THE PRINCIPLE OF MINIMUM MOMENTUM TRANSFER IN ELEMENTARY CHEMICAL REACTIONS AND POLANYI'S RULE

A. M. Brodskii, V. G. Levich,*
and V. V. Tolmachev

A complete quantum-mechanical calculation of the effective cross section for a chemical substitution reaction [1] of the form

$$R_1-R_2+R_3=R_1+R_2-R_3, \tag{1}$$

encounters considerable well known mathematical difficulties. Therefore a new procedure is developed below for studying the fundamental characteristics of these cross sections, based on a proposed simple principle which requires the minimum transfer of momentum for each of the three complex particles R_1, R_2, and R_3 participating in the reaction (considered here for simplicity to be structureless monatomics). The quantum-mechanical basis for this principle is given in [2].

The motion of the particles in reaction (1) at relatively low energy can be divided approximately into three stages: (a) quasiclassical movement of R_1-R_2 as a unit relative to R_3 up to the point of entry into the reaction zone; (b) quantum-mechanical transition from the bonded structure R_1-R_2 into the bonded structure R_2-R_3; and (c) quasiclassical movement of R_2-R_3 as a unit relative to R_1 on departure from the reaction zone. The motion of stages (a) and (c) can in fact be analyzed as quasiclassical potential scattering, taking into account the deformation of the bound molecule by the third particle. Since the laws of elastic scattering are known, the study of stages (a) and (c) does not present the principal difficulty, and therefore we focus our attention on the fundamental stage (b). Accordingly it is implicit in the following that all the initial and final conditions refer to values directly at the points of arrival and departure from the reaction zone, and not to the true asymptotic values of stages (a) and (c).

Suppose that initially R_3 moves with momentum $\mathbf{p}_i$ in the c.m. system toward the bound molecule R_1-R_2, and at the conclusion the bound molecule R_2-R_3 moves with momentum $\mathbf{p}_f$ away from R_1. Postulating that the momentum of the bound diatomic molecules is divided between the two constituent particles proportionally to their masses, it is easy to calculate the momentum transfer for each of the three particles:

$$\begin{aligned}\mathbf{q}_1&=-\frac{m_1}{m_1+m_2}\mathbf{p}_i+\mathbf{p}_f,\\ \mathbf{q}_2&=-\frac{m_2}{m_1+m_2}\mathbf{p}_i-\frac{m_2}{m_3+m_2}\mathbf{p}_f,\\ \mathbf{q}_3&=\mathbf{p}_i-\frac{m_3}{m_2+m_3}\mathbf{p}_f.\end{aligned} \tag{2}$$

(Since the analysis is performed in the c.m. system, $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3=0$.)

The momenta $\mathbf{p}_i$ and $\mathbf{p}_f$ are related by the law of conservation of energy,

$$p_i^2M/2m_3(m_1+m_2)=p_f^2M/2m_1(m_2+m_3)+Q', \tag{3}$$

where $Q'=Q+\varepsilon_f-\varepsilon_i$. Here Q is the heat of reaction (for a transition between standard states) referred to zero temperature; ε_f is the excitation energy of the molecule R_2-R_3 formed in the reaction; ε_i is the excitation energy of the molecule R_1-R_2 which disappears in the reaction; and $M=m_1+m_2+m_3$.

According to the proposed principle of minimum momentum transfer, the cross section $\delta(E, Q)$ for a reaction of the form (1) has a significant maximum at energy $E=p_i^2M/2m_3(m_1+m_2)$ and angle $\cos\theta=(\mathbf{p}_i\mathbf{p}_f)/p_ip_f$,

---

* Corresponding Member, Academy of Sciences of the USSR.

Institute of Electrochemistry, Academy of Sciences of the USSR. Translated from Doklady Akademii Nauk SSSR, Vol. 183, No. 4, pp. 852-855, December, 1968. Original article submitted June 28, 1968.

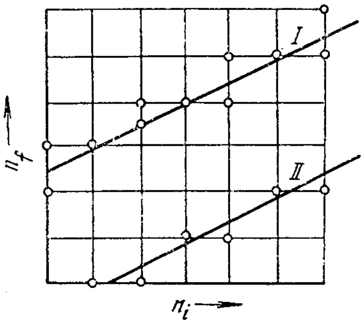

Fig. 1

for which each of the quantities q_1^2, q_2^2, and q_3^2 in (2) takes on the minimum allowed value consistent with the law of conservation of energy (3). (It is readily seen that the minima of all three quantities q_1^2, q_2^2, and q_3^2 are attained at the same values of E and Θ.)

