PHYSICAL CHEMISTRY

E. A. PSHENICHNOV

1962

SovietRxiv

Fig. 1. Double potential barrier. V_1, V_2 are the heights of the potential barriers; V_3 determines the position of the bottom of the potential well. E is the energy; $-a, -b, c$, and d are the turning points. The arrows show the directions of the incident, reflected, and transmitted waves.

Figure 1: Fig. 1. Double potential barrier. V_1, V_2 are the heights of the potential barriers; V_3 determines the position of the bottom of the potential well. E is the energy; $-a, -b, c$, and d are the turning points. The arrows show the directions of the incident, reflected, and transmitted waves.

Abstract

Full Text

PHYSICAL CHEMISTRY

E. A. PSHENICHNOV

ON THE TUNNEL EFFECT FOR A DOUBLE POTENTIAL BARRIER

(Presented by Academician V. N. Kondrat' ev, November 30, 1961)

The literature has repeatedly discussed the question of the possible existence, on the potential-energy curve representing the profile of the path of a chemical reaction, of a depression at the top of the activation barrier (see, for example, (^{1})). On the other hand, it is known (for example, (^{2})) that, when particles tunnel through two identical potential barriers, resonance effects arise if there are quasistationary states in the potential well between the barriers.

It is therefore of interest to consider what consequences should follow from the presence of a depression at the top of the activation barrier under conditions in which tunnel effects may be expected, i.e., in the course of a chemical reaction at sufficiently low temperatures.

Fig. 1. Double potential barrier. V_1, V_2 are the heights of the potential barriers; V_3 determines the position of the bottom of the potential well. E is the energy; $-a, -b, c$, and d are the turning points. The arrows show the directions of the incident, reflected, and transmitted waves.

For this purpose let us assume that the reaction coordinate (for example, in a reaction of exchange by light H or D atoms) is described by the potential curve $V(x)$ shown in Fig. 1. The expression for the reaction-rate constant may be written in the form (^{3})

$$k = B \int_0^{\infty} G(E) \exp\left(-\frac{E}{\Theta}\right) dE, \qquad (1)$$

where E is the energy; $\Theta = kT$; B is a pre-exponential factor, weakly dependent on the temperature T; and $G(E)$ is the transmission coefficient.

Assuming the conditions for the quasiclassical approximation to be satisfied, let us find $G(E)$ for the potential field $V(x)$ (Fig. 1). Suppose that a particle of mass μ and energy $V_3 < E < V_2$ ($V_2 < V_1$ are the heights of the potential barriers, and V_3 determines the position of the minimum) is incident from right to left. In the sense of the problem, in the region $x < -a$ there is only a wave going off to $-\infty$; i.e., the wave function has the form

$$\psi = \frac{C}{\sqrt{p}} \exp\left(\frac{i}{\hbar}\int_x^{-a} p\,dx\right), \tag{2}$$

where $p = \sqrt{2\mu[E - V(x)]}$, $C = \text{const}$. Continuing this solution into the region $x > d$ (for the rules of matching quasiclassical functions and their derivatives at the turning points $-a$, $-b$, c, and d, see, for example, (^{4,2})), we obtain

$$\psi = \frac{C}{\sqrt{p}} \exp\left(\frac{i}{\hbar}\int_d^{x} p\,dx\right)\left\{-i\cos\sigma\left[2e^{(\tau_1+\tau_2)} - \frac{1}{8}e^{-(\tau_1+\tau_2)}\right] - \operatorname{sh}(\tau_2-\tau_1)\sin\sigma\right\}$$
$$+\frac{C}{\sqrt{p}} \exp\left(-\frac{i}{\hbar}\int_d^{x} p\,dx\right)\left\{\cos\sigma\left[2e^{(\tau_1+\tau_2)} + \frac{1}{8}e^{-(\tau_1+\tau_2)}\right] - i\operatorname{ch}(\tau_2-\tau_1)\sin\sigma\right\}. \tag{3}$$

