# SEMICLASSICAL CALCULATION OF KINETIC PARAMETERS OF SOME SUBSTITUTION REACTIONS

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It has been shown [1] that in determining the shapes of potential energy surfaces, transitions of a system from an initial ($U_i$) to a final ($U_f$) state can be considered classically.† The activation energy of a transition between the surfaces $U_i$ and $U_f$ is then found by solving the system of equations‡

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

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

where $\alpha$ represents the partial derivative of the activation energy with respect to the reaction heat, and the set of coordinates $\xi_k^*$ determines the position of saddle points on the intersection surface of the terms $U_i$ and $U_f$. The corresponding expressions for the activation entropy and for the transmission coefficient $\varkappa$ are of the form [1, 2]

$$\exp(-\Delta S^{\neq}/k)=(2\pi\hbar^2/kT)^{1/2}\int\exp[-(U_i-E_a)/kT]\,dS^*\Big/\int\exp(-U_i/kT)\prod_k d\xi_k, \tag{3}$$

$$\varkappa=2|V|^2/\pi\hbar\sum_k\left[\frac{\partial(U_i-U_f)}{\partial\xi_k}\right]\dot{\xi}_k, \quad \varkappa\leqslant 1, \tag{4}$$

where $S^*$ denotes the intersection surface of the terms $U_i$ and $U_f$, V is the term splitting, and $E_a$ is the activation energy, equal to the distance between the minimum of the initial term to the value of $U_i$ at the point $\xi_k^*$.

We calculate below the quantities $\Delta S^{\neq}$ and $\varkappa$ for substitution processes of type AC + B → A + BC, taking place in a polar solvent under the conditions that the valence bond A–C (B–C) vibrational frequency exceeds significantly the solvent vibrational frequency B(A) and all three particles A, C, and B are collinear (the linear complex model). The first assumption implies that the intersection of the multidimensional initial state term $U_i$ (i.e., the intersection of the potential energy surfaces of the reagents and of the solvent) is steep along one of the classical coordinates $R_A$ and rather flat along another (see Fig. 1). The intersection of the $U_f$ term is, on the contrary, flat along the first coordinate and steep along the other. In the nearest-neighbor approximation we assume that the intermolecular interaction potential between B and AC depends on the distance between C and B only.

We denote by $R_A$, $R_B$, and $R_C$ the Cartesian coordinates of atoms A, B, C and by $u_i(R_A-R_C)$ and $v_i(R_C-R_B)$ the steep intermolecular and flat intermolecular interaction potentials of A and C and of B and AC, respectively.

†For harmonic potentials the vibrational frequency ($\omega$) of the oscillator serves as the quantum-classical criterion. If $\omega > 4kT/\hbar$, the system is quantum, and if $\omega < 4kT/\hbar$, it is classical. For more complicated potentials quantum-classical criteria are obtained in [3].

‡Using adiabatic potential energy surfaces in the calculations, Eqs. (1) for the determination of saddle point coordinates are conserved, but Eq. (2) is modified [4].

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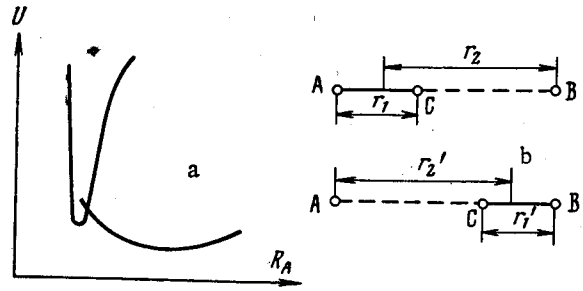


Fig. 1. a) Intersection of the terms $U_i$ and $U_f$ in particle A coordinates; b) coordinate notation in the linear complex model.

