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Abstract

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BIMOLECULAR PREASSOCIATION OF POLYATOMIC MOLECULES

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Processes of the type of spontaneous preassociation are apparently widespread and play an important role in the kinetics of reactions of complex molecules. This is connected with the fact that, for molecules with a number of atoms greater than two, there is a finite probability of formation of a complex arising in a process of the preassociation type. At the first moment after the elementary act the molecule is at a quasistationary level of the vibrational spectrum, characterizing the dynamic behavior of the bond that is breaking as a result of predissociation (or being formed during preassociation). This bond interacts with the other bonds in the molecule, which leads to intramolecular redistribution of energy. In the harmonic approximation, intramolecular energy exchange is described by introducing delocalized normal coordinates. Finally, the influence of anharmonicity reduces to redistribution of energy among normal vibrations. If the characteristic lifetime of the quasistationary level with respect to intramolecular energy redistribution, τ_0, is small in comparison with the time of energy exchange between normal vibrations, τ_{anh}, then the formation and decay of the complex can be characterized by two constants—the probability P of formation of a quasimolecule, the distribution of energy among the bonds in which would differ substantially from the initial δ-shaped distribution, and the lifetime τ with respect to spontaneous decay. It is essential here that, for $\tau_0 \ll \tau_{\text{anh}}$, the quantities P and τ are determined primarily by the harmonic and anharmonic parts of the intramolecular potential. It is precisely this circumstance that makes it possible to apply statistical theory to the calculation of τ (see, for example, ([1])).

The temperature dependence of the rates of processes of the type of reverse spontaneous dissociation (the temperature of translational motion is meant) was considered by V. I. Goldanskii ([2]). The parameters σ_i entering into the formulas of that work, having the meaning of cross sections of various processes, can evidently be written in the form $\sigma_i = \sigma_0 AP$, where σ_0 is the geometrical cross section of interaction and A is the steric factor of the transition state corresponding to the configuration at the point of quasi-intersection of electronic terms. Thus, within the framework of transition-state theory, P can be interpreted as a transmission coefficient. It should be borne in mind, however, that we are considering a nonequilibrium process, assuming preservation of the

Boltzmann distribution only over the translational and rotational degrees of freedom. On the other hand, it is clear that P can be represented in the form $P = W(1 - S)$, where W is the probability of a change of the electronic state in preassociation and S is the probability of decay during such a time t_0, which would be large in comparison with τ_0, but small in comparison with τ. The existence of such a time t_0 is ensured by the structure of the vibrational spectrum of a complex molecule, which, in turn, leads to a strong increase of τ with increasing number of degrees of freedom N.

For the calculation of S it is expedient to proceed from nonstationary perturbation theory, taking as the zeroth approximation the functions of the isolated bond A–B (of discrete and continuous spectra) and vibrational-

wave functions of fragment A (for simplicity it is assumed that B is an atom). Suppose that the interaction between the A—B bond and the normal vibrations of A is such that the width of the vibrational spectrum $\widetilde{AB}$, ω, is considerably smaller than the mean vibrational frequency ω_0 (this condition is satisfied by a group of characteristic vibrations in a complex molecule). Let a_k denote the amplitudes of the expansion of the complete vibrational function in terms of the zero-approximation functions, with a_0 assigned to the state in which all the vibrational energy is concentrated in the A—B bond. In addition, the expansion must include the functions of the continuous spectrum, with coefficients b_m. Then, neglecting states that contain the rapidly oscillating factor $\exp(i\omega_0 t)$, the system of equations can be written in the form

$$i\hbar\dot{a}_k = V_{k0}\exp[-i\Delta\omega_k t]\,a_0, \qquad k \neq 0,$$

$$i\hbar\dot{a}_0 = \sum_k V_{0k}\exp[i\Delta\omega_k t]\,a_k + \sum_m W_{0m}\exp[i\Delta\omega t]\,b_m, \tag{1}$$

$$i\hbar\dot{b}_m = W_{m0}\exp[-i\Delta\omega_m t]\,a_0,$$

where V_{k0} and W_{m0} are matrix elements of the interaction, and $\Delta\omega_k = E_0 - E_k$. The initial conditions are $a_k = b_m = 0$, $a_0 = 1$ at $t = 0$; thus we assume that the initial excitation of A may be neglected. The probability of decay S during the time t_0 is equal to

