ATOM – MOLECULE CONVERSIONS IN THE CONDENSED PHASE AT LOW TEMPERATURES

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Within the framework of the general quantum-mechanical theory of the kinetics of chemical reactions in a condensed phase [2], Vorotyntsev et al. [1] gave a calculation of the probability of an elementary act of chemical reaction for the low-temperature limit $T \to 0$. In the present paper a calculation will be made for analogous processes at low but non-zero temperatures satisfying the condition $kT \ll \hbar\Omega^{(m)}$, where $\Omega^{(m)}$ is the characteristic frequency of the oscillators in the medium. Both the temperature dependence W of the transition probability and the dependence of W on the free energy ΔF of the reaction will be investigated. Similarly to [1], it will be assumed that the reaction is kinetically controlled, i.e., that during a single "collision" of the reactants the probability of their conversion into products is small. This condition is especially important with processes taking place in solids, in which the diffusion coefficient is usually very small and the majority of processes are diffusionally controlled. Moreover, as previously in [1], we shall assume that the bond between the reacting species and the medium is a strong one, as is the case for example in reactions proceeding in a polar medium and accompanied by a large redistribution of charge. For definiteness, only exothermic processes ($\Delta F < 0$) are examined in what follows. In the case of an endothermic reaction an expression for W may be obtained by utilizing the expression $W_{if} = W_{fi} \exp(-\Delta F/kT)$, which ensues from the principle of microscopic reversibility for the forward (W_{if}) and the reverse (W_{fi}) processes.

The calculation of the transition probability W is performed within the framework of the general method [2] (see equation (1) of [1]), according to which the probability of an elementary act of reaction can be represented in the form [3]

$$W = \text{const} \cdot \Phi_i(Q^*, T/(1-\theta^*))\,\Phi_f(Q^*, T/\theta^*), \tag{1}$$

where Φ_i (or Φ_f) is a quantum-statistical function of the distribution according to the coordinates for the intramolecular degrees of freedom of the reactants (products) and the degree of freedom of the medium for the initial (final) state in the transitional configuration Q^* at an effective temperature of $T/(1-\theta^*)(T/\theta^*)$. The quantity θ^* has the meaning of a symmetry factor in the Brønsted relation

$$\theta^* = -d \ln W/\beta d\Delta F, \quad \beta = 1/kT. \tag{2}$$

Depending on the effective temperature for Φ_i and Φ_f, in (1) either a classical approximation (at high temperatures) or a quantum approximation (at low temperatures) can be used. The critical temperature (T_c), above which the classical Boltzmann distribution function can be used and below which the square of the modulus of the wave function of the ground state can be used as the distribution function, depends in general on the form of the potential energy curve of the system being considered [2]. In particular, in the harmonic approximation, for most cases that are of practical interest, T_c for any degree of freedom is mainly determined by the condition $2kT_c = \hbar\omega$, where ω is the vibration frequency for this degree of freedom. Corresponding to this, a series of limiting cases is possible: 1) If $\omega < 2/\beta\hbar(1-\theta^*) \equiv \Omega_c$, then the classical approximation can be used for Φ_i and Φ_f for the given oscillator (here we have taken into account that for exothermic processes within the framework of the model being considered [1] $\theta^* < 1/2$ and the condition $\theta^* < 2/\beta\hbar\theta^*$ is satisfied automatically); 2) with $\omega > 2/\beta\hbar\theta^* \equiv \Omega_q$ the behavior of the given oscillator will be quantized, i.e., along this degree of freedom the transition will proceed from an initial ground

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state to a final ground state; 3) finally, with $\Omega_c < \omega < \Omega_q$ a quantum approximation for Φ_i must be used, but a classical one for Φ_f. This means that in the initial state the oscillator was in the ground vibrational level, while in the final state it is at a highly excited vibrational level. Thus in accordance with the type of behavior of the various degrees of freedom during the reaction, all the degrees of freedom in the system (both the intramolecular ones and also the effective oscillators of the medium [1, 2]) can be divided into three groups: 1) purely classical ($\omega < \Omega_c$), 2) purely quantized ($\omega > \Omega_q$), and 3) "mixed" ($\Omega_c < \omega < \Omega_q$).

