CHARGE TRANSFER REACTIONS ACCOMPANIED BY A CHANGE IN THE COORDINATES OF A HEAVY PARTICLE. II

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We previously examined the elementary act of charge transfer in a polar medium, taking account not only of the reorganization of the solvent but also the changes in the coordinates of the heavy particle taking part in the reaction [1]. The aim of the present work was to examine various effects related to the quantum character of the vibrations of the heavy particle. We shall consider the latter in the harmonic oscillator approximation. We shall consider the case where after electron transfer, the coordinate of the heavy particle is far from the equilibrium value, i.e., where a greatly elongated bond is formed as a result of charge transfer. Because of the anharmonicity of the vibrations, the vibrational levels for marked elongation of the bond are extremely close, and the movement of the reacting particle in the final state, particularly when account is taken of the high values of the vibrational numbers, can be regarded as classical.

The activation energy associated with the reorganization of the solvent for a given coordinate of the particle R is equal to [2]

$$(E_s + \Delta U_i(R))^2 / 4E_s,$$

where E_s is the energy of reorganization of the solvent, and $\Delta U_i(R)$ is the difference in the energies of the initial and final states of the system for a constant coordinate R and the i-th vibrational level of the initial state and the equilibrium polarization of the solvent for the given conditions $\Delta U_i(R) = \Delta U_0(R) - n\varepsilon$, where ε is the magnitude of the vibrational quantum for the intermolecular vibrations of the reacting particle and n is the number of the level. Let us consider first the case where the charge transfer takes place with practically no change in R. The probability of transfer (or the quantity W proportional to it) can then be found by taking the sum over all levels.

$$W = \sum_0^\infty e^{-\frac{n\varepsilon}{kT}} \exp\left[-\frac{(E_s + \Delta U_0 - n\varepsilon)^2}{4E_s kT}\right]. \tag{1}$$

When the values of ε are not too large compared with kT, the summation can be replaced by integration with respect to n

$$W = \int_0^\infty e^{-\frac{n\varepsilon}{kT}} \exp\left[-\frac{(E_s + \Delta U_0 - n\varepsilon)^2}{4E_s kT}\right] dn. \tag{1a}$$

For the range $\Delta U_0 < E_s$, a transition from the level n = 0 is most probable.

Approximate integration of the rapidly changing function [3] gives for $\Delta U_0 < E_s - \sqrt{2E_s kT}$.

$$W = 2\frac{kT}{\varepsilon}\frac{E_s}{E_s - \Delta U_0} \exp - (E_s + \Delta U_0)^2/(4E_s kT), \tag{2}$$

and for $E_s - \sqrt{2E_s kT} < \Delta U_0 < E_s$ we obtain the result:

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$$W = \frac{1}{2\varepsilon}\left[\sqrt{2E_s kT} + \Delta U_0 - E_s + (3\sqrt{2E_s kT} + \Delta U_0 - E_s)\right.$$

$$\left. \times \exp\left[-\frac{2E_s kT - (E_s - \Delta U_0)^2}{4E_s kT}\right]\right] \exp\left[-\frac{(E_s + \Delta U_0)^2}{4E_s kT}\right]. \tag{2a}$$

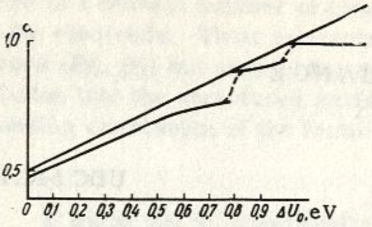

Fig. 1

For the range $\Delta U_0 \geq E_S$, the most probable transition is not from the ground level but from one of the excited levels $n = (\Delta U_0 - E_S)/\varepsilon$. The probability of the transition is equal to

$$W = 2\sqrt{\pi}\frac{\sqrt{E_s kT}}{\varepsilon} e^{-\Delta U_0/kT}. \tag{3}$$

The value of ΔU_0 for R = const is uniquely related to the difference in the minimum values of the internal energies of the initial and final states (the heat of the elementary act of the reaction Q), differing from it by a constant quantity – the energy of elongation of the bond up to the given value of R. Thus the dependence of W on ΔU_0 is similar in character to the dependence of W on Q. Thus from Eqs. (2) and (3) we can find the value of the transfer coefficient (Brönsted coefficient) $\alpha = -kTd \ln W/dQ = -kTd \ln W/d\Delta U_0$. For

