# THE REORGANIZATION ENERGY IN PROTON TRANSFER REACTIONS AT ELECTRODES AND IN HOMOGENEOUS PROTON TRANSFER REACTIONS

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The reorganization energy of the electrode reaction was estimated from data for the activation energy at the transition potential from barrierless to ordinary discharge, while the energy consumed in bringing the hydroxonium ion toward the electrode to a distance which is optimum for proton tunneling was taken into account. Data for the energy interval between barrierless and activationless homogeneous proton transfer for various classes of acids were used to estimate the reorganization energy of these reactions. The reorganization energy was found to be appreciably smaller than that following from the relations of Marcus, both for proton transfer at electrodes and for homogeneous proton transfer. Possible reasons for these differences are discussed, with particular mention of the importance of reduced reorganization of the near solvation sphere as compared to the isotropic dielectric model.

Together with the heat, $\Delta I$, of the elementary act, the solvent reorganization energy, $E_S$, is the parameter governing the activation energy of charge transfer processes. It is natural, therefore, that a knowledge of this parameter is important for all theoretical estimates of reaction rates.

A value of 20 to 30 kcal often is assumed for $E_S$ in calculations related to proton donor discharge reactions. It seemed that this figure on one hand is in order-of-magnitude agreement with the experimental activation energies, and on the other hand it is close to the result calculated with the Marcus relation [1]

$$E_s = N_A(\Delta e)^2\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_s}\right)\left(\frac{1}{2a}-\frac{1}{4R'}\right). \quad (1)$$

Here, $N_A$ is the Avogadro constant; $\Delta e$ is the charge being transferred, which equals the charge of an electron; $\varepsilon_0$ and $\varepsilon_S$ are the optical and static dielectric permittivity; $a$ is the ion's radius; and $R'$ is the distance from the electrode surface to the center of the ion. Assuming that $R' \simeq a$ and accepting $a \simeq 1.5$ Å for the radius of the $H_3O^+$ ion we obtain $E_S = 30$ kcal/mole, i.e., a figure close to that reported above.

For a homogeneous charge transfer reaction,

$$E_s = N_A(\Delta e)^2\left(\frac{1}{\varepsilon_0}-\frac{1}{\varepsilon_s}\right)\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{R}\right), \quad (2)$$

where $a_1$ and $a_2$ are the radii of the two reacting species, and R is the distance between their centers. Assuming $a_1 = a_2 = 1.5$ Å and $R = 2a = 3.0$ Å for the distance we find $E_S = 60$ kcal, a figure which is twice that for heterogeneous reactions.

It seemed to us, however, that the widespread opinion that estimates via the Marcus relations are in harmony with experiments in the case of proton transfer reactions is based on an insufficiently careful analysis of this problem. The best-founded way of experimental estimates of $E_S$ for electrode reactions is that using data for the activation energy of barrierless discharge.

Let us examine in more detail the situation existing here. The transition point from ordinary to barrierless discharge corresponds to the mutual disposition of terms shown in Fig. 1. Here, the initial state (1) represents the hydroxonium ion in the position just before discharge and the electron in the metal on the Fermi level at the corresponding potential; the final state (2) represents the adsorbed hydrogen atom and the water molecule in the position just after discharge. For the situation depicted in Fig. 1, the true activation energy of the elementary act equals the reorganization energy $E_S$.

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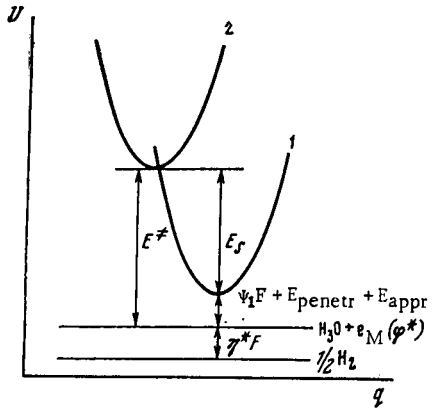


Fig. 1

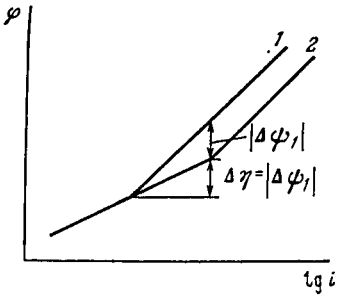


Fig. 2

Fig. 1. Schematic disposition of the potential curves at the transition potential from ordinary to barrierless discharge.

Fig. 2. Schematic polarization curves in the transition region from ordinary to barrierless discharge.

