CALCULATION OF THE ACTIVATION ENERGY OF ADIABATIC REACTIONS

É. D. German, R. R. Dogonadze, and V. K. Khidyreli

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A general procedure was developed in [1] for calculating the activation energy of nonadiabatic reactions not accompanied by interconversion of the quantum and classical degrees of freedom* and characterized by a low amount of splitting of the 2V terms of the initial (U_i) and the final (U_f) states (plotted as a function of the coordinates ξ_k of only the classical subsystem) near the saddle point on the surface of intersection of the terms. According to this procedure, the activation energy E_a^{nonad} is determined by the distance between the minimum of the initial term I_i and the value U_i at the saddle point ξ_k^*:

$$E_a^{nonad} = U_i(\xi_k^*) - I_i, \tag{1}$$

whose coordinates are found by resolving the system of equations

$$(1 - \alpha^{nonad})\,\partial U_i/\partial\xi_k + \alpha^{nonad}\,\partial U_f/\partial\xi_k = 0, \tag{2a}$$

$$U_i[\xi_k^*(\alpha^{nonad})] = U_f[\xi_k^*(\alpha^{nonad})]; \tag{2b}$$

here α^{nonad} is a function of the activation energy (E_a^{nonad}) and the heat of reaction ΔH:

$$\alpha^{nonad} = \partial E_a^{nonad}/\partial(\Delta H). \tag{3}$$

For a large group of reactions the formal calculation of E_a^{nonad} can be carried out [2] without a detailed knowledge of the shape of the potential energy surfaces U_i and U_f provided that: 1. the system of reagents (products) has one or more normal vibrations the frequencies of which undergo a sharp change during the reaction; 2. the deviation from symmetry of the potential energy surface is only slight near the saddle point; i.e., the coefficient α^{nonad} determining this symmetry is not too close to zero or unity.

We show below that also in the case when adiabatic reactions (when the splitting of the terms U_i and U_f is substantial compared with kT) satisfy analogous requirements, the formal expression of the activation energy E_a^{ad} can be found without the need for detailed information concerning the surface of the potential energy.

For determining this we shall consider a system of reagents (products) located in a polar solvent with two classical normal vibrations which rapidly change their frequency during the reaction.

Assume that the vibration along the coordinates R_X suddenly increases in frequency on transition from the initial state to the final state, while the vibration along the coordinates R_Y on the other hand rapidly decreases in frequency. In other words the cross section along the coordinates R_X of the term U_i is a shallow curve $v_i(R_X)$, while that of the term U_f is a steep curve $u_f(R_X)$. On the other hand the cross section along the coordinates R_Y of the term U_i

*According to the criterion fixed within the framework of harmonic approximation [3], the degrees of freedom are reckoned as quantum if $\hbar\omega > 4kT$, and they are regarded as classical if $\hbar\omega < 4kT$; here ω is the vibration frequency in the harmonic potential along the corresponding degree of freedom. Criteria of quantum and classical nature for potentials of more complex form were obtained in [4].

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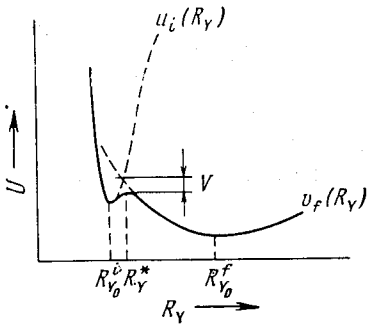

Fig. 1. Cross section of surface of potential energy along coordinate R_Y. The solid line indicates the lower adiabatic term, and the dotted line the nonadiabatic terms of the initial (u_i) and final (v_f) states.

is a steep curve $u_i(R_Y)$, while that of term U_f is a shallow curve $v_f(R_Y)$. (Compare Fig. 1, which shows the cross section U_i and U_f along the coordinate R_Y.)