Here the following notation has been introduced:

$$\frac{1}{\hbar}\int_{-a}^{-b} |p|\,dx = \tau_1, \qquad \frac{1}{\hbar}\int_{-b}^{+c} p\,dx = \sigma,$$

$$\frac{1}{\hbar}\int_{c}^{d} |p|\,dx = \tau_2.$$

Equating the second term in (3) to zero and regarding the penetrability as a small quantity ($e^{-(\tau_1+\tau_2)} \ll 1$), we obtain the condition for determining the quasiclassical levels E_n^0 and their width Γ:

$$\frac{1}{\hbar}\int_{-b}^{+c} \sqrt{2\mu[E_n^0 - V(x)]}\,dx = \left(n+\frac{1}{2}\right)\pi \qquad (n = 0, 1, 2, \ldots);$$

$$\Gamma = \frac{\hbar\omega}{2\pi} e^{-(\tau_1+\tau_2)}\operatorname{ch}(\tau_2-\tau_1), \qquad \text{where} \quad \frac{\pi}{\omega} = \mu\int_{-b}^{+c} dx\,\{2\mu[E_n^0 - V(x)]\}^{-1/2}.$$

The transmission coefficient is

$$G(E) = \left\{ \operatorname{ch}^2(\tau_2 - \tau_1) \left[\frac{4e^{2(\tau_1+\tau_2)}}{\operatorname{ch}^2(\tau_2 - \tau_1)} \cos^2\sigma + \sin^2\sigma \right] \right\}^{-1}. \tag{4}$$

For a symmetric potential curve $[V(+x) = V(-x)]$, putting $V_1 = V_2 \equiv V_0$, $\tau_1 = \tau_2 \equiv \tau$, we obtain the known (^{2}) result

$$G_{\mathrm{sym}}(E) = [4e^{4\tau}\cos^2\sigma + \sin^2\sigma]^{-1}. \tag{5}$$

It follows from (5) that at a value of E coinciding with one of the quasilevels, $G(E) = 1$. For $\Delta E < |E_n^0|$, from (4) and (5) we obtain, respectively,

$$G(E) = [\operatorname{ch}^2(\tau_2 - \tau_1)]^{-1} \frac{\Gamma^2}{\Gamma^2 + (\Delta E)^2}; \tag{4'}$$

$$G_{\mathrm{sym}}(E) = \frac{\Gamma^2}{\Gamma^2 + (\Delta E)^2}. \tag{5'}$$

Far from resonance $G(E) \simeq e^{-2(\tau_1+\tau_2)}$, $G_{\mathrm{sym}}(E) \simeq e^{-4\tau}$.

Having investigated the behavior of $G(E)$, let us now return to consideration of formula (1). Suppose that the potential field $V(x)$ has two identical barriers with a potential well between them, in which there is one quasistationary level E_0 with width Γ, and E_0 is appreciably smaller than the barrier height V_0. For a qualitative investigation of the role of the tunnel effect, we use the following rough approximation for $G(E)$:

$$\begin{aligned} &G(E) = 0 \quad \text{for} \quad 0 \le E < E_0 - \Gamma, \\ &G(E) = 1 \quad \text{for} \quad E_0 - \Gamma \le E \le E_0 + \Gamma, \\ &G(E) = 0 \quad \text{for} \quad E_0 + \Gamma < E < V_0, \\ &G(E) = 1 \quad \text{for} \quad V_0 \le E. \end{aligned} \tag{6}$$

From (1), taking (6) into account, we obtain

$$k = B_1 e^{-V_0/\Theta} \left[1 + 2\operatorname{sh}\left(\frac{\Gamma}{\Theta}\right) e^{(V_0 - E_0)/\Theta} \right], \tag{7}$$

where $B_1 = B\Theta$.

Let us consider the dependence of k on temperature.

1) At sufficiently high temperatures, $2\,\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right)\exp\left(\frac{V_0 - E_0}{\Theta}\right) \ll 1$ and $k \simeq B_1 \exp\left(-\frac{V_0}{\Theta}\right)$. The reaction proceeds by the classical path, over the barrier. The role of the tunnel effect is negligibly small. The dependence of k on Θ has a simple exponential form.

2) When the temperature is lowered, in some interval $\Delta\Theta$, depending, for a given form of the potential curve $V(x)$, on the effective mass μ, the relation $2\,\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right)\exp\left(\frac{V_0 - E_0}{\Theta}\right) \sim 1$ will hold. In this case $k(\Theta)$ does not have a simple exponential form. The over-barrier transition and the tunneling transition (through the quasistationary state) will be equally probable.

3) At sufficiently low temperatures, when $2\,\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right)\exp\left(\frac{V_0 - E_0}{\Theta}\right) \gg 1$, we have $k \simeq 2B_1\,\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right)\exp\left(-\frac{E_0}{\Theta}\right)$. The predominant role will be played by the tunneling transition through the quasistationary state. The isotopic effect is weaker than in the usual tunnel effect (in the case of a single barrier), approximately by a factor $\exp\left[\frac{E_0(\mu_1) - E_0(\mu_2)}{\Theta}\right]$, where $\mu_2 > \mu_1$. From comparison of items 1 and 3 it follows that, in the presence of a quasistationary state, as Θ decreases the effective activation energy is lowered ($E_0 < V_0$).