The principle of minimum momentum transfer has an obvious resemblance to the Franck-Condon principle, in that it allows the determination of the most probable quantum transitions in molecular systems (just as the well known Franck-Condon principle does in molecular spectroscopy). According to the Franck-Condon principle, the most probable electronic transition in a complex electronic-nuclear system occurs with the nuclei vibrationally unexcited and with zero momentum transfer for each nucleus. According to the principle of minimum momentum transfer, any electronic-nuclear transition in such a system occurs with the minimum momentum transfers for the nuclei which are consistent with the law of conservation of energy.

As an example, let us examine the momentum transfer for the first particle. From (3) we obtain at once

$$\begin{aligned} q_1^2 &= \left(\frac{m_1}{m_1+m_2}\right)^2 p_i^2 - 2\,\frac{m_1}{m_1+m_2}\cos\theta p_ipf + p^2f \\ &= \left(\frac{m_1}{m_1+m_2}\right)^2 p_i^2 - 2\,\frac{m_1}{m_1+m_2}\cos\theta p_i \sqrt{\frac{m_1(m_2+m_3)}{m_3(m_1+m_2)}\,p_i^2 - \frac{2m_1(m_2+m_3)}{M}\Big)\,Q'} \\ &\quad + \frac{m_1(m_2+m_3)}{m_3(m_1+m_2)}\,p_i^2 - \frac{2m_1(m_2+m_3)}{M}\,Q'. \end{aligned} \tag{4}$$

It is immediately evident from (4) that the expression has a minimum at cos Θ = 1, i.e., at Θ = 0. Thus the most favorable angle for reaction is determined simply by the elastic scattering in stages (a) and (c), in full agreement with experiment [3]. Assuming further that cos Θ = 1, we calculate the derivative $\partial q_1^2/\partial p_i$ and set it equal to zero. Solving the resulting equation, we obtain the energy corresponding to a maximum in the effective cross section:

$$\begin{aligned} E_0 &= Q'\,\frac{\gamma+1}{2} \quad \text{for} \quad Q' \geqslant 0, \\ E_0 &= |Q'|\,\frac{\gamma-1}{2} \quad \text{for} \quad Q' \leqslant 0, \end{aligned} \tag{5}$$

where $\gamma = \sqrt{1 + 4\cos^2\psi/\sin^4\psi}$, in which $\psi = \arctan\sqrt{m_2M/m_1m_3}$.

Equations (5) show that for Q' ≥ 0 the maximum in the effective cross section does not occur at the threshold energy E = Q', but rather at a higher energy E = E_0 > Q'. In the case where Q' ≤ 0 the maximum in the effective cross section does not lie at the threshold energy E = 0 for the reaction, but rather at a higher energy E = E_0 > 0.

Supposing for simplicity that the excitation is exclusively due to the vibrational modes,* i.e., that $\varepsilon_f = n_f\hbar\omega_f$ and $\varepsilon_i = n_i\hbar\omega_i$, where ω_f and ω_i are the frequencies corresponding to the vibrational quanta, and n_f and n_i are the quantum numbers, important conclusions can be derived from (5) regarding the relative reaction rates for varying excitation of the initial and final bound molecules. The optimal values of n_f and n_i will be those lying near the lines in Fig. 1. In particular, for the most interesting case in which the reactant excitation is entirely thermal (where mainly the low vibrational quanta are excited), the following conclusions may be drawn:

1. For an endothermic reaction (Q > 0), the most favorable situation (in the sense of minimized momentum transfer) will exist when the initial bound molecule R_1-R_2 is excited to a quantum-number value $n_i = n_i^{cr}$ or $n_i^{cr} + 1$, while the final bound molecule R_2-R_3 is practically unexcited ($n_f = 0$),

$$n_i^{cr}\,\hbar\omega_i < Q < (n_i^{cr}+1)\,\hbar\omega_i. \tag{6}$$

---

* The additional calculation for rotations does not modify the essential conclusions of the present work, since the conversion of a significant part of the heat of reaction into rotational energy of the bound molecule being produced, and also the reverse process, seem quite unlikely; actually, not only is the minimization of momentum transfer necessary, but also in addition the minimization of angular momentum transfer. We remark, however, that in the complete absence of coupling between vibration and rotation the reaction is forbidden by the conservation laws.

