ON THE THEORY OF SIMPLE SUBSTITUTION REACTIONS IN THE LIQUID PHASE

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In studying the kinetics of the elementary act of homogeneous and heterogeneous reactions of the type

$$AB + C \rightleftarrows A + BC; \quad AB^z + e \rightleftarrows A^{z-1} + B_{ads} \tag{1}$$

Dogonadze et al. [1] assumed that the transfer of the particle B takes place between stationary reagents A and C (or A and the electrode) which are at a defined distance from each other in a given reaction volume. In this paper the reactions of type (1) will be used to investigate the effect of the relative motions of the reagents A and C within the reaction zone on the transfer probability in unit time W_{if}. We will use the simplest "linear collision" model in which all the three particles move along one straight line. Let us assume that the particle B in the molecules AB and BC represents a harmonic oscillator with constant frequencies ω_{AB} and ω_{BC}, respectively ($\gg kT/\hbar$) whose values are independent of the distance between the particles A and C. Thus, the corresponding potential energies may be written in the form

$$U_{AB} = {}^1/_2\mu_{AB}\omega_{AB}^2 (r_{AB} - r_{AB}^0)^2 + J_{AB}; \quad U_{BC} = {}^1/_2\mu_{BC}\omega_{BC}^2 (r_{BC} - r_{BC}^0)^2 + J_{BC}, \tag{2}$$

where $\mu_{AB} = m_A m_B/(m_A + m_B)$, $\mu_{BC} = m_B m_C/(m_B + m_C)$ are the reduced masses, $r_{AB} = r_A - r_B$, $r_{BC} = r_B - r_C$; r_{AB}^0 and r_{BC}^0 are the equilibrium lengths of the chemical bonds A–B and B–C, respectively, and J_{AB} and J_{BC} are the corresponding energies at the minimum points.

As far as the potential energy describing the interaction between the reagents, U_i (or the products, U_f), as a whole is concerned, we shall adopt a model based on the following qualitative assumptions. When the distance between the reagents is small and $R_i \equiv R_{AB} - r_C$ (where R_{AB} represents the coordinate of the center of gravity of the molecule AB) becomes smaller than a fixed quantity R_{0i}, a repulsion develops which increases with decreasing value of R_i. An increase of R_i into the $R_i > R_{0i}$ region can also lead to an increase of the potential energy U_i both because of the repulsion between the reagent molecules and the solvent and because of the attraction between the molecules of reagents at a larger distance from each other. However, this part of the potential curve does not play any significant role, in particular, for the obtaining of qualitative results.

The general formula for W_{if} [2] may be approximated in the form

$$W_{if} \simeq B \int_{c-i\infty}^{c+i\infty} d\theta \int dR_i dr_{AB} \left(\prod_k dq_k\right) \left[\int \rho_\nu dE_\nu e^{-\beta(1-\theta)E_\nu} \{\Phi_\nu^i(R_i)\}^2\right]$$
$$\times \left[\int \rho_{\nu'} dE_{\nu'} e^{-\beta\theta E_{\nu'}} \{\Phi_{\nu'}^f(R_f)\}^2\right] \exp\left\{\beta\theta\Delta J_{if} - \left[\frac{\mu_{AB}\omega_{AB}}{\hbar}(r_{AB} - r_{AB}^0)^2 \right.\right.$$
$$\times \operatorname{th}\frac{\beta(1-\theta)\hbar\omega_{AB}}{2} + \frac{\mu_{BC}\omega_{BC}}{\hbar}(r_{BC} - r_{BC}^0)^2 \operatorname{th}\frac{\beta\theta\hbar\omega_{BC}}{2}\Big]$$
$$\left. - \sum_k \left[(q_k - q_{k0}^i)^2 \operatorname{th}\frac{\beta(1-\theta)\hbar\omega_k}{2} + (q_k - q_{k0}^f)^2 \operatorname{th}\frac{\beta\theta\hbar\omega_k}{2}\right]\right\},$$

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where $\Phi_{v(v')}^{i(f)}(R)$ are the wave functions describing the relative motions of reagents (products); $\beta = 1/kT$; $R_f = r_A - R_{BC}$; ω_k, q_{k0}^i, and q_{k0}^f are the frequencies and equilibrium values of the normal coordinates of the solvent q_k corresponding to a mean value of the polarization of the medium in the initial and the final states; and B is a constant comprising a number of pre-exponential factors. The quantities in brackets are proportional to the mean Gibbs probabilities $f_i(R_i)$ and $f_f(R_f)$ (with effective temperatures $T_{eff}^i = T/(1-\theta)$ and $T_{eff}^f = T/\theta$) expressing the probability of finding the reagents and the reaction products at distances R_i and R_f from each other, respectively.