Within the approximations adopted, the initial state term can then be written in the form

$$U_i = \frac{1}{2}\sum \hbar\omega_k q_k^2 + u_i(R_A - R_C) + v_i(R_C - R_B) + I_i. \tag{5a}$$

Introducing similarly potentials $u_f(R_C - R_B$ and $u_f(R_A - R_C)$, the final state term can be written

$$U_f = \frac{1}{2}\sum \hbar\omega_k (q_k - q_{k_0})^2 + v_f(R_A - R_C) + u_f(R_C - R_B) + I_f. \tag{5b}$$

The terms $I_i$ and $I_f$ in (5a, b) are the values of $U_i$ and $U_f$ at their minima. The first terms in (5a, b) are the solvent potential energies within the dielectric formalism [5].

To integrate (1) it is convenient to transform to the Jacobi coordinates $r_1$, $r_2$, and $r_3$ (Fig. 1b), related to the Cartesian coordinates by

$$r_1 = (1 + m_A/m_C)R_A + (m_B/m_C)R_B,\quad r_2 = -[1 + m_B/(m_A + m_C)]R_B,$$
$$r_3 = [m_A R_A + m_B R_B + m_C R_C]/(m_A + m_B + m_C), \tag{6}$$

where $m_A$, $m_B$, and $m_C$ are the masses of atoms A, B, and C. In the final state it is convenient to introduce the Jacobi coordinates $r_1'$ and $r_2'$:

$$r_1' = (m_A/m_C)R_A + (1 + m_B/m_C)R_B,\quad r_2' = -[1 + m_A/(m_B + m_C)]R_A. \tag{7}$$

The relation between $r_1$, $r_2$ and $r_1'$, $r_2'$ is of the form

$$r_1' = [m_A/(m_C + m_A)]r_1 - r_2,\quad r_2' = -[Mm_c/(m_B + m_C)(m_A + m_C)]r_1 - [m_B/(m_B + m_C)]r_2, \tag{8}$$

where $M = m_A + m_B + m_C$.

We denote by $\mu_{1i}$, $\mu_{1f}$, $\mu_{2i}$, and $\mu_{2f}$ the reduced masses

$$\mu_{1i} = m_C m_A/(m_C + m_A),\quad \mu_{1f} = m_C m_B/(m_C + m_B);$$
$$\mu_{2i} = m_B(m_C + m_A)/M,\quad \mu_{2f} = m_A(m_B + m_C)/M,$$

and by $\omega_{1i}$, $\omega_{1f}$, $\omega_{2i}$, and $\omega_{2f}$ the corresponding vibrational frequencies. Recalling that the intersection of the steep and flat terms $u_{i(f)}$ and $v_{i(f)}$ occurs [6] close to the minimum of the $u_{i(f)}$ term (Fig. 1), which allows us to approximate $u_{i(f)}$ by a harmonic potential in this region, we rewrite (5a, b)

$$U_i = \frac{1}{2}\sum \omega_k^2 \eta_k^2 + \frac{1}{2}\omega_{1i}^2(\xi_1 - \xi_{10}^i)^2 + v_i(\mu_{1i}^{1/2}m_C^{-1}\xi_1 - \mu_{2i}^{-1/2}\xi_2), \tag{9}$$

$$U_f = \frac{1}{2}\sum \omega_k^2(\eta_k - \eta_{k_0})^2 + v_f(\mu_{1i}^{-1/2}\xi_1) + \frac{\omega_{1f}^2 m_A m_B}{(m_A + m_C)(m_B + m_C)}$$
$$\times\left[\xi_1 - \xi_{10}^f - \left(\frac{m_C M}{m_A m_B}\right)^{1/2}(\xi_2 - \xi_{20}^f)\right]^2 + \Delta I,$$

where $\xi_1 = \mu_{1i}^{1/2}r_1$, $\xi_2 = \mu_{2i}^{1/2}r_2$, $\eta_k = (\omega_k/\hbar)^{-1/2}q_k$; $\xi_{10}^{i(f)}$ and $\xi_{20}^{i(f)}$ are the equilibrium values of $\xi_1$ and $\xi_2$ in the initial and final states, and $\Delta I = I_f - I_i$.

