6) $\xi_1 + c_2 \simeq z_1^2 + \rho_1^2$, we obtain

$$\int\varphi_i\,\nabla\varphi_j\,d\vec{S}_2 = \frac{e^2}{a_2}\left(1-\frac{a_1^2-c_1^2}{3R^2}\right)\left[\int\frac{d\sigma}{\sqrt{a_2^2-\rho_2^2}\sqrt{(R+c_2\sqrt{1-\rho_2^2/a_2^2})^2+\rho_2^2}}+\right.$$

$$\left.+\int\frac{d\sigma}{\sqrt{a_2^2-\rho_2^2}\sqrt{(R-c_2\sqrt{1-\rho_2^2/a_2^2})^2+\rho_2^2}}\right] = \frac{4\pi e^2}{R}\left(1-\frac{a_1^2-c_1^2}{3R^2}-\frac{a_2^2-c_2^2}{3R^2}+0\left(\frac{a^4}{R^4}\right)\right). \tag{15}$$

From Eqs. (15), (9), and (5) in case II we obtain the following expression for E_S^{II}:

$$E_s^{II} = \frac{Ce^2}{2}\left[\frac{1}{\sqrt{a_1^2-c_2^2}}\operatorname{arctg}\frac{\sqrt{a_1^2-c_1^2}}{c_1}+\frac{1}{\sqrt{a_2^2-c_2^2}}\operatorname{arctg}\frac{\sqrt{a_2^2-c_2^2}}{c_2}-\frac{2}{R}+\frac{2(a_1^2-c_1^2)}{3R^3}+\frac{2(a_2^2-c_2^2)}{3R^3}\right]. \tag{16}$$

It is easy to see that on passing to spherical ions where $c_1 \to a_1$ and $c_2 \to a_2$ Eqs. (14) and (16) change into Eq. (2), and if only one of the reagents is spherical, e.g., the electron donor, from Eqs. (14) and (16) we obtain

$$E_s^I = \frac{Ce^2}{2}\left[\frac{1}{a_1}+\frac{1}{\sqrt{a_2^2-c_2^2}}\operatorname{arctg}\frac{\sqrt{a_2^2-c_2^2}}{c_2}-\frac{2}{R}-\frac{a_2^2-c_2^2}{3R^3}\right], \tag{17}$$

$$E_s^{II} = \frac{Ce^2}{2}\left[\frac{1}{a_1}+\frac{1}{\sqrt{a_2^2-c_2^2}}\operatorname{arctg}\frac{\sqrt{a_2^2-c_2^2}}{c_2}-\frac{2}{R}+\frac{2(a_2^2-c_2^2)}{3R^3}\right]. \tag{18}$$

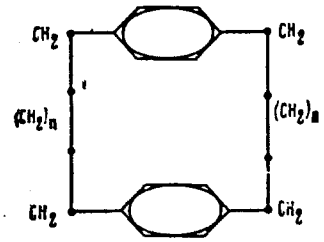


Fig. 4

The method developed above for calculation of E_S can be used, for example, in the evaluation of the activation energy of intramolecular electron-transfer reactions in radical anions containing benzene rings [7]. Case I corresponds to electron transfer between benzene rings lying in one plane and linked by a polymethylene chain (Fig. 3).

Case II corresponds to electron transfer in a cyclic structure obtained by joining benzene rings with two polymethylene chains (Fig. 4). By using 1.4 Å for the distance between the C–C atoms in the benzene ring, 1.09 Å for the length of the C–H bond, and 0.72 and 0.37 Å for the radii of the C and H atoms, we can take $c_1 = c_2 = 0.72$ Å and $a_1 = a_2 = 2.86$ Å as parameters characterizing the electron-density distribution in the ring. In the case of diphenylmethane (Fig. 3, n = 1) for example, the distance R is 8.26 Å, and in the case of paracyclophane (Fig. 4, n = 1) R is 6.52 Å. The corresponding E_S^I and E_S^{II} values are

$$E_s^I = C \cdot 5.04 \text{ eV}; \quad E_s^{II} = C \cdot 4.97 \text{ eV}. \tag{19}$$

On the condition that in the region where $\omega > kT/h$ there are dielectric losses only at optical frequencies, the parameter C contained in Eq. (1) can be expressed in terms of the optical and static dielectric constants of the solvent:

$$C = \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}. \tag{20}$$

Substituting Eq. (20) in Eq. (19) and taking account of the relation between the activation energy of electron transfer and the solvent reorganization for zero heat of reaction

$$E_a = \frac{E_s}{4}, \tag{21}$$

we obtain an expression for E_a^I and E_a^{II}.

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