On denoting by ω_k the solvent polarization fluctuation frequencies which did not vary during the reaction process and by q_k the corresponding normal coordinates, if the potential energy of the classical subsystem is read off from the minimum of the initial term, i.e., on taking $I_i = 0$, then the terms U_i and U_f can be represented in the following form:

$$U_i = \frac{1}{2}\sum \hbar\omega_k q_k^2 + u_i(R_Y) + v_i(R_X), \tag{4a}$$

$$U_f = \sum \hbar\omega_k (q_k - q_{k0})^2 + u_f(R_X) + v_f(R_Y) + \Delta I, \tag{4b}$$

where the first term in U_i and U_f denotes the potential energy of the solvent in the initial and final states, respectively, written within the framework of dielectric formalism, and the quantity $\Delta I = I_f - I_i = I_f$ virtually (to within the accuracy of kT) coincides with the thermal process ($\Delta I \approx \Delta H$).

In the case of adiabatic reactions where the splitting of the terms U_i and U_f is substantial, in order to calculate the activation energy (E_a^{ad}) it is necessary to plot the entire adiabatic surface of the potential energy (U_-) as a function of the classical coordinates, which can be expressed in twin-level approximation by the terms U_i and U_f:

$$U_- = {}^1/_2(U_i + U_f) - {}^1/_2\sqrt{(U_i - U_f)^2 + 4V^2}. \tag{5}$$

Here the quantity E_a^{ad} is determined by the distance between the minimum of the initial term U_i and the saddle point on the surface U_-, i.e.,

$$E_a^{ad} = U_-(\xi_k^*) - I_i = U_-(\xi_k^*). \tag{6}$$

In order to find the coordinates (ξ_k^*) of the saddle point on the adiabatic surface, we introduce the coefficient α^{ad} of the adiabatic reactions in accordance with the following relation:

$$\alpha^{ad} = \partial E_a^{ad}/\partial(\Delta H) = \partial E_a^{ad}/\partial(\Delta I) \tag{7}$$

bearing in mind that at the point (ξ_k^*) the derivatives $\partial U_-/\partial\xi_k$ are equal to zero, i.e.,

$$\left.\frac{\partial U_-}{\partial \xi_k}\right|_{\xi_k=\xi_k^*} = \left[\frac{1}{2}\left(\frac{\partial U_i}{\partial \xi_k} + \frac{\partial U_f}{\partial \xi_k}\right) - \frac{1}{2}\,\frac{U_i - U_f}{\sqrt{(U_i - U_f)^2 + 4V^2}}\left(\frac{\partial U_i}{\partial \xi_k} - \frac{\partial U_f}{\partial \xi_k}\right)\right]_{\xi_k=\xi_k^*}. \tag{8}$$

On the basis of (6) and (8) we can rewrite (7) as follows:

$$\alpha^{ad} = \partial U_-(\xi_k^*)/\partial(\Delta I) + \sum (\partial U_-/\partial\xi_k)_{\xi_k^*}(\partial\xi_k^*/\partial(\Delta I)) = \partial U_-/\partial(\Delta I),$$

or

$$\alpha^{ad} = {}^1/_2 + ({}^1/_2)\,(U_i(\xi_k^*) - U_f(\xi_k^*))/\sqrt{(U_i - U_f)^2 + 4V^2}. \tag{9}$$

On inserting (9) into (8) we get a system of equations for determining the coordinates of the saddle point $\xi_k^*(\alpha^{ad})$:

$$(1 - \alpha^{ad})\,\frac{\partial U_i(\xi_k^*)}{\partial \xi_k} + \alpha^{ad}\,\frac{\partial U_f}{\partial \xi_k} = 0, \quad k = 1, 2, \ldots, N. \tag{10}$$

Equations (10) are completely identical formally with the corresponding Eqs. (2a) for nonadiabatic reactions. Here, although the coordinates of the saddle point $\xi_k^*(\alpha^{ad})$ coincide with the coordinates $\xi_k^*(\alpha^{nonad})$ for nonadiabatic terms, the coefficient α^{ad} according to (9) is determined from solution of another equation:

$$U_i[\xi_k^*(\alpha^{ad})] = U_f[\xi_k^*(\alpha^{ad})] + (2\alpha^{ad} - 1)\sqrt{\{U_i[\xi_k^*(\alpha^{ad})] - U_f[\xi_k^*(\alpha^{ad})]\}^2 + 4V^2}, \tag{11}$$

which at $V \to 0$ turns into the corresponding equation for the nonadiabatic reactions.