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta U_0}{E_s}\right) - \frac{kT}{E_s - \Delta U_0}. \tag{4}$$

For $E_S - \sqrt{2E_S kT} < \Delta U_0 < E_S$

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta U_0}{E_s}\right) - \frac{1}{2E_s}\cdot\frac{2E_s kT + [2E_s kT - (3\sqrt{2E_s kT} + \Delta U_0 - E_s)(E_s - \Delta U_0)]\exp\left[-\frac{2E_s kT - (E_s - \Delta U_0)^2}{4E_s kT}\right]}{\sqrt{2E_s kT} + \Delta U_0 - E_s + (3\sqrt{2E_s kT} + \Delta U_0 - E_s)\exp\left[-\frac{2E_s kT - (E_s - \Delta U_0)^2}{4E_s kT}\right]}. \tag{4a}$$

For $\Delta U_0 \geq E_S$

$$\alpha = 1. \tag{5}$$

The results of the calculation from Eqs. (4) and (5) (it is assumed that $E_S = 1$ eV, i.e., $E_S = 40$ kT) are given in Fig. 1* and compared with the results which follow from the equations obtained without allowance for the intermolecular vibrations [2]:

$$\alpha = \frac{1}{2}(1 + \Delta U_0/E_s). \tag{6}$$

The most characteristic difference between Eqs. (4), (5), and (6) is that allowance for the quantum character of the vibrations leads to the conclusion that there is a limiting value $\alpha = 1$, whereas according to Eq. (6), α can increase without limit. The existence of a set of comparatively close quantum levels always leads to the limit $\alpha = 1$. For electrode reactions this limit follows from the nature of the distribution of electrons in a metal [4], and for bulk reactions it follows from the quantization of the intermolecular (and in some cases intramolecular [5]) vibrations, examined above. Another interesting feature is that calculation according to Eq. (4) gives smaller values of α than calculation according to Eq. (6); the physical reason for this is clear; as ΔU_0 increases, there is an increase in the contribution of the excited vibrational levels, for which ΔU is less than ΔU_0 and hence less than the value of α.

It was assumed above that for all conditions, R = const. In actual fact, however, the particle is vibrating, so that the coordinate R is changing. The probility that it is situated at a given point is given by the square of the wave function ψ_n, which for the harmonic oscillator (see for example [6]) has the form

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*The breaks in the functions giving the dependence of α on ΔU_0 are probably due to the approximate nature of the integration. Figure 1 gives only the positive values of ΔU_0, since for large negative values, a significant and subsequently the chief contribution is made by transitions to excited levels of the final state, which are not examined within the framework of the present paper.

$$\psi_n = \left(\frac{1}{2^n n! \sqrt{\pi}}\right)^{1/2} H_n(s) e^{-1/2 s^2}. \quad (7)$$

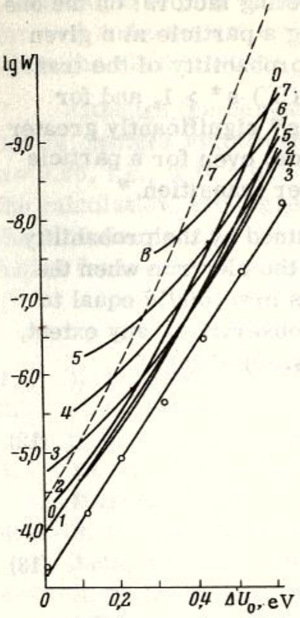

Fig. 2

Here the distance S is measured from the equilibrium position and is expressed as fractions α of the classical amplitude of the vibrations, and H_n is an Hermitian polynomial. The jump-over of an electron for different R leads to different values for the energy of the final state in accordance with U(R) relationship for the final state. By approximating this relationship to a straight line*, we obtain the dependence of the quantity $\Delta U_n(s)$ on the coordinate of the vibrating particle.

$$\Delta U_n(s) = \Delta U_0 - n\varepsilon - Ks \quad (8)$$

Here, ΔU_0 relates to the zeroth vibrational level and the equilibrium value of the coordinate (s = 0), (s = 0), $K = (dU/dR)\,\alpha$.

