KINETICS OF ELECTROCHEMICAL PROCESSES

VI. QUANTUM-MECHANICAL THEORY. ROLE OF THE INTERDEPENDENT CHARACTER OF THE MOTION OF INDIVIDUAL ATOMS IN REACTIONS IN WHICH POLYATOMIC SYSTEMS PARTICIPATE

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Chemical reactions between polyatomic reagents are examined. The problem of the participation in the formation of the transition configuration of atoms whose equilibrium positions do not change as a result of the reaction is investigated. The conditions under which the motion of these atoms in the process of transition can be disregarded are elucidated. The transition configurations of some homogeneous addition reactions and electrode reactions with transfer of solid particles in a linear complex model are calculated.

In theoretical examinations of electrochemical reactions that include a step involving adsorption of atoms on the electrode, one usually does not take into account the fact that the atoms of the electrode effect the vibrational motion, and it is supposed that they are fixed in the crystal lattice points [1]. The validity of this sort of approximation is not obvious, since the adsorbed particles, which are essentially impurities in the solid, participate in collective vibrations of the lattice atoms and, as is well known, may significantly reorganize the vibrational spectrum.

A situation of this type, in which the transition occurs in a system made up of a large number of particles, the motions of which are interdependent, is generally extremely widespread in chemical reactions. All homogeneous reactions involving transfer of heavy particles and in which polyatomic molecules participate, including polymerization, electrochemical reactions accompained by adsorption of particles on the electrode, reactions involving the dissolving and deposition of metals, etc., are processes of this type. The interdependent character of the motions of individual atoms leads to the necessity for the construction of potential energy surfaces as functions of the coordinates of a large number of particles, and this makes the calculation extremely complicated. However, in a number of cases one can attempt to simplify the picture by excluding from consideration those atoms whose equilibrium positions do not undergo changes as a result of the reaction. In the present paper, the problem of when this sort of approach is justified and in what cases the motion of the atoms whose equilibrium positions do not change as a result of the reaction should nevertheless be taken into account is investigated for several model examples. In particular, the addition of an atom to a long chain of atoms, which can be considered as the first step in modeling metal deposition and dissolving reactions (for the reverse process) and polymerization reactions, is discussed. The results obtained for this model make it possible to draw several conclusions relative to the occurrence also of other reactions in complex polyatomic systems.

1. Model with Two Degrees of Freedom

As a first example, let us consider the addition of atom (or ion) C to molecule (charged or uncharged) AB.

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$$AB+C \rightleftharpoons ABC. \quad (1)$$

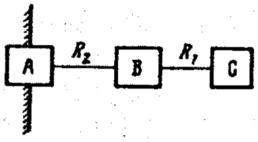

Fig. 1

It is assumed that reaction (1) proceeds in a polar solvent and that as a result of the reaction there is pronounced redistribution of the charge in the reactants and considerable reorganization of the polarization of the medium around the reactants. We will subsequently describe the solvent within the framework of the model developed in [2], according to which the potential energy of the medium in the initial and final states can be written in the form

$$U_s^i=\frac{1}{2}\sum_{\varkappa}\hbar\omega_{\varkappa}(q_{\varkappa}-q_{\varkappa 0}^i)^2;$$
$$U_s^f=\frac{1}{2}\sum_{\varkappa}\hbar\omega_{\varkappa}(q_{\varkappa}-q_{\varkappa 0}^f)^2, \quad (2)$$

where $\omega_{\varkappa}$ are the frequencies at which dielectric absorption occurs in the solvent, $q_{\varkappa}$ are the normal coordinates of the dynamic polarization of the solvent, and $q_{\varkappa 0}^{i,f}$ are the equilibrium values of the normal coordinates.