In evaluating the integral in (4) by the Laplace method it is necessary to expand $U_i$ and $U_f$ in series up to quadratic terms close to the saddle points. For this purpose it is convenient to represent the $U_i$ and $U_f$ terms as follows, separating the contributions corresponding to the potential energy of the solvent:

$$U_i = \frac{1}{2}\sum \omega_k^2 \eta_k^2 + \bar{U}_i(\xi_1, \xi_2), \quad U_f = \frac{1}{2}\sum \omega_k^2 (\eta_k - \eta_{k_0})^2 + \bar{U}_f(\xi_1, \xi_2) + \Delta I. \tag{9a}$$

Since the solvent components of $U_i$ and $U_f$ do not contain linear terms, the series expansion of the $U_i$ and $U_f$ terms reduces essentially to approximating $\bar{U}_i(\xi_1, \xi_2)$ and $\bar{U}_f(\xi_1, \xi_2)$ by quadratic forms

$$\bar{U}_{i(f)} = U_{i(f)}(\xi_1^*, \xi_2^*) + B_1^{i(f)}(\xi_1 - \xi_1^*) + B_2^{i(f)}(\xi_2 - \xi_2^*)$$
$$+ \frac{1}{2} B_{11}^{i(f)}(\xi_1 - \xi_1^*)^2 + \frac{1}{2} B_{22}^{i(f)}(\xi_2 - \xi_2^*) + B_{12}^{i(f)}(\xi_1 - \xi_1^*)(\xi_2 - \xi_2^*), \tag{10}$$

where, by (2) and (5) the saddle point coordinates $\xi_1^*$, $\xi_2^*$ are determined by the expressions

$$\xi_1^* = \xi_{10}^i - \frac{\alpha}{1-\alpha}\frac{v_f'}{\mu_{1i}^{1/2}\omega_{1i}^2},$$
$$\xi_2^* = \xi_{20}^f + \left(\frac{m_A m_B}{M m_C}\right)^{1/2}(\xi_{10}^i - \xi_{10}^f) + \frac{1-\alpha}{\alpha}\mu_{2i}^{1/2}\frac{v_i'}{\mu_{1f}\omega_{1f}^2} - \frac{\alpha}{1-\alpha}\left(\frac{m_A m_B}{M m_C}\right)^{1/2}\frac{v_f'}{\mu_{1i}\omega_{1i}^2}. \tag{11}$$

Since the potentials $v_i$ and $v_f$ are much smoother than $u_i$ and $u_f$, we approximately represent them by linear functions close to the saddle points; i.e., we assume that the second derivatives $v_i''$ and $v_f''$ vanish at the saddle points. Using this approximation and performing the integration, we finally obtain the following expression for the activation entropy and for the coefficient $\varkappa$:

$$\Delta S^{\neq} = k \ln\left\{\frac{\hbar\omega_{ef}}{\sqrt{\alpha(1-\alpha)kT}}\left[\frac{(m_A + m_C)(m_B + m_C)}{m_C M}\right]^{1/2}\frac{\omega_{2i}}{\omega_{1f}}\right\}; \tag{12}$$

$$\varkappa = 2|V|^2 \Big/ \left|\frac{\hbar^2 kT}{2\pi^3\alpha^2}\left\{2E_s\alpha^2(\omega_{ef}^s)^2 + \left[\frac{\mu_{1i}^{1/2}v_i'}{m_C} - \frac{\alpha}{1-\alpha}\frac{v_f'}{\mu_{1i}^{1/2}}\right]^2 + \frac{(v_i')^2}{\mu_{2i}}\right\}\right|^{1/2}, \tag{13}$$

where

$$\omega_{ef}^2 = \left\{\alpha^2(\omega_{ef}^s)^2 + \left(\left[\frac{\mu_{1i}^{1/2}}{m_c}v_i' - \frac{\alpha}{1-\alpha}\frac{v_f'}{\mu_{1i}^{1/2}}\right]^2 + \frac{(v_i')}{\mu_{2i}}\right)\Big/ 2E_s\right\}\Big/\left\{\alpha^2\right.$$
$$\left. + \left(\frac{1}{\alpha}\frac{(v_i')^2}{\mu_{1f}\omega_{1f}^2} + \frac{\alpha^2}{(1-\alpha)^3}\frac{(v_f')^2}{\mu_{1i}\omega_{1i}^2}\right)\Big/ 2E_s\right\}. \tag{14}$$

The quantities appearing in Eqs. (13) and (14) have the following meaning: $\omega_{ef}^s$ denotes an effective frequency of the solvent polarization fluctuation, $E_s$ is the reorganization energy of the solvent [1], and $v_i'$ and $v_f'$ are the slopes of the potentials $v_i$ and $v_f$ close to the saddle points.