Analysis of expression (11) [or (9)] reveals an important conclusion concerning the limits of variation of α^{ad} as a function of ΔI (the heat of reaction). Since the quantity $|(U_i - U_f)[(U_i - U_f)^2 + 4V^2]^{-1/2}|$ is always less than unity at $V \neq 0$, it follows that on variation in ΔI throughout the range of heats from $-\infty$ to ∞, $|2\alpha^{ad} - 1| < 1$, i.e., $0 < \alpha^{ad} < 1$.

Equations (10), together with condition 2., according to which $\alpha^{ad} \sim 1/2$, give the well-known relations for the coordinates of a saddle point obtained earlier [5] on calculating the activation energy of nonadiabatic reactions (compare Fig. 1):

$$R_X^* \cong R_{X_0}^f, \quad R_Y^* \cong R_{Y_0}^i, \quad q_k = \alpha^{ad} q_{k_0}. \tag{12}$$

Thus, according to (10), the intersection of the potentials $u_{i,f}(R_{Y,X})$ and $v_{f,i}(R_{X,Y})$ occurs near the minima $u_i(R_Y)$ and $u_f(R_X)$.

In general it is impossible to resolve Eq. (11). An approximate solution can be found however, bearing in mind that the potential $v_{f,i}(R_{X,Y})$ is far smoother than $u_{i,f}(R_{Y,X})$ (compare Fig. 1). This, after expanding $v_{i,f}(R_{X,Y})$ into a series near the point $R_{X_0}^f(R_{Y_0}^i)$, allows us to restrict ourselves to the linear terms:

$$v_i(R_X) = E_r^X + A_X(R_X - R_{X_0}^f), \quad v_f(R_Y) = E_r^Y - A_Y(R_Y - R_{Y_0}^i). \tag{13}$$

The quantities $E_r^X = v_i(R_{X_0}^f) \approx v_i(R_X^*)$ and $E_r^Y = v_f(R_{Y_0}^i) \approx v_f(R_Y^*)$ contained in the expansion (13) are termed the reorganization energies relative to the coordinates R_X and R_Y, respectively (for more details of these parameters (see [1, 2]); $A_X = |\partial v_i / \partial R_X|_{R_X = R_X^f}$, and $A_Y = |\partial v_f / \partial R_Y|_{R_Y = R_Y^i}$, are the slopes of the linearized terms $v_i(R_X)$ and $v_f(R_Y)$ at the points $R_{X_0}^f$ and $R_{Y_0}^i$. Since, as was mentioned earlier, the intersections $u_i(R_Y)$ and $v_f(R_Y)$ and $u_f(R_X)$ and $v_i(R_X)$ occur near the minimum of $u_i(R_Y)$ and $u_f(R_X)$, respectively, the latter can be approximated with good accuracy in this range by parabolic potentials of frequencies ω_X and ω_Y:

$$u_i(R_Y) = 1/2 M_Y \omega_Y^2 (R_Y - R_{Y_0}^i)^2; \quad u_f(R_X) = 1/2 M_X \omega_X^2 (R_X - R_{X_0}^f)^2, \tag{14}$$

where M_X and M_Y are the effective masses of the oscillators.

Equations (10) and expressions (13) and (14) give the relations between $R_X^*(R_Y^*)$ and $R_{X_0}^f(R_{Y_0}^i)$

$$R_X^* = R_{X_0}^f + \frac{\alpha^{ad} - 1}{\alpha^{ad}} \frac{A_X}{M_X \omega_X^2}; \quad R_Y^* = R_{Y_0}^i + \frac{\alpha^{ad}}{1 - \alpha^{ad}} \frac{A_Y}{M_Y \omega_Y^2}, \tag{15}$$

These enable the accuracy of approximations (12) to be estimated if $A_X(A_Y)$ and $\omega_X(\omega_Y)$ are known.