If the mass of atom A considerably exceeds the masses of atoms B and C ($m_A \gg m_B$, m_C), i.e., particle A can be assumed to be at rest during the reaction, and if we restrict ourselves to the model of a linear complex (all three particles A, B, and C lie on a single straight line during the reaction), in this case, in addition to the degree of freedom of the solvent, only two degrees of freedom of the reactants that describe the relative position of particles A and B and C will participate in the reaction (Fig. 1). Using the harmonic approximation for the description of the intramolecular vibrations, we write the potential energies of molecule AB and of molecule ABC formed in the final state in the form

$$U_{AB}=\frac{1}{2}g_2^i(R_2-R_{20}^i)+I_i;$$
$$U_{ABC}=\frac{1}{2}g_2^f(R_2-R_{20}^f)^2+\frac{1}{2}g_1^f(R_1-R_{10}^f)^2+I_f, \quad (3)$$

where g_1^f, g_2^i, and g_2^f are the force constants and R_{10}^i, R_{10}^f, and R_{20}^f are the equilibrium values of the lengths of the chemical bonds of BC and AB in the initial (i) and final (f) states, and I_i and I_f are the minimum values of the potential energy of the entire system.

To describe U_{ABC} we adopted a model in which the interaction of each atom only with its nearest neighbors is taken into account [3]. Thus the potential energies of the entire system in the initial and final states have the form

$$U^i=U_s^i+U_{AB}+U_{AB/C}; \quad U^f=U_s^f+U_{ABC}, \quad (4)$$

where $U_{AB/C}$ describes the potential energy of particle C and the energy of its interaction with molecule AB. Depending on the character of the process, term $U_{AB/C}$ may have different forms.

Case in Which Particle C is Free. Let us first consider the case in which particle C is not chemically bonded to any particles whatsoever in the solvent. In our adopted model of interaction between nearest neighbors, $U_{AB/C}$ depends only on the distance between particles B and C:

$$U_{AB/C}=U_{AB/C}(R_1). \quad (5)$$

It should be noted that because of the presence of interaction between particles B and C, their motions are not independent. It is well known that normal coordinates that are expressed in the form of several linear combinations of the coordinates of the individual atoms can be introduced into the harmonic approximation for the description of the vibrations in molecule ABC. This makes it possible to find the frequencies of the normal vibrations (ω_1^f and ω_2^f) and the wave functions. However, the introduction of normal coordinates is impossible for the initial state for an arbitrary form of potential $U_{AB/C}(R_1)$, which describes the repulsion between atoms B and C at short distances, and finding the initial wave function proves to be extremely difficult.

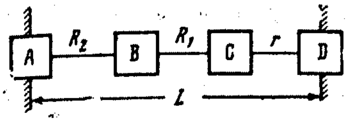

Fig. 2

a) An accurate calculation for a sufficiently arbitrary form of potential $U_{AB/C}(R_1)$ can be made when the frequencies of the normal vibrations (ω_1^f and ω_2^f) in molecule ABC, the frequency (ω^i) of the vibrations of isolated molecule AB, and potential $U_{AB/C}(R_1)$ satisfy the classical conditions

$$\hbar\omega^i,\ \hbar\omega_1^f,\ \hbar\omega_2^f \ll kT,$$
$$\left[\left(\frac{\partial U_{AB/C}}{\partial R_1}\right)^2 \cdot \hbar^2/m_C\right]^{1/3} \beta(1-\alpha) \ll 1, \quad \beta=\frac{1}{kT} \ . \tag{6}$$

As shown in [4], transition of the system from the initial state to the final state is realized in this case through the saddle point on the intersection of the initial and final potential energy surfaces. Simple calculation for the values of the normal coordinates of the solvent and the distances between the atoms in the reactants and the transition configuration gives

$$q_\kappa^* = (1-\alpha) q_{\kappa 0}^i + \alpha q_{\kappa 0}^f;$$
$$R_2^* = [(1-\alpha) g_2^i R_{20}^i + \alpha g_2^f R_{20}^f]/[(1-\alpha) g_2^i + \alpha g_2^f]. \tag{7a}$$

The R_1^* value is determined from the equation

$$(1-\alpha)\partial U_{AB/C}(R_1)/\partial R_1 + \alpha g_1^f (R_1 - R_{10}^f) = 0, \tag{7b}$$

where α is the transport coefficient.