We use the equations obtained to evaluate the activation entropy of nucleophillic substitution reactions $CH_3X + Y^- \rightarrow CH_3Y + X^-$ [X(Y) = Cl, Br, I]. In this case it is understood that $v_i(v_f)$ is the interaction potential between the ion $Y^-(X^-)$ and the molecule $CH_3X(CH_3Y)$ depending on the distance between C and $Y^-$(C and $X^-$), $\omega_{1i}(\omega_{1f})$ is the vibrational frequency of the valence bond C–X in $CH_3X$ (C–Y in $CH_3Y$), $\omega_{2i}(\omega_{2f})$ is the vibrational frequency of the $X^-(Y^-)$ ion, which is of the same order of magnitude as the reciprocal Debye relaxation time, and $m_A$ and $m_B$ are the masses of particles A and B. The protons are quantum particles and do not affect the quantity $\Delta S^{\neq}$ since their motion is of subbarrier character.

Consider first, for estimates, symmetric processes in which X = Y. Equations (13) and (14) simplify and acquire the form

$$\varkappa = 2|V|^2 \Big/ \left|\frac{\hbar^2 kT}{\pi^3\alpha^2}\left[\alpha^2 E_s(\omega_{ef}^s)^2 + (v')^2/\mu\right]\right|^{1/2}, \tag{15}$$

$$\omega_{ef}^2 = [\alpha^2 E_s (\omega_{ef}^s)^2 + (v')^2/\mu]/[\alpha^2 E_s + (v')^2/\alpha\mu_{1i}\omega_{1i}^2], \quad (16)$$

where $v' = |v_i'| = |v_f'|$, $\mu = m_X m_C/(2m_X + m_C) = mm_C/M$.

The parameters entering (15) and (16) are of the following orders of magnitude. According to [6], the reorganization energy of the solvent ($H_2O$) can be taken as $\sim 2.5$ eV. The symmetry coefficient of the reactions considered is close to $^1/_2$ [6]. The frequencies $\omega_{1i}$ and $\omega_{1f}$ are well-known from infrared spectra [7]. The solvent effective frequency $\omega_{ef}^s$ is of the order of the reciprocal Debye relaxation time. Analysis of experimental data on the kinetic isotope effect [8] in the reaction $CH_3I + I^- \rightarrow I^- + CH_3I$ ($k_H/k_D = 1.1$) by means of Eq. (15) allows us to make a qualitative lower bound estimate of the slope v' close to the transition configuration: $v' \geq 2.5 \cdot 10^{-3}$ eV/Å. (This qualitative estimate of v' does not contradict the quantum chemical calculations of Zhidomirov and Chuvylkin, and also those of Fujimoto and Fukui, who obtained for v' values of the order of 1-2 eV/Å.)

Substituting in Eq. (16) the numerical values of the parameters leads to the frequency $\omega_{ef} \sim 10^{12}$ sec$^{-1}$. Using for $\omega_{2i}$ the value $\sim 10^{12}$ sec$^{-1}$ and taking into account that for $\varkappa \sim 1$ the preexponent is related to $\Delta S^{\neq}$ by $\log A = \log (ekT/h) + \Delta S^{\neq}/2.3k + \log G$ (G is the reaction volume at 1 mole-particle [1]), we obtain for log A a value $\sim 9.7$. This result is in good agreement with the experimental preexponent values [9, 10], lying in the interval $\sim 10^9 - 10^{10}$ for the reactions considered.

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