$$S = \sum_m |b_m(t_0)|^2. \tag{2}$$

Carrying out the integration over m, we obtain

$$S = 2\gamma\int_0^{t_0} |a_0(t)|^2\,dt, \tag{3}$$

where 2γ is the predissociation rate constant. After eliminating b_m from (1), which can be done in general form by using the condition of continuity of the spectrum of the dissociated state and the weak dependence of W_{m0} on m, (1) takes the form

$$i\hbar\dot{a}_k = V_{k0}\exp[-i\Delta\omega_k t]\,a_0,$$

$$i\hbar\dot{a}_0 = -i\hbar\gamma a_0 + \sum_k V_{0k}\exp[i\Delta\omega_k t]\,a_k. \tag{4}$$

This system, with the initial conditions $a_0(t=0)=1$, can be reduced to the integral equation

$$a_0(t) = \overline{a}_0(t) + \gamma\int_{-\infty}^{\infty}\overline{a}_0(t-\tau)\,\theta(t-\tau)\,a_0(\tau)\,d\tau. \tag{5}$$

Here $\overline{a}_0(\tau)\theta(\tau)$ is the Green' s function of system (4) for $\gamma=0$, which is expressed through the solution of the vibrational problem with the initial conditions $\overline{a}_0(0)=1$, and $\theta(\tau)$ is the unit function. The solution of (5) can be found by the Laplace-transform method:

$$a_0(t) = \frac{1}{2\pi i}\int\psi_0(ip)\exp(ipt)\,dp, \qquad \psi_0(p) = \overline{\psi}_0(p)\,[1+\gamma\overline{\psi}_0(p)]^{-1}, \tag{6}$$

where

$$\overline{\psi}_0(p) = \int_{-\infty}^{\infty}\overline{a}_0(t)\theta(t)\exp(-pt)\,dt. \tag{7}$$

Let us now note that S in (3) practically does not depend on t_0 for $t_0 \gg \tau_0$, so that one may put $t_0=\infty$, if at the same time one neglects the contribution to the integral from very large times, corresponding to the return of the system to the initial state. Substituting (6) and (7) into (3), we find

$$S = \frac{\gamma}{\pi}\int\left|\frac{\overline{\psi}_0(ip)}{1+\gamma\psi_0(ip)}\right|^2 dp. \tag{8}$$

Here, in order to calculate $\overline{\psi}_0(p)$ from (7), one should neglect the contribution of $\overline{a}_0(t)$ at large t. Thus (7) and (8) reduce the problem of the predissociation of a complex molecule along one of its bonds to the problem of beats in a system of harmonic oscillators described by the system (4) with $\gamma=0$.

Let us now consider two special cases of the solution of the system (4).

Strong coupling. Suppose that the interaction between the bonds is sufficiently large, so that the relation $\omega\tau_0 \ll 1$ is fulfilled. Under this condition a decrease in the energy of the bond A–B will be accompanied by multiquantum excitation of the normal vibrations of A. The solution can be found if, from the correct vibrational functions of AB, one constructs a wave packet which at $t = 0$ would give a function localized on A–B. For this purpose we use the relation

$$\varphi_n(x_0) = \sqrt{n!}\sum \frac{b_{01}^{p_1} \dots b_{0N}^{p_N}}{\sqrt{p_1! \dots p_N!}}\, \varphi_{p_1}(Q_1) \dots \varphi_{p_N}(Q_N), \tag{9}$$

where $\varphi_n(x_0)$ is the vibrational function of the n-th level of A–B; $\varphi_{p_k}(Q_k)$ is the function of the p_k-th level of the normal vibration Q_k of the entire AB system; b_{0m} are the coefficients of the transformation of the bond coordinate x_0 to the normal coordinates Q_k