The probability of a transition for given n and s is determined as

$$w_n(s) = \frac{1}{2^n n! \sqrt{\pi}} H_n^2(s) e^{-s^2} \exp\left[-\frac{(E_s + \Delta U_0 - n\varepsilon - Ks)^2}{4E^s kT}\right] \quad (9)$$

and the total probability of a transition for the n-th level is found by integrating with respect to s:

$$W_n = \int_{-\infty}^{\infty} w_n(s)\, ds. \quad (10)$$

The most probable transformation is that for a distance s* satisfying the condition for a maximum value of the function under the integral sign:

$$(4E_s kT + K^2) s^* - (E_s + \Delta U_0 - n\varepsilon) K - 4E_s kT \left(\frac{d \ln H_n}{ds}\right)_{s^*} = 0. \quad (11)$$

For n = 0 we have $d \ln H_0/ds = 0$ and

$$s_0^* = \frac{(E_s + \Delta U_0) K}{4E_s kT + K^2} \quad (11a)$$

and for n = 1 we have $d \ln H_1/ds = 1/s$ and

$$s_1^* = \frac{(E_s + \Delta U_0 - \varepsilon) K + \sqrt{(E_s + \Delta U_0 - \varepsilon)^2 K^2 + 16 E_s kT (4E_s kT + K^2)}}{2(4E_s kT + K^2)}. \quad (11b)$$

For higher values of n the derivative d ln Hn/ds can be represented in the form of a series $n/s + f_1/s^3 + f_2/s^5 + \ldots$, where $n \leqslant f_1 < f_2 \ldots$. Estimation shows that in certain cases of practical interest (e.g., of a type such as the anodic liberation of chlorine), s* is significantly greater than unity, and for values of n which are not too large in the above expansion it is possible to neglect all terms except the first. Then with allowance for the fact that the main contribution to the integral (10) is made by s > 0, we obtain

$$s_n^* \simeq \frac{(E_s + \Delta U_0 - n\varepsilon) K + \sqrt{(E_s + \Delta U_0 - n\varepsilon)^2 K^2 + 16 E_s kT (4E_s kT + K^2) n}}{2(4E_s kT + K^2)}. \quad (11c)$$

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*For extensive elongation of the final bond, e.g., the adsorption bond between an atom or radical and an electrode, the curvature of the corresponding term is small.

The value of the optimum distance for a transition is determined by two competing factors: on the one hand, departure from the maximum values of ψ_n^2 decreases the probability of finding a particle at a given point, and, on the other hand, ΔU and the activation energy are decreased, i.e., the probability of the transition increases. It is important to note that for the above example (the discharge of Cl^-) $s^* > 1$, and for the normal and partly for the excited levels the transition takes place for values of s^* significantly greater than the classical values of the corresponding amplitudes of vibration. In other words, even for a particle as heavy as Cl, its quantum behavior is significant and the transition is a sub-barrier transition.*

In the calculation it was assumed that the probability of the process is determined by the probability of the production of a favorable configuration of the heavy subsystem; jump-over of the electron when the optimum configuration is attained, however, takes place with a probability χ which is practically equal to unity and hence is independent of the coordinate R. If, however, this dependence is observed to any extent, it can formally be taken into account by the quantity K. For $n=0$ we obtain from Eqs. (9)-(11a)

$$W_0=\frac{1}{2\sqrt{\pi}}\exp\left[-\frac{(E_s+\Delta U_0)^2}{4E_skT}\cdot\frac{4E_skT}{4E_skT+K^2}\right], \tag{12}$$

$$\alpha=\frac{1}{2}\left(1+\frac{\Delta U_0}{E_s}\right)\frac{4E_skT}{4E_skT+K^2}. \tag{13}$$