The main contribution in the integral (3) is made by a small region in the vicinity of the transition point $\{\theta^*, R_i^*, r_{AB}^*, q_k^*\}$ whose position determines the configuration of the system in its transition state. The criteria for the classical and quantum-mechanical behavior of the vibrational intramolecular degrees of freedom during a reaction were obtained in [1, 2]. The nature of the behavior of the degrees of freedom corresponding to the relative motions of the reagents (products) is determined by the form of the expressions for $f_i(R_i)$ and $f_f(R_f)$ in the transition point R_i^*, R_f^*. For the sake of simplicity, let us assume that the process occurs in the normal region [1, 2], i.e., $\theta^* \equiv \alpha$ is not close to 0 or 1.

1. If the conditions given below are satisfied within the entire regions

$$\beta(1-\alpha)(\hbar^2 F_i^2(R_i)/\mu_i)^{1/3} \ll 1, \quad \beta\alpha(\hbar^2 F_f^2(R_f)/\mu_f)^{1/3} \ll 1, \tag{4}$$

(where $F_{i(f)} = dU_{i(f)}/dR_{i(f)}$ and μ_i and μ_f are the reduced masses of the reagents and of the products, respectively), then one can use the classical formulas for $f_i(R_i)$ and $f_f(R_f)$

$$f_i(R_i) \sim \exp[-\beta(1-\theta)U_i(R_i)], \quad f_f(R_f) \sim \exp[-\beta\theta U_f(R_f)]. \tag{5}$$

Thus for W_{if} one obtains the expression $W_{if} = A\exp(-\beta E_a - \sigma)$, where the energy of activation E_a and the tunneling factor σ [2] are given as

$$E_a = U_i(R_i^*) + [E_s - \Delta J_{if} - U_i(R_i^*) + U_f(R_f^*)]^2/4E_s, \tag{6}$$

$$\sigma = \mu_{AB}\omega_{AB}(r_{AB}^* - r_{AB}^0)^2/\hbar + \mu_{BC}\omega_{BC}(r_{BC}^* - r_{BC}^0)^2/\hbar, \tag{7}$$

where E_s is the energy of reorganization of the solvent [1].

If, along with (4), the following conditions also apply

$$\beta(1-\theta^*)\,dU_i/dR_i, \quad \beta\theta^*\,dU_f/dR_f \ll 2\mu_{AB}\omega_{AB}r_{AB}^0/\hbar, \quad 2\mu_{BC}\omega_{BC}r_{BC}^0/\hbar, \tag{8}$$

then the configuration of the reagents in the transition state is determined by

$$r_{AB}^* \simeq r_{AB}^0; \quad r_{BC}^* \simeq r_{BC}^0; \quad R_i^* \simeq \tilde{R}_i; \quad R_f^* \simeq \tilde{R}_f. \tag{9}$$

The value of σ reaches zero. This result corresponds to the following qualitative interpretation of the transfer. The reagents A and C approach each other in such a manner that the distances between the particle B and A or C equal the corresponding equilibrium lengths of the chemical bonds A–B and B–C, respectively. As a result of fluctuation in the solvation cosphere, the coordinates describing the state of the medium have the values $\{q_k^*\}$ corresponding to the transition configuration. This configuration corresponds to the rupture of the A–B bond and to the formation of the B–C bond. The first term in (6) is related to the relative motion of the reagents and the second term takes into account the reorganization of the solvation cosphere.

When the repulsion between the reagents becomes stronger for $R_{i(f)} < \tilde{R}_{i(f)}$ so that the conditions of (8) are not satisfied but the inequalities (4) still hold, the values of the coordinates r_{AB}^*, r_{BC}^*, R_i^*, and R_f^* are higher than the values given by (9) and have to be found from the equations

$$\beta(1-\theta)\frac{dU_i}{dR_i}\frac{m_A}{m_A+m_B} + \beta\theta\frac{dU_f}{dR_f} + \frac{2\mu_{AB}\omega_{AB}}{\hbar}(r_{AB} - r_{AB}^0) = 0,$$

$$\beta(1-\theta)\frac{dU_i}{dR_i} + \beta\theta\frac{dU_f}{dR_f}\frac{m_C}{m_C+m_B} + \frac{2\mu_{BC}\omega_{BC}}{\hbar}(r_{BC} - r_{BC}^0) = 0. \tag{10}$$

In this case, the transfer occurs as follows. By means of classical motion, the reagents approach each other until their distance is R_i^*. The distance between the particles A and C is higher than the sum of the equilibrium lengths

of chemical bonds $r_{AB}^0 + r_{BC}^0$. In this situation and at the corresponding configuration of the solvation cosphere, a quantum–mechanical rearrangement of the reagents results in the rupture of the A–B bond and the formation of the B–C bond. The tunneling factor is different from zero and is determined by Eq. (7). Equation (6) holds for E_a, R_i^* and R_f^* being given by (10).

