CALCULATION OF SOLVENT REORGANIZATION ENERGY IN CHARGE-TRANSFER REACTIONS IN POLAR MEDIUM

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In an early paper of Marcus [1], where the classical model of the polar solvent is used for calculating the probability of electron transfer in a polar medium, the following expression was obtained for the activation energy of the reaction:

$$E_a = (E_s + I_f - I_i)^2 / 4E_s, \tag{1}$$

where E_S is the energy of solvent repolarization during charge transfer, and I_f and I_i are the equilibrium energies of the final and initial state of the system. In this theory, the parameter E_S was expressed in terms of the static and optical dielectric permittivity of the medium and of the distribution of the vector of electrical induction in the initial and final state:

$$E = \frac{1}{8\pi}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)\int (\vec{D}_i - \vec{D}_f)^2 dv. \tag{2}$$

The development of the quantum theory of chemical reactions in polar media has shown [2] that in the general case, the reorganization energy of a polar medium is expressed in terms of a complex, space- and time-dependent dielectric permittivity $\varepsilon(\omega, k)$:

$$E_s = \frac{1}{8\pi}\sum_k (\vec{D}_k^f - \vec{D}_k^i)^2 \frac{2}{\pi}\int_0^{kT/\alpha(1-\alpha)\hbar} \frac{d\omega}{\omega}\frac{\operatorname{Im}\varepsilon(\omega, k)}{|\varepsilon(\omega, k)|^2}, \tag{3}$$

where $\vec{D}_k^{i,f}$ is the Fourier component of the vector of electrical induction, k is the wave vector, and α is the transfer coefficient. In the longwave approximation ($k \to 0$), Eq. (3) can be transformed into

$$E_s = \frac{1}{8\pi}\left[\frac{1}{2\pi}\int_0^{kT/\alpha(1-\alpha)\hbar} \frac{d\omega}{\omega}\frac{\operatorname{Im}\varepsilon(\omega, 0)}{|\varepsilon(\omega, 0)|^2}\right]\int (\vec{D}^i - \vec{D}^f)^2 dv = \frac{c}{8\pi}\int (\vec{D}^i - \vec{D}^f)^2 dv. \tag{4}$$

The important difference between this expression and (2) is in the fact that only "classical" frequencies $\omega < kT/\alpha(1-\alpha)\hbar$ contribute to the reorganization energy of the medium, whereas the factor $1/\varepsilon_{op} - 1/\varepsilon_{st}$ corresponds to an integration over all frequencies, right up to the frequency ω_e corresponding to the electronic motion. Calculations employing the experimental relation $\operatorname{Im}\varepsilon(\omega)$ for water have shown [3] that the integral over frequencies in (4) gives approximately 80% of the value of $1/\varepsilon_{op} - 1/\varepsilon_{st}$.

The model of solid, conducting spheres [1] has been suggested for calculating the space integral of $(\vec{D}_i - \vec{D}_f)^2$. According to this model, the first solvation sheath of reacting ions is saturated, and together with the ions forms spheres within which the induction goes to zero, so that the molecules of the first solvation sheath are, as it were, "metallized." Thus, the integral in (4) is taken over an infinite volume excluding the two spheres (see Fig. 1):

$$\int_{\infty - v_a - v_b} (\vec{D}_i - \vec{D}_f)^2 dv = \int_{\infty - v_a - v_b} \vec{D}_i^2 dv + \int_{\infty - v_a - v_b} \vec{D}_f^2 dv - 2\int_{\infty - v_a - v_b} \vec{D}_i \vec{D}_f dv. \tag{5}$$

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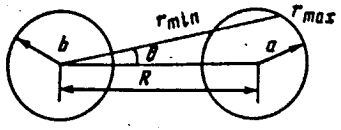


Fig. 1

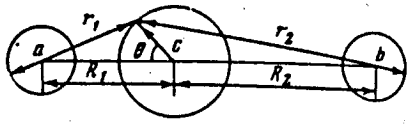


Fig. 2

However, the expression obtained in [1] for

$$\int (\vec{D}_i - \vec{D}_f)^2 dv = 4\pi e^2 (1/a + 1/b - 2/R) \tag{6}$$

corresponds to a situation where the integrals of $\vec{D}_i^2$ and $\vec{D}_f^2$ in [5] have in truth been calculated over all space excluding only either v_a or v_b, respectively.