We shall begin the analysis of the kinetic parameters with an investigation of the dependence of the symmetry factor θ^* on T and ΔF. For a qualitative discussion the general inferences of the quantum theory of chemical reactions can be utilized [2, 4]. According to [2, 4], when ΔF varies from 0 (symmetrical reactions) to $-E_r$ (strongly exothermic reactions; E_r is the total reorganization energy of the system [2]) the symmetry factor θ^* decreases monotonically from $1/2$ to 0. Let us first examine the normal region [2] where θ^* is close to $1/2$. Here $\Omega_c \simeq \Omega_q = 4/\beta\hbar$, i.e., the mixed subgroup is virtually absent and all the degrees of freedom can be separated only into the classical and the quantized types. If it is assumed throughout from now on that the condition $\Omega^{(i)} > 4/\beta\hbar$ is fulfilled for the intramolecular degrees of freedom, i.e., that they are quantized in the normal region, we infer that only the low-frequency modes of the effective oscillators of the medium are related to the classical subsystem ($\omega < 4\beta\hbar$). Since all the quantized degrees of freedom ($\omega > 4\beta\hbar$) perform a transition from the ground level of the initial state to the ground level of the final state, all the free energy ΔF of the reaction is consumed in excitation of the classical degrees of freedom. Hence the equation [2] $\theta^* \simeq 1/2 + |\Delta F|/2E_r^c$ ($|\Delta F| < E_r^c$) is valid for θ^*, E_r^c being the reorganization energy of only the classical degrees of freedom of the medium [2], which energy can be represented in the form of the product of a factor determining the change in the field generated by the reactants during the reaction and a factor having the meaning of the strength of the oscillators in the medium. The first factor is completely determined by the intramolecular properties of the reactants, while the second one is determined within the scope of a linear model by the properties of the medium and is proportional to Im $G(\mathbf{k}, \omega)/\omega$, where $G(\mathbf{k}, \omega)$ is the Green's retarding function of the field operators of the medium. For example, as regards the electrostatic interaction of the reactants with the medium $G(\mathbf{k}, \omega)$ is connected with the complex dielectric constant: $\varepsilon(\mathbf{k}, \omega) = [1 - 4\pi G \cdot (\mathbf{k}, \omega)]^{-1}$. At low temperatures E_r^c is proportional to Im $G(\mathbf{k}, \omega)/\omega|_{\omega=0} \cdot 4kT/\hbar$, i.e., it depends approximately linearly on the temperature. Thus the width of the normal region, equal to E_r^c, must depend substantially on the behavior of Im $G(\mathbf{k}, \omega)$ in the low-frequency region. In particular, if Im $G(\mathbf{k}, \omega) = 0$ with $\omega < \Omega_q \neq 0$, then with $\beta > 4/\hbar\Omega_q$ the normal region will be practically absent.

Let us now consider the unactivated region [2, 4] ($|\Delta F| > E_r^c$), in which θ^* is close to zero. Here $\Omega_c \ll \Omega_q$, and it is necessary to examine separately the purely classical, the mixed, and the purely quantized subsystems. In the unactivated region the activation energy over the classical degrees of freedom is equal to zero. The oscillators of the mixed subgroup execute a transition from the initial ground state to the final excited state the energy of which equals the energy of reorganization along a given degree of freedom. Finally, the quantized subgroup executes a transition from the initial ground state to the final ground state.

A calculation gives the following expression for the symmetry factor with $|\Delta F| \ll E_r^{(m)}$ ($E_r^{(m)}$ is the reorganization energy of the medium):

$$\theta^* = [\operatorname{arctg}(\pi\lambda/\beta|\Delta F|)]/\pi; \quad \lambda = (\pi\hbar)^{-1} \sum_{\mathbf{k}} |\Delta F_{\mathbf{k}}| d \operatorname{Im} G(\mathbf{k}, \omega)/d\omega|_{\omega=0}, \tag{3}$$