We know [2] that the apparent real activation energy, $E^{\neq}$ (at constant overvoltage and solution composition), that can be measured can be described in the potential diagram as the distance from the energy level which corresponds to the energy level of the $H_3O^+$ ion in the bulk solution and of the electron on the Fermi level at a given overvoltage to the point of intersection of the initial and final term; the distance from the level of gaseous hydrogen to the above Fermi level is $\eta F$.

In the case under discussion, the difference between $E^{\neq}$ and $E_S$ corresponds to the energy difference of $H_3O^+$ in the position just prior to discharge and in the bulk solution. This difference is due to three elements: The $\psi_1$-effect, the work of incorporation of the $H_3O^+$ ion into the first monolayer of water molecules, and the work of bringing the ion toward the electrode to a distance that is optimum for tunneling:

$$E^{\neq} = E_s + \psi_1 F + E_{\text{penetr}} + E_{\text{appr}} \qquad (3)$$

Figure 2 shows schematic polarization curves in the transition region from ordinary to barrierless discharge for two different solutions associated with different values of the $\psi_1$-potential. The activation energies that can be measured in the transition points differ by the overpotential difference $E_2^{\neq} = E_1^{\neq} - \Delta\eta F$. For a calculation of $E_S$ we want to know the quantity $E^{\neq} - \psi_1 F$, according to (3). In the transition point of curve 2, this is given by $E_2^{\neq} - \psi_1(2)F = E_1^{\neq} - \psi_1(1)F + \Delta\psi_1 F - \Delta\eta F$, where $\Delta\psi_1$ is the negative displacement of $\psi_1$ in curve 2 relative to curve 1. Under the conditions of constant $\psi_1$, the slopes of the Tafel lines for ordinary and barrierless discharge differ by a factor of two; one can see from Fig. 2, therefore, that $\Delta\eta = \Delta\psi_1$, i.e., $E_2^{\neq} - \psi_1(2)F = E_1^{\neq} - \psi_1(1)F$. Thus, for the difference which we want to know, it is irrelevant which of the experimental curves we select for the calculation. For example, from the data of [3] one can find the value of $E^{\neq}$ in the transition point from ordinary to barrierless discharge in 6.0 M KI + 0.55 M HCl solution; this is 13.7 kcal. The $\psi_1$-potential in this solution can be found from the displacement of the polarization curve of ordinary discharge relative to that in a solution not containing surface-active ions. It is −0.30 V. Hence $E^{\neq} - \psi_1 F = 20.6$ kcal.

The component $E_{\text{penetr}}$ arises since hydrogen is discharged which is present in the inner part of the double layer rather than at the outer Helmholtz plane; but the properties of the so-called dielectric interlayer of the double-layer capacitor, i.e., of the first water monolayer next to the electrode, are greatly different from the bulk properties [4]. Quantity $E_{\text{penetr}}$ turns out to be inaccessible to direct experimental determination. It can be estimated from the following considerations. The work of penetration must be sufficiently large so that hydrogen ion adsorption in the inner layer would be negligibly low relative to that in the outer layer. Moreover, this low extent of adsorption must be preserved when the $\psi_1$-potential is strongly displaced in the negative direction, which causes the $H_3O^+$ concentration in the inner layer to increase by several orders of magnitude. We shall assume that the amount of $H_3O^+$ in the inner layer will not surpass 1% of their total amount at the electrode surface, even when the concentration in the first monolayer has been raised by three orders of magnitude ($\psi^1 - \psi^0 = 180$ mV). Then $E_{\text{penetr}} = 2.3\ RT \cdot 5 \simeq 7$ kcal. We note that an estimate of $E_{\text{penetr}}$ which was based on a certain model of dielectric permittivity distribution in the double layer gave a figure of 5 to 10 kcal [5]. One can see that the contribution of $E_{\text{penetr}}$ practically compensates that of the $\psi_1$-effect.