2. For an exothermic reaction ($Q < 0$), the most favorable situation (in the sense of minimized momentum transfer) will exist when the initial bound molecule R_1-R_2 is practically unexcited, while the final bound molecule R_2-R_3 is excited to quantum-number values $n_f = n_f^{cr}$ or $n_f^{cr} + 1$, where

$$n_f^{cr} h\omega_f < |Q| < (n_f^{cr} + 1)\hbar\omega_f. \tag{7}$$

By keeping only those contributions to the effective total cross section for endothermic and exothermic reactions which come from the processes which have been shown to be the most probable, and carrying out the usual temperature averaging over the Maxwell distribution, an expression may be derived for the reaction rate constant in the form

$$k(T) = Ae^{-E_1/kT} + Be^{-E_2/kT}, \tag{8}$$

in which, for an endothermic reaction,

$$E_1 = (Q - n_i^{cr}\hbar\omega_i)\frac{\Upsilon+1}{2}, \quad E_2 = ((n_i^{cr} + 1)\hbar\omega_1 - Q)\frac{\Upsilon-1}{2} \tag{9}$$

and for an exothermic reaction,

$$E_1 = ((n_f^{cr} + 1)\hbar\omega_f - |Q|)\frac{\Upsilon+1}{2}, \quad E_2 = (|Q| - n_f^{cr}\hbar\omega_f)\frac{\Upsilon-1}{2}. \tag{10}$$

In the temperature range of interest to us, Eq. (8) may be approximated by the equation

$$k(T) = Ce^{-Ea/kT}, \tag{11}$$

i.e., Eq. (8) reduces to the form of the Arrhenius law, with

$$E_a = -\frac{\partial \ln k(T)}{\partial (1/kT)} = \frac{E_1 Ae^{-E_1/kT} + E_2 Be^{-E_2/kT}}{Ae^{-E_1/kT} + Be^{-E_2/kT}} = \lambda E_1 + \mu E_2, \tag{12}$$

using the parameters $\lambda + \mu = 1.\ 0 \leqslant \lambda \leqslant 1,\ 0 \leqslant \mu \leqslant 1.$

Thus for an endothermic reaction, ($Q > 0$), we have

$$E_a = \left[-\left(\lambda\Upsilon - \frac{\Upsilon-1}{2}\right)n_i^{cr} + (1-\lambda)\frac{\Upsilon-1}{2}\right]\hbar\omega_i + \left(\lambda\Upsilon - \frac{\Upsilon-1}{2}\right)Q \tag{13}$$

and for an exothermic reaction

$$E_a = \left[\left(\lambda\Upsilon - \frac{\Upsilon-1}{2}\right)n_f^{cr} + \lambda\frac{\Upsilon+1}{2}\right]\hbar\omega_f - |Q|\left(\lambda\Upsilon - \frac{\Upsilon-1}{2}\right). \tag{14}$$

Equations (13) and (14) explain theoretically the well known empirical rule of Polanyi for reactions [Eq. (1)] in homologous series.*

We have not touched here on the question of the spread in energy of the maxima; this calculation gives a small correction to the value of the activation energy. The indicated spread Δ in the reaction cross section maxima is related to the momentum uncertainty of the individual particles in the bound molecules, and a detailed calculation shows that it is given by

$$\Delta^2 = 2\frac{(1+n_i)\hbar\omega_i(1+n_f)\hbar\omega f}{(1+n_i)\hbar\omega_i + (1+n_f)\hbar\omega_f}|Q'|\frac{\cos^2\psi}{\sin^4\psi}. \tag{15}$$

The experimentally observed order for the constant term and the coefficient in Polanyi's formula follows from Eqs. (13) and (14). Here, however, the sum of the Polanyi coefficients for the forward and reverse reactions does not equal unity, since the reactions proceed in different temperature regions. The present results also account for the departures from Polanyi's rule when there are sharp mass changes, and they explain the specific isotope effect (as

---

* It should be noted that Eqs. (11) and (13), and (11) and (14), for forward and reverse reactions (endothermic and exothermic) hold true in different temperature intervals. Hence it is not at all surprising that the difference between the effective activation energies of (13) and (14) is not equal to the heat of reaction.

for example in going from hydrogen reactions to deuterium reactions). The diagram of Fig. 1 provides the basis for an explanation of the particular chemical reactivity toward further endothermic reactions of the products of exothermic reactions before their thermalization (i. e., in the nascent state).

LITERATURE CITED

1. S. Benson, The Foundations of Chemical Kinetics, McGraw-Hill, New York (1964).
2. A. M. Brodskii, V. G. Levich, and V. V. Tolmachev, Dokl. Akad. Nauk SSSR, 182, No. 5 (1968).
3. L. Prigogine (editor), Progress in Chemical Physics, Vol. 10 (1966).
4. N. N. Semenov, On Some Problems of Chemical Kinetics and Reactivity [in Russian], Moscow (1958).