which is valid both in the normal region ($\beta|\Delta F| < \pi\lambda$) and in part of the unactivated region ($\beta|\Delta F| > \pi\lambda$). Here $\Delta F_{\mathbf{k}}$ is the difference between the Fourier forms of the field generated by the reactants and products in the medium [1], λ is a dimensionless parameter characterizing the reorganization of the medium in the course of the reaction. In particular, with a resonance approximation of the frequency spectrum [2] at a characteristic frequency Ω_R and resonance width Γ in the long-wave approximation ($k \to 0$), $\lambda = 2\Gamma E_r^{(m)}/\pi\hbar^2\Omega_R^2$. Equation (3) is also valid when there are intramolecular degrees of freedom, if a number of relations between ΔF, $E_r^{(m)}$, the reorganization energy $E_r^{(i)}$, and the Ω_i are satisfied for the intramolecular degree of freedom. An expression for θ^* in a highly deactivated region is given by Eq. (12) of [1].

Low-temperature reactions possess a number of peculiar features as compared with high-temperature reactions both in the condensed and in the gas phase. We note first of all that although in the normal region an activation of the group of low-frequency oscillators in the medium occurs, experimentally the Arrhenius temperature dependence of the rate constant may be masked owing to a temperature dependence of the number of classical oscillators. Because of this the value of βE_a may in general prove to be independent of T and the entire dependence on T will be determined by the temperature variation of the tunnelling factor σ. Moreover, even in the normal region

the symmetry factor θ^* does not fully reflect the dependence of the activation energy E_a on ΔF because of a considerable dependence of σ on ΔF, whereas in the unactivated region $\theta^* \to 0$ at $T \to 0$. Hence in the unactivated region the dependence of ln W on ΔF is chiefly determined by the quantity $d\sigma/d\Delta F \approx \beta\theta^*$, which according to (3) is equal to $\lambda/|\Delta F|$ and does not depend on T when $T \to 0$.

Calculation of the transition probabilities gives expressions with a concrete form which depend on the form of absorption spectrum of the medium (Debye spectrum, resonance spectrum, etc.). In particular, in the case of the resonance approximation for $G(0, \omega)$ the expressions for W in the normal and unactivated regions have the form

$$W \simeq \frac{\beta L^2}{\hbar}\left(\frac{\hbar^2\Omega_R^2}{2\Gamma E^{(m)}}\right)^{1/2}\left(\frac{\pi}{\gamma\beta\hbar\Omega_R}\right)^{4\Gamma E_r^{(m)}/\pi\hbar^2\Omega_R^2}\exp\left\{\frac{\beta|\Delta F|}{2}-\frac{F_r^{(m)}}{\hbar\Omega_R}\right\}, \tag{4}$$

$$|\Delta F| < 16\Gamma E_r^{(m)}/\pi\beta\hbar^2\Omega_R^2;$$

$$W \simeq \frac{2L^2}{\hbar|\Delta F|}\left(\frac{2\Gamma E_r}{\hbar^2\Omega_R^2}\right)^{1/2}\left(\frac{\pi e\hbar\Omega_R|\Delta F|}{4\gamma\Gamma E_r^{(m)}}\right)^{4\Gamma E_r/\pi\hbar^2\Omega_R^2}\exp(-E_r^{(m)}/\hbar\Omega_R), \tag{5}$$

$$16\Gamma E_r^{(m)}/\pi\beta\hbar^2\Omega_R^2 < |\Delta F| \ll E_r^{(m)},$$

where $\ln\gamma \simeq 0.57$.

As follows from (4), when $\Delta F = 0$ W depends exponentially on T and tends to zero when $T \to 0$. In general the nature of the dependence of W on T is essentially determined by the behavior of Im $G(\mathbf{k}, \omega)/\omega$ when $\omega \to 0$. If this quantity remains finite as $\omega \to 0$, then with $\Delta F = 0$ and $T \to 0$ W is reduced to zero. If when $\omega \to 0$ Im $G(\mathbf{k}, \omega)/\omega$ tends to zero according to some exponential law, then W will remain finite. In that case when $T = 0$ W as a function of ΔF will undergo a sudden change at $\Delta F = 0$.

Equations of the type of (4), (5) can also be readily generalized to include the case of intramolecular degrees of freedom with defined relations between the system parameters. Expressions for W in the region of strongly exothermic processes ($|\Delta F| \sim E_r$) are presented in [1].

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