Inserting Eqs. (13), (14), and (15) into (11), we get an equation for determining α^{ad} in the form

$$2\alpha^{ad} - 1 - (\Delta j / E_s) + (\varepsilon_Y / E_s)[\alpha^{ad}(2 - \alpha^{ad})/(1 - \alpha^{ad})^2] - \varepsilon_X(1 - (\alpha^{ad})^2)/(\alpha^{ad})^2$$
$$= (2\alpha^{ad} - 1)\left\{(4V^2/E_s) + \left[2\alpha^{ad} - 1 - (\Delta j / E_s) + \frac{\varepsilon_Y}{E_s} \frac{\alpha^{ad}(2 - \alpha^{ad})}{(1 - \alpha^{ad})^2} - \frac{\varepsilon_X(1 - (\alpha^{ad})^2)}{E_s(\alpha^{ad})^2}\right]^2\right\}^{1/2},$$

where $E_s = 1/2 \sum \hbar \omega_k q_{k_0}^2$ is the energy of reorganization of the solvent, $\Delta j = \Delta I + E_r^Y - E_r^X$ is the effective heat of reaction along the coordinate of the solvent, $\varepsilon_X = A_X^2 / 2M_X \omega_X^2$, and $\varepsilon_Y = A_Y^2 / 2M_Y \omega_Y^2$. In this equation the quantities V/E_s, ε_Y/kT, and ε_X/kT are small parameters. Solution of (16) by the defined-root method gives the following expression for α^{ad}:

$$\alpha^{ad} = \frac{1}{2} + \frac{\Delta j}{2E_s} + \frac{V}{E_s} \frac{\Delta j}{\sqrt{E_s^2 - \Delta j^2}}. \tag{17}$$

Now introducing the coordinates of the saddle point into (6) and on the basis of (17), we get the final expression for the activation energy of adiabatic reactions as follows:

$$E_a^{ad} = E_a^{nonad} - V\sqrt{1 - \Delta j^2 / E_s^2}, \tag{18}$$

where E_a^{nonad} is the activation energy of the nonadiabatic reaction

$$E_a^{\text{nonad}} = E_r^X + (E_s + \Delta I + E_r^Y - E_r^Y)^2/4E_s. \quad (19)$$

As an illustration of the application of the results obtained above, we will now consider the processes of nucleophilic substitution in methyl halides $CH_3Y + X^- \rightarrow CH_3X + Y^-$. In these reactions the cross section of the terms U_i and U_f along the coordinate of the particle Y, i.e., the cross section along the coordinate R_Y, is as illustrated in Fig. 1, the frequency of the valence vibrations of the C–Y bond in the CH_3Y molecule being far in excess of the vibration frequency of the Y^- ion in the solvent [5]. On the other hand, the vibrations along the coordinates R_X rapidly increase in frequency during the reaction. The magnitude of the coefficient α of the reactions considered here is close to $1/2$ [5]. Thus, these reactions belong to the class of processes where the results obtained above are appreciable.

We first estimate the accuracy of the approximations employed (12). The frequency $\omega_{X(Y)}$ is ~ 400-$700\,cm^{-1}$ [5]. The reduced mass $M_{X(Y)}$ is equal to 10 units in order of magnitude. The slope $A_{X(Y)}$ of the sloping term close to the point of intersection, according to the calculations of Fujimoto,* carried out within the framework of the extended method of Huckel for the system $Cl^- + CH_3Cl$, is ~ 2 eV/Å. According to the calculations of Zhidomirov and Chuvylkin† using the CNDO method, for the reaction $Cl^- + CH_3F$ the slope is ~ 1 eV/Å. It follows from these data that $R_X^* - R_{X_0}^f \approx 0.1$ Å (according to the data of Zhidomirov and Chuvylkin) and ≈ 0.2 Å (according to the data of Fujimoto). Thus, the error in the activation energy on replacing R_X^* by $R_{X_0}^f$ and R_Y^* by $R_{Y_0}^i$ is ~ 0.6 and 2.5 kcal/mol, respectively, for the first and second calculations. Hence, the parameters E_a are ~ 20 kcal/mol in magnitude, and the approximations (12) are correct. In order to calculate E_a^{ad} according to (21) it is necessary to find the splitting V. Estimates of the magnitude of V show that $V \ll kT$, since the contribution of the second term to E_a^{ad} is small compared with the contribution of the first term. This means that $E_a^{ad} \approx E_a^{\text{nonad}}$, and the allowance for the decrease in the activation energy through splitting of the terms is not extensive in the processes under consideration here.

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