Equation (13) becomes Eq. (6) as $K \to 0$, i.e., as $s^* \to 0$, as was assumed in the derivation of Eq. (6). The smaller value of α from Eq. (13) compared with Eq. (6) is due to the fact that with increase in ΔU_0, closer approach of the discharging particle to the electrode (closer approach of the partners in the redox reaction) becomes favorable, so that the quantity $\Delta U = \Delta U_0 - Ks^*$, which determines directly the activation energy of the process of reorganization of the solvent, increases more slowly than ΔU_0. For higher vibrational levels within the framework of the approximation corresponding to Eq. (11c) (for $n=1$ this solution is exact), we obtain

$$W_n=\frac{1}{2^n n!\sqrt{\pi}}H_n^2(s^*)e^{-s^{*2}}\exp\left[-\frac{(E_s+\Delta U_0-n\varepsilon-Ks^*)^2}{4E_skT}\right]\sqrt{\frac{s^{*2}}{2(Bs^{*2}+n)}}, \tag{14}$$

where s^* is determined by the relationships (11a)-(11c) [Eq. (12) is a particular case of Eq. (14), where the dependence of s^* on the other parameters is expressed in explicit form], and $B=(4E_SkT+K^2)/4E_SkT$.

The total probability is

$$W=\sum_0^\infty e^{-n\varepsilon/kT}W_n. \tag{15}$$

To estimate the contribution of different levels for real values of the parameters, we carried out the numerical calculation from Eqs. (14) and (15), assuming $K=5kT$ and $\varepsilon=2kT$.† For each level we restricted ourselves to the range of values of ΔU_0 in which the error introduced by the approximation (11c) did not exceed ~2-3% of W.

The results of the calculation are given in Fig. 2. In can be seen from the figure that for $\Delta U_0=0$ the chief contribution to the process is made by the zeroth and first levels, after which the second, third, etc.,

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*The estimate of K necessary for the calculation was made on the basis of the value of $dU/dR \simeq 70$-80 kcal/Å · mole, obtained from the potential curves for Cl−X bonds (where X = halogen) for elongation of the bond by ~0.8 Å [1], and the value of $a=0.04$ Å, obtained from the potential curve for KCl (it was assumed that this curve is close to U(R) for the Cl^-−electrode system), with allowance for the difference in the reduced masses. The value is $K \simeq 3$ kcal/mole = 5 kT.

†As noted above, the value K = 5 kT corresponds approximately to the discharge of the Cl^- ion. For this case we estimated $\varepsilon = kT$. This version of the calculation was also carried out by us and gave results similar to those indicated in Fig. 2. In this case, however, a reliable approximation could be obtained in a narrower range ΔU_0, so that we give as an illustration the more fully developed version $\varepsilon = 2$ kT.

levels begin to play a decisive role. For comparison, the broken line gives the results of the calculation for $n=0$ and constant $s=0$. It can be seen that when account is taken of the possibility of approach of the ion to the electrode, the probability of the transition increases considerably.

Although the curvature of the plot of $\log W_n - \Delta U_0$ for each of the levels in the range considered $\Delta U_0 = 0.6$ eV changes significantly, for the total probability curve it is practically constant and corresponds to $\alpha \simeq 0.46$, i.e., it is close to that frequently observed experimentally.* In view of the approximate nature of the calculation, this agreement can be taken as satisfactory. The fact that α is practically constant, despite the increase in ΔU_0, is related to two effects, compensating the influence of ΔU_0: the increase in the contribution from excited levels and the approach of the discharging particle to the electrode.

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*The deviations from the straight line corresponding to $\alpha = 0.46$ do not exceed ~20 mV.