2. When the coordinate values R_i^* and R_f^* determined from (10) are in the region where the potentials U_i and U_f are so steep that conditions (4) are not satisfied. Eqs. (5) for $f_i(R_i)$ and $f_f(R_f)$ are not applicable. In general, an exact calculation of the $f_i(R_i)$ and $f_f(R_f)$ values for any given values of the potentials U_i and U_f is not possible. However, below we shall discuss a certain group of potentials for which a general solution giving qualitative results is possible.

Let the potentials U_i and U_f slowly [in terms of satisfying conditions (4) and (8)] change up to a certain point $\hat{R}_i > \bar{R}_i$, $\hat{R}_f > \bar{R}_f$ beyond which a steep increase of the potential occurs so that conditions (4) and (8) at $R_i < \hat{R}_i$ and $R_f < \hat{R}_f$ are not satisfied. Let us further assume that the energy interval for the transition between the first and the second region of the potential change is $\delta E \lesssim kT$ and that R_i^* and R_f^* are in a region where a quasi-classical approximation is applicable. Then, for the region $R_i < \hat{R}_i$ and $R_f < \hat{R}_f$ the following expressions may be used for $f_i(R_i)$ and $f_f(R_f)$:

$$f_{i(f)} \sim \exp\left[-U_{i(f)}(\hat{R}_{i(f)})/kT_{\text{eff}}^{i(f)}\right] \exp\left[-\frac{2}{\hbar}\int_{R_{i(f)}}^{\hat{R}_{i(f)}} \sqrt{2\mu_{i(f)}\left[U_{i(f)}(R) - U_{i(f)}(\hat{R}_{i(f)})\right]}\, dR\right]. \tag{11}$$

At the same time, E_a is still expressed by (6) with the substitution $R_i^* \to R_i$ and $R_f^* \to R_f$; however, the formula for σ changes and has the form

$$\sigma = \frac{\mu_{AB}\omega_{AB}}{\hbar}(r_{AB}^* - r_{AB}^0)^2 + \frac{\mu_{BC}\omega_{BC}}{\hbar}(r_{BC}^* - r_{BC}^0)^2 + \frac{2}{\hbar}\int_{R_i^*}^{\hat{R}_i} \sqrt{2\mu_i\left[U_i(R) - U_i(\hat{R}_i)\right]}\, dR + \frac{2}{\hbar}\int_{R_f^*}^{\hat{R}_f} \sqrt{2\mu_f\left[U_f(R) - U_f(\hat{R}_f)\right]}\, dR, \tag{12}$$

where r_{AB}^*, r_{BC}^*, R_i^*, and R_f^* are determined from the condition that the value of σ has to be at the minimum. As previously, the first two terms in (12) correspond to the exponential character of overlap between the wave functions of fundamental vibrational states of molecules AB and BC and the last two terms correspond to the penetration of the reagents as a whole into the region inaccessible for classical mechanics. In this case, the approaching of the reagents by means of classical motion occurs up to the distance $\hat{R}_i$ only.

The equation for the determination of $\{q_k^*\}$ and the transmission coefficient $\alpha = \theta^*$ are identical in both cases and have the form

$$\Delta J_{if} = U_f(R_f) - U_i(R_i) + \sum_k \left\{\frac{1}{2}\hbar\omega_k (q_k - q_{k0}^f)^2 - \frac{1}{2}\hbar\omega_k (q_k - q_{k0}^i)^2\right\}, \tag{13}$$

$$(1-\theta)(q_k - q_{k0}^i) + \theta(q_k - q_{k0}^f) = 0.$$

Similarly, one can discuss intermediate cases where conditions (4) are satisfied only for one of the potentials (U_i or U_f), as well as the barrierless ($\alpha \sim 1$) and activationless ($\alpha \sim 0$) regions.

It follows from this study that, in a general case, the nature of the behavior of a degree of freedom during the reaction is determined by the form of the expression for the diagonal elements of the corresponding density matrix $f(R)$ within the space important for the transfer. In the case of potentials for which the first derivative with respect to the coordinate R is a monotonic function of R, the criteria determining the classical or quantum–mechanical behavior are the conditions of the Eq. (4). It is difficult to derive general expressions describing the criteria for potentials given in a more complex form. It is easier to obtain the latter separately in each actual case by means of an approximate determination of the partition function of $f(R)$ in the desired coordinate region.

LITERATURE CITED

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