TABLE 1. Typical Energy Intervals for Various Reactions

| Acid | Base | Energy interval, kcal |
|---|---|---|
| Acetic | Amines | 10-11 |
| Maleic | " | 10 |
| Fumaric | " | 11 |
| Phenol | " | 10-11 |
| Carboxylic acids, nitrophenol | Aniline | $\geqslant 11$ |
| Phenols, acetic acid, acid pyrophosphate | Imidazole | 8 |
| Phenols, inorganic oxygen acids, glucose | Ammonia | 7 |
| Thioglycol | Amines | 14 |
| Ketones | $OH^-$ | 18 |
| Acetylacetone | Anions of carboxylic acids, phenols, carbohydrates, $OH^-$, $HS^-$, $P_2O_7$, $H_2O$, pyridine | 23 |

The very sharp dependence of the tunneling probability on distance is responsible for the appreciable energy expenditure in bringing the ion closer to the electrode, since the expenditure of energy for this approach is made profitable by this dependence [6]. The repulsion potentials which must be overcome during the approach are not known for the $H_3O^+$–metal system, so that quantitative calculations are impossible here. The order of magnitude can be estimated from the analogy to other systems, and in particular to the system CH...O, for which the repulsion potentials are better known. A calculation of the tunneling conditions for this system yielded the result that the approach to the distance which is optimum for proton tunneling requires the expenditure of 7.6 kcal [6]. One can assume by analogy that for the electrode reaction, too, $E_{appr}$ amounts to a few, e.g., 5, kcal in magnitude.*

By taking into account the elements listed here one comes to values of $E_S$ for hydrogen ion discharge on mercury which are appreciably lower than the ones usually adopted, viz., to $E_S$ of about 7 to 9 kcal.

Let us now discuss the problem of reorganization energies in homogeneous proton transfer. One can see from the large amount of experimental data obtained primarily in the work of Eigen [8] that the reaction will pass from the region of a diffusion-limited reaction rate into that of ordinary kinetics and further into a kinetic region where product diffusion is limiting, the determining factor being $\Delta pK$, i.e., the standard free energy of the reaction. Allowing for the small size of the activation energy of diffusion, we can assume that the boundaries between these regions are close to the boundaries of the regions of activationless and barrierless proton transfer, respectively. Typical energy intervals which for different reaction series are separating the regions of barrierless and activationless reactions are presented in Table 1.

Consider the schematic potential curves of Fig. 3. The sum of the absolute value of the equilibrium $\Delta I$ for processes at the boundaries between barrierless and activationless reactions ($\Delta I_1$ and $\Delta I_2$) differs from twice the reorganization energy by the difference between the energies, $E_{appr\,1} - E_{appr\,2}$, required to bring the reactants to the optimum distance. Within any given reaction series, this difference cannot be a large quantity, so that to a first approximation one can assume that $E_S \simeq (\Delta I_1 + |\Delta I_2|)/2$, i.e., half the interval between two regions with the limiting values of $\alpha = 0$ and $\alpha = 1$. Turning now to the data of Table 1 we can conclude that for reactions of O–H or N–H acids with O or N bases, i.e., for reactions of partners linked by a sufficiently strong hydrogen bond, a low reorganization energy of 4 to 6 kcal is found. For reactions of C–H acids, the reorganization energy is substantially higher (9 to 12 kcal), while thioglycol takes up an intermediate position. However, in all cases the experimental values are much lower than the estimate obtained from the Marcus relation. It must be taken into account here that for C–H acids, the charge transfer distance ought to be larger than the sum of radii of the charged groups (as assumed in the estimate reported at the beginning of the present paper), since the charge in the anions of these acids is centered, not at the C atom but at other, more remote atoms, in particular at the oxygen atoms bound to the C of nitro and carbonyl groups. In accordance with Eq. (2), this leads to a higher reorganization energy [9].

*The feasibility of this analogy follows from data for the activation energies of hydrogen evolution in light and heavy water. A calculation of the contribution of $E_{appr}$ to the difference between these energies in the systems CH–O and CD–O yields about 0.8 kcal, while from experimental data for hydrogen and deuterium evolution on mercury one can estimate that $\Delta E_{appr} \simeq 0.7$ kcal [7].

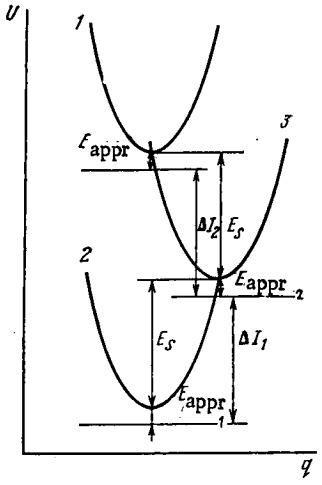


Fig. 3. Scheme of the potential curves for an activationless (1 → 3) and a barrierless (2 → 3) homogeneous reaction. Horizontal lines indicate the energy levels of the reactants prior to their approach to optimum tunneling distance.

Thus, both for homogeneous and heterogeneous proton transfer reactions, the experimental data lead to the conclusion that the reorganization energy has substantially lower values than those following from the Marcus relation. The question arises, of course, as to the origin of this difference.