It follows from (7a) that if, as a result of the reaction, force constant g_2 and the equilibrium value R_{20} of the A−B bond length remain unchanged ($g_2^i = g_2^f$, $R_{20}^i = R_{20}^f$), $R_2^* = R_{20}$ in the transition configuration, i.e., chemical bond A−B does not stretch during activation, and, in addition to the change in the normal coordinates of the solvent, there is approach of particle C to atom B, which is in its equilibrium position. Thus, in this case the motion of particle B during the reaction can be disregarded.†

It follows from (7b) that the larger the g_1^f value (i.e., the higher the frequency of the vibrations in molecule ABC) and the smaller the $\partial U_{AB/C}/\partial R_1$ value (i.e., the weaker the repulsion of particle C away from atom B), the closer the R_1^* and R_{10}^f values.

b) Extrapolating this result in the case in which the force constants $g_2^i = g_2^f$ and g_1^f are so large that the corresponding vibrational frequencies satisfy the quantum conditions [4]

$$\hbar\omega^i,\ \hbar\omega_1^f,\ \hbar\omega_2^f \gg kT, \tag{8}$$

but potential $U_{AB/C}(R_1)$, as before, satisfies classical conditions (6), one can assert that in this case in the normal region ($\alpha \sim 1/2$) bond A−B remains unstretched ($R_2^* = R_{20}$) in the transition configuration under the condition $R_{20}^i = R_{20}^f$, while particle C approaches atom B up to a distance that is practically equal to the equilibrium value of the length of chemical bond B−C in molecule ABC ($R_1^* \approx R_{10}^f$). In particular, this conclusion is confirmed by analytical calculation for potentials $U_{AB/C}$ that have parabolic shapes.

In all of the cases considered above, the general expression for the activation energy has the form

$$E_a = U^i(q_\kappa^*, R_1^*, R_2^*) - I_i = U_s^i(q_\kappa^*) + U_{AB/C}(R_1^*) + [U_{AB}(R_2^*) - I_i]. \tag{9a}$$

If the state of particle B does not change as a result of the reaction, i.e., $g_2^i = g_2^f$ and $R_{20}^i = R_{20}^f$, term $U_{AB}(R_2^*) - I_i$ reverts to zero, and formula (9a) takes on the form

$$E_a = U_s^i(q_\kappa^*) - U_{AB/C}(R_1^*). \tag{9b}$$

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† If $R_{20}^i = R_{20}^f$, the transition configurations and the activation energies will be identical for both $g_2^i = g_2^f$ and $g_2^i \neq g_2^f$. However, since a change in the force constant of the chemical bond affects the value of the preexponential factor, its dynamic characteristics must be taken into account in the calculation of the transition probability, even if the equilibrium length of this chemical bond does not change as a result of the reaction.

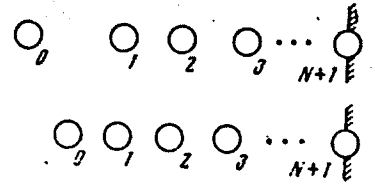

Fig. 3

c) When potential $U_{AB/C}(R_1)$ satisfies the quantum condition, one cannot perform an accurate calculation for a potential of arbitrary form. However, for a model potential of, for example, parabolic form,

$$U_{AB/C}(R_1)=\frac{g_1^i}{2}(R_1-R_{10}^i)^2. \tag{10}$$

It can be shown that in this case the motion of atom B must be taken into account, even if its equilibrium position does not change as a result of the reaction ($R_{20}^i = R_{20}^f$).

Case in Which Particle C is Bonded. If particle C in the initial state is chemically bonded to another molecule (or atom) D that has a considerably higher mass, such that it can be considered to be at rest at a certain fixed distance L from particle A during the reaction, potential $U_{AB/C}$ will depend not only on the distance R_1 between atoms B and C but also on the distance between C and D, i.e., on the degree of stretching of chemical bond C–D (Fig. 2):

$$U_{AB/C}=U^{(1)}_{AB/C}(R_1)+U^{(2)}_{AB/C}(r-r_0^i), \tag{11}$$

where r_0^i is the equilibrium value of the length of chemical bond C–D. In this case, in the final state, when bond C–D is broken and molecule ABC has been formed, yet another term $U_{CD}(r-r_0^f)$, which describes the repulsion between atoms C and D in which r_0^f is the equilibrium distance between atoms C and D in the final state, will appear in potential energy U^f in (4).

