

# CALCULATION OF THE SOLVENT REORGANIZATION ENERGY IN REACTIONS WITH COMPLEX CHARGE REDISTRIBUTION IN THE REACTANTS

Yu. I. Kharkats

UDC 541.138

The solvent reorganization energy,  $E_s$ , is an important parameter of the quantum theory of chemical and electrochemical reactions occurring in polar media. The activation energy of a process is substantially determined by it. For example, when reorganization of the inner sphere of the reactants does not occur and the free energy of the reaction is low (the normal domain of reactions), the free energy of activation constitutes one fourth of  $E_s$ . For reactions occurring in the barrierless domain, the free energy of activation coincides with  $E_s$ .

In the long-wave approximation, the solvent reorganization energy is determined by the dielectric properties of the polar medium and by the charge distribution in reactants and reaction products [1]:

$$E_s = \frac{0.8}{8\pi} \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \int_{\text{other solvent volume}} (\vec{D}_i - \vec{D}_f)^2 dv. \quad (1)$$

Here  $\epsilon_{op}$  and  $\epsilon_s$  are the optical and the static dielectric permittivity of the solvent,  $\vec{D}_i$  and  $\vec{D}_f$  are the vectors of electric induction set up in the medium by the charge distribution before and after the reaction.\*

The first calculation of solvent reorganization energy had been performed by Marcus [2], who specified an expression for  $E_s$  for charge transfer between two spherical ions which he regarded as rigid spheres of radii  $a_1$  and  $a_2$  separated by a distance  $R$  and with a homogeneous distribution of the charges over the surface of the spheres

$$E_s = \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right). \quad (2)$$

Subsequent analysis showed [3] that the ions' own volumes had not been taken into account correctly by Marcus in deriving Eq. (2). Calculations allowing for this factor, as well as for mutual polarizability of the ions, a variation of reactant radii during the reaction, and reactant nonsphericity, and also calculations of  $E_s$  in more complex systems were performed in a number of papers [4-13].

In the present communication we report a calculation of solvent reorganization energy in reactions accompanied by charge transfer or redistribution in reactants with a complex charge distribution. The reactants and reaction products will be described as a set of an arbitrary number,  $N$ , of spherical particles which are distributed in an arbitrary manner in the polar medium. Each particle can have a charge  $z_k^i$  in the initial state and a charge  $z_k^f$  in the final state. The radii of the particles will be labeled  $a_k$ , the coordinates of their centers will be labeled  $\vec{R}_k$ , and the dielectric permittivity of the reactants will be labeled  $\epsilon_i$ .

When determining the distribution of the induction vectors  $\vec{D}_i$  and  $\vec{D}_f$  in the polar medium we shall take into account that each of the charges  $z_k^i, f$  brings forth induced dipole moments in all remaining dielectric spheres. To find these dipole moments one can utilize the solution obtained in the problem of a spherical cavity within a dielectric in an homogeneous external field [10, 14]. Corrections of a higher order with respect to parameter  $(a/R)^2$  are obtained when inhomogeneity of the external field and a charge redistribution on the reactants resulting from their interaction with the induced dipoles are taken into account; these will not be discussed here.

Thus, electric inductions  $\vec{D}_i$  and  $\vec{D}_f$  can be written down, in terms of the model being discussed, as

\* The numerical factor of 0.8 in (1) arises when the quantum properties of the medium are taken into account.

$$\vec{D}_{i,j} = -\nabla \left[ \sum_{k=1}^N \left( \frac{z_k}{|\vec{r}_k|} + \sum_{\substack{m=1 \\ m \neq k}}^N \left( \frac{\vec{d}_{mk} \cdot \vec{r}_m}{|\vec{r}_m|^3} \right) \right] \quad (3)$$

where  $\vec{r}_k$  is a vector issuing from the center of the k-th sphere, and  $\vec{d}_{mk}$  is the dipole moment induced by charge  $z_k$  on sphere m [10, 14]:

$$\vec{d}_{mk} = \frac{z_k a_m^3 \vec{R}_{mk}}{|\vec{R}_{mk}|^3} \left( \frac{\varepsilon_s - \varepsilon_i}{2\varepsilon_s + \varepsilon_i} \right), \quad \vec{R}_{mk} = \vec{R}_m - \vec{R}_k. \quad (4)$$