One of the reasons undoubtedly is the assumed lack of frequency dispersion of the dielectric permittivity contained in the Marcus relation. An inclusion of this effect based on the corresponding experimental data induced Dogonadze and Kuznetsov to introduce a correction factor close to 0.8 into Eqs. (1) and (2) [10]. This correction produces lower calculated $E_S$ but cannot be regarded as the main reason for the differences between theory and experiment.

Another possible reason is partial screening of the charged group from the solvent by nonpolar groups bound to it. This effect is very sensitive to the molecule's geometry, and basically can be large [11, 12]. It merits special analysis with respect to a number of specific reactions. It must be noted, however, that for cathodic hydroxonium ion discharge, this effect is absent, and for a number of homogeneous reactions of simple molecules, in all likelihood it is small.

As a third reason one can cite a substantial decrease in the charge transfer distance, R, relative to the sum of ionic radii (for electrode processes, of R' relative to $a$). It had been shown previously, in fact [6], that a substantial approach of the species relative to their equilibrium distance is optimum for tunneling in a number of cases (electrode reactions, homogeneous reactions of C–H acids). When R' is reduced by 0.3 Å (precisely this order of magnitude must be expected for optimum approach), this has the effect that $E_S$ decreases to 53 kcal. It must be pointed out, however, that reactant approach against the repulsion forces is associated with deformation of the particles and with a decrease in their effective radius, which has the effect of raising $E_S$ somewhat. Quantitative estimates are difficult to obtain here; it is clear, however, that this effect, too, cannot fully settle the differences found between the Marcus relations and experiment. We note that in certain cases, particularly for homogeneous reactions of hydrogen-bonded species, the contribution from this effect should not be large.

Finally, in cases where the immediate neighborhood of the reacting species is undergoing much less reorganization, one expects a more significant decrease in reorganization energy than in cases where the solvent properties are uniform right up to the reactant molecule itself. This effect can be linked to several reasons: spatial dispersion of the dielectric permittivity (in cases where the electric field close to the ion changes substantially over distances which are smaller than or comparable with the correlation radius of the solvent dipole positions); dielectric saturation of the solvent in the strong electric field close to an ion or charged group of small size; and nonelectrostatic interactions, in particular the formation of hydrogen bonds between the water molecules and the reactants, which results in a certain dipole orientation which has little relation to the charge present in the molecule. In the last case, one actually is talking about including the first solvation sheath into the reactant species: The water molecules are regarded as ligands in some com-

plex, and the loss or acquistion of a proton by this complex is associated with relatively little reorganization of its coordination sphere. An example of such a hydration complex is $H_9O_4^+$ which is prevalent in aqeuous solution and which can be regarded as an $H_3O^+$ ion strongly hydrogen-bonded to three water molecules. By approximating this complex by a sphere of 3 Å radius and assigning the same size to the other reacting complex we obtain $E_S = 30$ kcal, i.e., $E_S$ has been reduced by a factor of two relative to the reaction of "nonhydrated" species.

It must be said that it will be difficult to distinguish experimentally between the three reasons listed above, and they overlap even in theoretical respects, since under certain aspects they differ more in description than in the physical reality of the effect. Without going into a detailed review of the mechanisms one still can conclude that this effect, i.e., less reorganization of the near hydration sphere, very substantially reduces the reorganization energy of the medium.

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# THE EFFECT OF IONIC ADSORPTION ON ELECTROCHEMICAL REACTION KINETICS


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In terms of statistical mechanics, the local probability of the elementary act of irreversible electrochemical one-electron reactions is averaged while allowing for the electric double layer set up by the indifferent electrolyte and by ions specifically adsorbed at the metal/solution interface. An expression for the current density as a function of double-layer parameters is obtained and analyzed for the case where the discharging ions are situated outside the Helmholtz layer.


The effect of impurity ion adsorption on ionic mass transport processes in electrochemical systems has been discussed in [1]. In the present work we discuss the problem how one can quantitatively calculate the effect of adsorption of electrochemically indifferent ionic solution components on the elementary act of electrochemical reactions and on the actual kinetic step of the entire electrode process. The effect of ionic atmosphere and layer structure on the elementary act of electrochemical reactions has been discussed in [2, 3]; in [2], the problem of the effect of adsorption has also been considered in general terms. In the following discussion of the effect of specific ionic adsorption on the elementary act of electrochemical reactions, we explicitly examine the procedure of statistical averaging over the entire ensemble of ions including those in the adsorbed layer. Cases of localized ionic adsorption (regular distribution and ionic adsorption on randomly


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