Different cases that correspond to the classical or quantum behavior of the different degrees of freedom are possible. We will restrict ourselves to an examination of only the completely classical case. Since in this case the transition is realized through the saddle point, the point of minimum energy at the intersection of the initial and final potential energy surfaces (U^i and U^f) will correspond to the transition configuration. Simple calculations with allowance for the fact that the R_1, R_2, and r values are interrelated by the expression

$$r+R_1+R_2=L, \tag{12}$$

lead to the following system of equations that determines this point:

$$\begin{gathered}(1-\alpha)g_2^i(R_2-R_{20}^i)+\alpha g_2^f(R_2-R_{20}^f)-(1-\alpha)\frac{\partial U^{(1)}_{AB/C}(R_1)}{\partial R}-\alpha g_1^f(R_1-R_{10}^f)=0,\\ (1-\alpha)g_2^i(R_2-R_{20}^i)-(1-\alpha)\frac{\partial U^{(2)}_{AB/C}(r-r_0^i)}{\partial r}+\alpha g_2^f(R_2-R_{20}^f)-\alpha\frac{\partial U_{CD}(r-r_0^f)}{\partial r}=0.\end{gathered} \tag{13}$$

As before, the $q_\varkappa^*$ values are determined by Eqs. (7a). It can be shown by investigation of this system of Eqs. (13) that even if $R_{20}^i = R_{20}^f$ and $g_2^i = g_2^f$, R_2^* is not equal to R_{20}. In this case the expression for the activation energy has the form

$$E_a=U_s^i(q_\varkappa^*)+[U_{AB}(R_2^*)-I_i]+U^{(1)}_{AB/C}(R_1^*)+U^{(2)}_{AB/C}(r^*-r_0^i). \tag{14}$$

In contrast to (9b), term $U_{AB}(R_2^*)-I_i$ now does not revert to zero and, in addition, yet another term $U^{(2)}_{AB/C}(r^*-r_0^i)$ appears. This is due to the fact that the approach of particle C to atom B when the position of atom B is fixed proves to be "disadvantageous," since too high an energy is required for this because of the attraction of particle C to molecule D. It proves to be "more favorable" to the system if a certain shift of atom B toward particle C occurs during activation and the stretching of chemical bond C–D is not too great. Thus in this case also it proves to be necessary to take into account the motion of particle B during the reaction.

2. Model with Many Degrees of Freedom. Linear Chain of Atoms

As a second example, let us examine the addition of an ion to a linear chain of atoms in a polar solvent (Fig. 3). Both homogeneous reactions and heterogeneous processes – polymerization, deposition or dissolving (for the reverse reaction) of metals, and adsorption – can be modeled to a rough approximation by this process. Since the result for a sufficiently long chain should not depend on the conditions at its opposite end, for simplicity we will assume that this end of the chain is fixed, i.e., shift x_{N+1} of the atom of the chain with number N+ 1 is zero at all times.

In the nearest-neighbor approximation, the potential energy of the atoms in the initial (U_i^L) and final (U_f^L) states can be written in the form [3]

$$U_i^L=\sum_{l=3}^{N+1}\frac{g_l^i}{2}(x_l^i-x_{l-1}^i)^2;\quad U_f^L=\sum_{l=2}^{N+1}\frac{g_l^f}{2}(x_l^f-x_{l-1}^f)^2;\ x_{N+1}^i=x_{N+1}^f=0, \tag{15}$$

where g_l^i and g_l^f are the force constants, and x_l^i and x_l^f are the shifts of the l-th atom from the initial and final equilibrium positions. Shifts x_l^i and x_l^f are interrelated by the expression

$$x_l^i+\sum_{k=l}^{N}a_k^i=x_l^f+\sum_{k=l}^{N}a_k^f, \tag{16}$$

where a_k^i and a_k^f are the equilibrium distances between the k-th and (k = 1)-th atoms in the initial and final states. The final state differs from the initial state in that atom C adds to the chain and the number of atoms in it increases by one. Summation in the first summation in (15) therefore is performed from $l = 3$, while the summation in the second is performed from $l = 2$.