From (3) we obtain

$$(\vec{D}_i - \vec{D}_j)^2 = \left[ \nabla \left( \sum_{k=1}^N u_k + \sum_{k=1}^N \sum_{\substack{m=1 \\ m \neq k}}^N w_{mk} \right) \right] \left[ \nabla \left( \sum_{n=1}^N u_n + \sum_{n=1}^N \sum_{\substack{l=1 \\ l \neq n}}^N w_{ln} \right) \right], \quad (5)$$

where

$$u_k = \frac{\delta z_k}{r_k}, \quad w_{mk} = \frac{\delta \vec{d}_{mk} \cdot \vec{r}_m}{r_m^3}, \quad \delta \vec{d}_{mk} = \delta d_{mk} \frac{\vec{R}_{mk}}{R_{mk}} \quad (6)$$

and

$$\delta z_k = z_k' - z_k, \quad \sum_{k=1}^N \delta z_k = 0, \quad \delta d_{mk} = \frac{\delta z_k a_m^3}{R_{mk}^2} \left( \frac{\varepsilon_s - \varepsilon_i}{2\varepsilon_s + \varepsilon_i} \right). \quad (7)$$

Changing in (1) from an integration over solvent volume to integrals over the surfaces of spheres we obtain

$$E_s = \frac{0.8}{8\pi} \left( \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right) \sum_{p=1}^N \int_{S_p} d\vec{S}_p \left[ \sum_{k=1}^N u_k + \sum_{k=1}^N \sum_{\substack{m=1 \\ m \neq k}}^N w_{mk} \right] \nabla \left[ \sum_{n=1}^N u_n + \sum_{n=1}^N \sum_{\substack{l=1 \\ l \neq n}}^N w_{ln} \right]. \quad (8)$$

Here the arrow written in  $d\vec{S}_p$  indicates that the internal normal to the surface,  $S_p$ , of the sphere is used in the integration.

In evaluating the integrals contained in (8) it was found that some of them are zero, and that others yield contributions to  $E_s$  which have a higher order of smallness with respect to parameter  $a^2/R^2$  than the terms describing the effects of mutual polarizability and the effects resulting when the reactants' own volumes are cut off. We shall retain in (8) only those integrals which yield a contribution to  $E_s$  up to the order of  $a^3/R^4$  inclusively. Among the integrals containing  $u \nabla u$ , these are

$$\int_{S_p} d\vec{S}_p u_p \nabla u_p = \frac{4\pi (\delta z_p)^2}{a_p}; \quad (9)$$

$$\int_{S_p} d\vec{S}_p u_k \nabla u_p = \frac{4\pi (\delta z_k) (\delta z_p)}{R_{kp}}, \quad (k \neq p) \quad (10)$$

$$\int_{S_p} d\vec{S}_p u_k \nabla u_n = -\frac{4\pi (\delta z_k) (\delta z_n) a_p^3}{3R_{pk}^3 R_{pn}^3} (\vec{R}_{pk} \cdot \vec{R}_{pn}), \quad (k \neq p, n \neq p). \quad (11)$$

Among the integrals containing  $w \nabla u$  and  $u \nabla w$ , one must retain

$$\int_{S_p} d\vec{S}_p u_k \nabla w_{pn} = \frac{8\pi (\delta z_k)}{3R_{pk}^3} (\delta \vec{d}_{pn} \cdot \vec{R}_{pk}), \quad (k \neq p, n \neq p) \quad (12)$$

$$\int_{S_p} d\vec{S}_p w_{mk} \nabla u_p = \frac{4\pi (\delta z_p)}{R_{pm}^3} (\delta \vec{d}_{mk} \cdot \vec{R}_{pm}), \quad (m \neq k, m \neq p) \quad (13)$$

$$\int_{S_p} d\vec{S}_p w_{pk} \nabla u_n = -\frac{4\pi (\delta z_n)}{3R_{pn}^3} (\delta \vec{d}_{pk} \cdot \vec{R}_{pn}), \quad (k \neq p, n \neq p). \quad (14)$$