$$x_0 = \sum_{m=1}^{N} b_{0m} Q_m. \tag{10}$$

The summation in (9) is over all p_k satisfying the relation $\sum_k p_k = n$. Formula (9) is a consequence of the theorem on the addition of Hermite polynomials ([3]), in which terms proportional to ω/ω_0 have been discarded. Introducing time factors in (9) (a factor $\exp[ip\Delta\omega_k t]$ must be assigned to each function φ_{p_k}) and calculating the overlap integral between the function $\varphi_n(x_0, t)$ thus obtained and the initial function $\varphi_n(x_0)$, we obtain

$$\overline{a}_0(t) = \langle \varphi_n(x_0),\ \varphi_n(x_0, t)\rangle = \left[\sum b_{0k}^2 \exp(i\Delta\omega_k t)\right]^n. \tag{11}$$

Since we are interested in times t of the order of τ_0, and, by assumption, $\tilde{\omega}\tau_0 \ll 1$, one can simplify (11) by expanding the exponential functions in series. In addition, for the most interesting case of large n, the power of the polynomial can be approximated near its maximum by an exponential function. Then we find

$$\overline{a}_0(t) = \exp\left[in\Omega_1 t - n\Omega_2^2 t^2\right], \tag{12}$$

where $\Omega_1 = \sum b_{0k}^2 \Delta\omega_k, \quad \Omega_2^2 = \frac{1}{2}\sum b_{0k}^2 \Delta\omega_k^2$.

If one uses the possibility of choosing different integration contours···

···of integration in (6), then $\overline{\psi}_0(ip)$ can be written in the form

$$\overline{\psi}_0(ip) = \frac{1}{\Omega_2^2} \exp\left[-\frac{p^2}{4\Omega_2^2}\right] \int_{ip/2\Omega_2}^{\infty} \exp(-s^2)\, ds. \tag{13}$$

Weak coupling. In this case the condition $\tilde{\omega}\tau_0 \gg 1$ is satisfied, so that it is necessary to investigate the behavior of $\overline{a}_0(t)$ in (11) for large values of the arguments in the exponentials. This can be done when the dependence of b_{0m} on m is known. For a large number of vibrational degrees of freedom, if the inequality $\tilde{\omega}\tau_0/N \ll 1$ is fulfilled, the spectrum $\Delta\omega_k$ may be regarded as continuous. If, in addition, V_{0k} depend only weakly on k and the main contribution to the deactivation of n is made by one-quantum transitions $0 \to 1$ in A, then one may put $V_{0k} \sim v\sqrt{n}$. Then $\overline{a}_0$ takes the form

$$\overline{a}_0(t) = \exp\left[-\frac{\pi}{2}\eta\tilde{\omega}t\right], \tag{14}$$

where $\eta = 2v^2 f(0)n/\hbar^2$ and $f(\Delta\omega)$ is the frequency-distribution spectrum in A. This solution is valid for $\tilde{\omega}t \gg 1$. Substituting (14) into (6)–(8), we obtain

$$S = \gamma\left[\gamma + \frac{\pi}{2}\eta\tilde{\omega}\right]^{-1}. \tag{15}$$

The transition to the case of strong coupling within the framework of this model can be made by assuming that $v \ll \hbar\Delta\omega_k$. In this case the coefficients b_{0m} can be calculated by perturbation theory, which gives

$$\Omega_2^2 = 2Nv^2/\hbar^2. \tag{16}$$

Putting $f \sim N/\tilde{\omega}$ in (14), one can express Ω_2^2 in terms of η. Then we obtain

$$\overline{a}_0(t) = \exp[-\eta(\tilde{\omega}t)^2]. \tag{17}$$

Thus (14) and (17) show the differences between the strong- and weak-coupling approximations. Since η is determined from the condition of an appreciable decrease of the exponential, the strong- and weak-coupling approximations correspond, obviously, to the cases $\eta \gg 1$ and $\eta \ll 1$.

Let us note that the proposed model of complex formation can be used to estimate the lower pressure limit at which bimolecular preassociation is still possible as one of the stages of a complex chemical process. In doing so, it should be borne in mind that the assumptions made concerning the character of the vibrational spectrum may differ substantially from reality (for example, the bimolecular preassociation of CO and O).

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Note: Figure translations are in progress. See original paper for figures.