The potential energy of the entire system in the initial and final states has the form:

$$U^i=U_s^i+U_i^L+U_{LC}+I_i;\quad U^f=U_s^f+U_f^L+I_f, \tag{17}$$

where U_{LC} is the potential energy of particle C with allowance for its interaction with the last atom of the chain. As in the case of the model with two degrees of freedom, two fundamental cases can be considered.

1) Case in Which Particle C is Free. Let us consider the case in which potential U_{LC}, just as in relation (5), depends only on the distance between particle C and the last atom of the chain, i.e., it depends only on the difference $R_1 = x_2^i-x_1^i$:

$$U_{LC}=U_{LC}(x_2^i-x_1^i). \tag{18}$$

a) If all of the frequencies of the normal vibrations of the chain in the initial and final states and potential U_{LC} satisfy the classical conditions of the (6) type, it is not difficult to show that one must take into account the motion of only those atoms (usually found near the end of the chain) whose position (and corresponding force constants) changes as a result of the reaction, while the remaining atoms can be assumed to be fixed in their equilibrium positions, since their shifts to the transition configuration prove to be equal to zero ($x_k^* = 0$).

For those atoms whose position changes, their shifts to the transition configuration are determined by the system of equations

$$(1-\alpha)g_l^i(x_l^i-x_{l-1}^i)+\alpha g_l^f(x_l^f-x_{l-1}^f)=0,\quad l\geqslant 3.$$

In particular, if the parameters of the chain (force constants and equilibrium distances between the atoms) do not change as a result of the reaction, the vibrations of the atoms of the chain during the reaction can generally be disregarded. In the transition configuration all of the atoms of the chain will be found in their equilibrium positions ($x_k^* = 0$), while atom C will occupy a certain intermediate position (between the initial and final), and the x_1^* value in the transition configuration will be determined by an equation similar to (7b):

$$(1-\alpha)\frac{\partial U_{LC}}{\partial r}+\alpha g_2x_1=0. \tag{19}$$

It is seen from (19) that the larger the force constant (g_2) in the chain and the weaker the repulsion of atom C away from the chain, the lower the x_1^* value.

b) Extrapolating this result to the case in which the force constants are so large that there are both classical and quantum frequencies in the vibrational spectrum of the chain and the parameters of the chain do not change as a result of the reaction, it can be asserted that in this case also the shifts of all of the atoms of the chain from equilibrium positions x_k* in the transition configuration are equal to zero, while atom C is found in a position that practically coincides with its equilibrium position in the chain in the final state, i.e., $x_1* \cong 0$.

The general expression for the activation energy of the process under consideration has the form

$$E_a = U_s^i(q_\varkappa^*) + U_i^L(x_k^{i*}) + U_{LC}(x_2^{i*} - x_1^{i*}). \tag{20}$$

When the chain parameters do not change, this expression is simplified and becomes similar to (9b):

$$E_a = U_s^i(q_\varkappa^*) + U_{LC}(-x_1^*). \tag{21}$$

Thus activation is realized here through the dipoles of the medium and through approach of atom C to the end of the chain. The vibrations of the chain do not participate in the activation process.

2) Case In Which Particle C is Bonded. If particle C is bonded to a certain atom (or molecule) D of sufficiently great mass, such that it can be considered to be stationary during the reaction, potential U_{LC} will depend both on the distance between atom C and the end of the chain $(x_2^i - x_1^i)$ and on the distance r between C and D [compare this with Eq. (11)]:

$$U_{LC} = U_{LC}^{(1)}(x_2^i - x_1^i) + U_{LC}^{(2)}(x_1^i); \quad x_1^i = r - r_0^i. \tag{22}$$

In addition, term $U_{CD}(r - r_0^f)$, which describes the repulsion of particle C (bonded to the chain of atoms) away from atom D, will appear in the potential energy of the final state.

Calculation shows that in this situation, in contrast to the preceding case, the approach of particle C to the end of the chain when the position of the atoms of the chain is fixed proves to be unfavorable, since the potential energy of the system in this case increases markedly because of the attraction of particle C to atom D. As a result, in the transition configuration, the x_k* values prove to be other than zero, and this indicates motion of the atoms of the chain toward atom C during activation.