4) In problems of chemical kinetics the condition $\left(\frac{\Gamma}{\Theta}\right) \ll 1$ is usually fulfilled down to very low temperatures. Therefore the expression for k (see item 3) can be written in the form

$$k \simeq B_1 \frac{2\Gamma}{\Theta} e^{-E_0/\Theta} = B\,\frac{\hbar\omega}{\pi}\exp\left[-2\tau(E_0) - \frac{E_0}{\Theta}\right]. \tag{8}$$

Then the ratio of the reaction-rate constants for isotopes (for example, H, D) is

$$\frac{k(\mu_2)}{k(\mu_1)} = \frac{B(\mu_2)\,\omega(\mu_2)}{B(\mu_1)\,\omega(\mu_1)} \exp\left\{\frac{E_0(\mu_1) - E_0(\mu_2)}{\Theta} - 2\left[\tau(E_0(\mu_2)) - \tau(E_0(\mu_1))\right]\right\}. \tag{9}$$

In (9) the pre-exponential factor is, in order of magnitude, equal to unity and depends only weakly on the mass of the isotopes. For $\mu_2 > \mu_1$, $2\{\tau[E_0(\mu_2)] - \tau[E_0(\mu_1)]\} > 0$ and $\frac{E_0(\mu_1) - E_0(\mu_2)}{\Theta} > 0$. Hence it follows that, for values of Θ satisfying the condition

$$\frac{E_0(\mu_1) - E_0(\mu_2)}{2\{\tau[E_0(\mu_2)] - \tau[E_0(\mu_1)]\}\,\Theta} > 1, \tag{10}$$

it may turn out that $k(\mu_1) < k(\mu_2)$. In this case there will be an inverse isotopic effect, i.e., the reaction rate in the case of the heavier isotope is greater than for the lighter one.

A calculation with the symmetric curve $V(x) = V(-x)$ of M-shaped form, with $V_1 = V_2 = V_0 = 12$ kcal, $V_3 = 6$ kcal, $OA = 0.3 \cdot 10^{-8}$ cm, and $A - B = 0.7 \cdot 10^{-8}$ cm (Fig. 1), leads to the value of the quasilevel $E_0(\mu_H) = 9$ kcal and $E_0(\mu_D) = 8.4$ kcal, where μ_H is the mass of the hydrogen atom and μ_D is the mass of deuterium. In this case the condition in item 2 is fulfilled for $\mu = \mu_H$ already at $T \sim 300$°K, whereas for $\mu = \mu_D$ only at $T < 240$°K. At $T \simeq 200$°K, for H we have $2\,\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right) \exp\left(\frac{V_0 - E_0}{\Theta}\right) \simeq 30$, while for D $2\,\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right) \exp\left(\frac{V_0 - E_0}{\Theta}\right) \simeq 4$. For the chosen values of the parameters of $V(x)$, even at very low temperatures $\mathrm{sh}\left(\frac{\Gamma}{\Theta}\right) \sim \frac{\Gamma}{\Theta}$ (at $T \simeq 10$°K

$\Gamma/\Theta \simeq 0.2$). The left-hand side in (10) is equal to unity at $T \simeq 100$°K. At $T \simeq 50$°K

$$\exp\left\{\frac{E_0(\mu_H) - E_0(\mu_D)}{\Theta} - 2\left[\tau(E_0(\mu_D)) - \tau(E_0(\mu_H))\right]\right\} \simeq 15$$

(see formula (9)).

Thus, at temperatures of 10–50°K, one may expect the manifestation of an inverse isotope effect.

In conclusion I express my deep gratitude to Prof. N. D. Sokolov for numerous discussions and a number of valuable comments.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
21 XI 1961

REFERENCES

1. S. Glasstone, K. Laidler, H. Eyring, *The Theory of Rate Processes*, IL, 1948.
2. I. I. Gol' dman, V. D. Krivchenkov, *Collection of Problems in Quantum Mechanics*, Moscow, 1957.
3. H. Eyring, D. Walter, D. Kimball, *Quantum Chemistry*, IL, 1948.
4. L. D. Landau, E. M. Lifshitz, *Quantum Mechanics*, Moscow–Leningrad, 1948.