It is of interest to estimate the magnitude of the terms $-\int_{v_b} \vec{D}_i^2 dv - \int_{v_a} \vec{D}_f^2 dv$ which have been dropped in such a calculation:

$$\int_{v_b} \vec{D}_i^2 dv = e^2 \iiint_{v_b} \frac{dr}{r^2} \sin\theta d\theta d\varphi = 2\pi e^2 \int_0^{\arcsin \frac{b}{R}} d\theta \sin\theta \int_{R\cos\theta - \sqrt{b^2 - R^2\sin^2\theta}}^{R\cos\theta + \sqrt{b^2 - R^2\sin^2\theta}} \frac{dr}{r^2}$$

$$= \frac{2\pi e^2 R}{R^2 - b^2} \left[\frac{b}{R} - \left(1 - \frac{b^2}{R^2}\right) \ln \frac{R+b}{\sqrt{R^2 - b^2}} \right] \equiv f(R, b). \tag{7}$$

Thus, in the model of conducting spheres we obtain

$$E_s = \frac{c}{8\pi} \int (\vec{D}_i - \vec{D}_f)^2 dv = \frac{c}{8\pi} \left[\frac{4\pi e^2}{a} + \frac{4\pi e^2}{b} - \frac{8\pi e^2}{R} - f(R, a) - f(R, b) \right]. \tag{8}$$

An evaluation shows that the two last terms in (8) yield a value of 6% of that being determined by Eq. (6), in the case of ions having the same size: $a = b$, $R = 2a$. The corresponding activational factor for the normal reaction range ($|I_f - I_i| \ll E_S$) and, e.g., $E_S = 2$ eV leads to a 3.3-fold increase in the reaction rate constant. For the case where the ions have different radii, there is an increase in the relative contribution of $f(R, a)$ and $f(R, b)$ to E_S. For example, when $b = 3a$ and $R = a + b$, this contribution amounts to 15.8% of E_S, and the rate constant increases by a factor of approximately 24.

The model of conducting spheres allows us to estimate the effect of a bridging ion on the mutual disposition of the initial and final state terms of the system in outer-sphere bridge charge-transfer reactions.

For the sake of simplicity, we shall consider the model where the two reacting ions and the bridging ion between them are all on one straight line (Fig. 2). Without the bridging particle, but otherwise unchanged arrangement of the reacting ions, E_S is determined by Eq. (8), where $R = R_1 + R_2$. In the presence of the bridging particle, this value E_S^0 must be reduced by the contributions from the integral over the region v_c:

$$E_s = E_s^0 - \frac{c}{8\pi} \int_{v_c} (\vec{D}_i - \vec{D}_f)^2 dv = E_s^0 - \frac{c}{8\pi} f(R_1 c) - \frac{c}{8\pi} f(R_2, c) + \frac{c}{4\pi} \int_{v_c} \vec{D}_i \vec{D}_f dv. \tag{9}$$

In evaluating the last integral in (9) it is convenient to change over to the integral over the surface:

$$2\int_{v_c} \vec{D}_i \vec{D}_f dv = 2\int_{v_c} \vec{\nabla}(\varphi_i \nabla \varphi_f) dv = -2\int_{s_c} \varphi_i \vec{\nabla} \varphi_f d\vec{S}_{\text{outer}} =$$

$$= -\frac{\pi e^2}{\sqrt{R_1 R_2}} \int_0^{\pi} \frac{\sin\theta \, d\theta \, (c/R_2 + \cos\theta)}{\sqrt{A - \cos\theta} \sqrt{(B + \cos\theta)^3}} = \frac{\pi e^2}{\sqrt{R_1 R_2}} \left\{ \frac{2(R_1 + R_2)}{\sqrt{R_1 R_2}(A + B)} - \right.$$

$$\left. - \arcsin \frac{A - B + 2}{A + B} + \arcsin \frac{A - B - 2}{A + B} \right\} = g(R_1, R_2, c), \tag{10}$$

where $A = (R_1^2 + c^2)/2cR_1$, $B = (R_2^2 + c^2)/2cR_2$.

We thus obtain for the system being considered

$$E_s = \frac{c}{8\pi}\left\{\frac{4\pi e^2}{a} + \frac{4\pi e^2}{b} - \frac{8\pi e^2}{R} - f(R_1 + R_2, b) - f(R_1 + R_2, a) - f(R_1, c) - f(R_2, c) + g(R_1, R_2, c)\right. \quad (11)$$

By estimating the importance of the various terms in (11) for the case $a = b = c$ and $R_1 = R_2 = 2$ one can see that the contribution from the terms $f(R_1 + R_2, a) + f(R_1 - R_2, b)$ is 0.2%, and that from $f(R_1, c) + f(R_2, c)$ is 4%, and that from $g(R_1, R_2, c)$ is 2.2% of the first three terms, which correspond to Marcus's equation. Thus, the total correction amounts to a reduction of E_S by 6.4%. The correction term increases with the radius of the bridging particle. For example, the corresponding contribution to E_S is 13% for the case $c = 3a$, $a = b$, $R = a + b + 2c$.

A bridging ion next to the reacting particles can also have an effect upon the solvation energy of the reagents; it will increase the equilibrium energies of the initial and final state of the system. We note that we are dealing here not with a direct electrostatic influence, but with a volume effect that does not depend on the sign of the bridging ion's charge. Thus, this volume effect leads to some approach between the terms of initial and final state (decrease of E_S), and raises them, because the solvation energy is reduced by an amount which is proportional to $f(R_1, c)$ and $f(R_2, c)$; this must lead to a decrease in the energy of activation of the process.

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