However, in the case of a sufficiently long chain of atoms, the parameters of which do not change as a result of the reaction, the situation proves to be substantially different from that which occurred for the addition to a small molecule [see (13)-(14)]. Although in this case the distances between the atoms of the chain approaches the C atom by a certain distance, the magnitude of this distance, i.e., $x_2^{i*} - x_1^{i*}$, and the position of particle C relative to atom D, i.e., x_1^{i*}, are determined only by the potentials of repulsion of atom C away from the end of the chain and away from atom D (U_{LC}^1 and U_{CD}) and also by the potentials of the attraction to the D atom and to the atom situated at the end of the chain [$U_{LC}^{(2)}$ and $1/2\, g_2^f (x_2^f - x_1^f)^2$]. It should be noted that in contrast to (13), the parameters of the starting chain, i.e., terms of the $g_2(R_2 - R_{20})$ type [see (13)], do not enter into the equations that determine the $x_2^{i*} - x_1^{i*}$ and x_1^{i*} values. This result is due to the fact that an increase in the distance between the atoms of the chains $(x_l^{i*} - x_{l-1}^{i*})$ is of the order of $\sim 1/N$, where N is the number of atoms in the chain. Therefore, when there are a sufficiently large number of atoms $(N \to \infty)$, the eigenenergy of the chain in the transition configuration is zero:

$$U_i^L(x_k^{i*}) \sim \sum_l^{N+1} \frac{g_l^i}{2}(x_l^{i*} - x_{l-1}^{i*})^2 \sim \frac{g_i}{2} N \cdot \frac{1}{N^2} \sim \frac{1}{N} \to 0. \tag{23}$$

Thus, in this case the behavior of the atom at the end of the original chain is similar to the behavior of the free atom, and the transition configuration is therefore determined only by interactions between this atom and particle C and between particle C and atom D, and the expression for the activation energy has the form

$$E_a = U_s^i(q_\varkappa^*) + U_{LC}^{(1)}(x_2^{i*} - x_1^{i*}) + U_{LC}^{(2)}(x_1^{i*}). \tag{24}$$

It should be noted that, in contrast to (14), the term $U_i^L(x_k^{i*})$, which in this case would be similar in meaning to the $[U_{AB}(R_2^*) - I_i]$ term in relation (14), does not enter into relation (24). This is due to the fact that when the chain of atoms is sufficiently long, an increase in the chain length by a magnitude of the order of the interatomic distances requires almost no expenditure of energy. This result is valid for both a chain with a purely classical spectrum of vibrations and for a chain in which both classical and quantum vibrations are present. Since the indicated stretching of the chain is realized through motion along the classical degrees of freedom, it is necessary only that the chain be sufficiently long and that it contain the number of classical vibrations that are necessary for this sort of stretching.

In conclusion, we present the result for the case in which the repulsion between atoms C and D in the final state [$U_{CD}(r-r_0^f)$] can be disregarded. It then turns out that the C–D bond in the transition configuration is practically undeformed ($r^*-r_0^i = x_1^{i*} \approx 0$) and atom C can be considered to be fixed in its initial equilibrium position. The distance between atom C and the end of the chain in the transition configuration ($x_2^{i*}-x_1^{i*}$) is determined by an equation similar to (19):

$$(1-\alpha)\frac{\partial U_{LC}^{(1)}(x_2^i-x_1^i)}{\partial(x_2^i-x_1^i)}+\alpha g_2(x_2^i-x_1^i)=0; \quad x_1^{i*}\approx 0, \tag{25}$$

and the term $U_{LC}^{(2)}(x_1^{i*})$ is absent in Eq. (24) for the activation energy.

The general conclusion flowing out of the examination above consists in the fact that in the general case even those atoms whose equilibrium positions are not changed as a result of the reaction participate in the formation of the transition configuration in reactions involving the participation of polyatomic systems. However, the motion of these atoms during the reaction can be disregarded for some types of processes, particularly the deposition and dissolving of metals, adsorption of atoms on the electrode, and some homogeneous addition reactions.

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