Finally, among the integrals containing  $w \nabla w$  one must retain

$$\int_{S_p} \vec{dS}_p w_{pk} \nabla w_{pn} = \frac{8\pi}{3a_p^3} (\vec{d}_{pk} \cdot \vec{d}_{pn}). \quad (k \neq p, n \neq p) \quad (15)$$

Putting integrals (9) to (15) into (8) and collecting similar terms we obtain, with (7),

$$E_s = 0.8 \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_s} \right) \left\{ \sum_{p=1}^N \left[ \frac{(\delta z_p)^2}{2a_p} + \sum_{\substack{h=1 \\ h \neq p}}^N \frac{(\delta z_p)(\delta z_h)}{2R_{ph}} + \sum_{\substack{h=1 \\ h \neq p}}^N \sum_{\substack{l=1 \\ l \neq p}}^N \frac{(\delta z_h)(\delta z_l) a_p^3 (\vec{R}_{ph} \cdot \vec{R}_{pl})}{R_{ph}^3 \cdot R_{pl}^3} \left( \frac{3\varepsilon_s^2}{(2\varepsilon_s + \varepsilon_l)^2} - \frac{1}{2} \right) \right] \right\}. \quad (16)$$

Expression (16) generalizes a previous result for solvent reorganization energy during charge transfer between two spherical reactants [10]. It also comprises as a particular case the solvent reorganization energy during the synchronized occurrence of several charge transfer reactions [4]. With relation (16) one can also generalize previous results concerning the effect of a bridging particle on the activation energy of charge transfer [9] and concerning solvent reorganization energy during electron transfer from an electrode to a dipolar reactant when image forces are included [5].

We note in conclusion that in the case of aqueous solutions frequently met, one has  $\varepsilon_i \ll \varepsilon_s$  and relation (16) can be simplified when the expression in parentheses in the third term is replaced by  $1/4$ .

The author thanks R. R. Dogonadze and A. M. Kuznetsov for discussing the work.

#### LITERATURE CITED

1. R. R. Dogonadze and A. M. Kuznetsov, *Élektrokhimiya*, **7**, 763 (1971).
2. R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).
3. Yu. I. Kharkats, *Élektrokhimiya*, **9**, 881 (1973).
4. L. I. Krishtalik, *Mol. Biol.*, (Moscow) **7**, 884 (1973).
5. W. R. Fawcett and Yu. I. Kharkats, *J. Electroanal. Chem.*, **47**, 413 (1973).
6. Yu. I. Kharkats, *Élektrokhimiya*, **10**, 612 (1974).
7. Yu. I. Kharkats, *Élektrokhimiya*, **10**, 1137 (1974).
8. Yu. I. Kharkats and G. M. Chonishvili, *Élektrokhimiya*, **11**, 172 (1975).
9. Yu. I. Kharkats and G. M. Chonishvili, *Élektrokhimiya*, **11**, 175 (1975).
10. Yu. I. Kharkats, *Élektrokhimiya*, **12**, 592 (1976).
11. Yu. I. Kharkats, *Élektrokhimiya*, **12**, 1284 (1976).
12. Yu. I. Kharkats, *Élektrokhimiya*, **12**, 1370 (1976).
13. Yu. I. Kharkats, *Élektrokhimiya*, **12**, 1866 (1976).
14. H. Frohlich, *Theory of Dielectrics*, Second edition, Clarendon Press, Oxford (1958) [Russian translation: *Izd. Inostr. Lit.*, Moscow (1960)].