KINETICS OF EXOTHERMIC REACTIONS BETWEEN MOLECULES AND MOLECULAR IONS

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The exothermic reaction between a molecular ion and a molecule $A^+ + B \rightarrow C^+ + D$ proceeds by formation of a long-lived complex $(AB)^+ = (CD)^+$ if the kinetic energy of A^+ and B is less than 0.1 eV. The cross section for formation of $(AB)^+$, due to polarization interaction, is of the order of 10^{-15}–10^{-14} cm^2. The probability of dissociation of $(AB)^+$ into C^+ and D is close to unity provided the state of the complex is independent of the initial particles $(A^+$ and B or C^+ and D); this assumption is justified. A detailed calculation of the $H_2^+ + H_2 \rightarrow H_3^+ + H$ cross section is given.

1. For the reaction

$$A^+ + B \rightarrow C^+ + D \tag{1}$$

to occur a close approach of the molecules A^+ and B is necessary so that the distance between their centers of inertia r is of the order of their dimensions, i.e., on the order of 2b, where b $= \hbar^2/m_e e^2$ is the Bohr radius.

The necessary condition can be found by means of classical mechanics if it is assumed that at large distances (r > 4b) the interaction of the ion with the molecule is given by the potential

$$U = -\alpha_i b^3 e^2/2r^4, \tag{2}$$

where α_i is the polarizability of the molecule in atomic units. The impact parameter of the collision (a) should satisfy the condition of impact of particles at the center of inertia:

$$a_i^2 \leqslant \sqrt{4\alpha_i b^3 e^2/m_i v_i^2} \,,$$

where m is the reduced mass and v_i is the velocity of relative motion of the molecules A^+ and B (i = 1) or of the molecules C^+ and D (i = 2). Thus the cross section for collisions producing close interaction between A^+ and B or between C^+ and D is

$$\sigma_i = \pi a_i^2 = \pi \sqrt{4\alpha_i b^3 e^2/m_i v_i^2}. \tag{3}$$

In the kinetics of the reaction we are concerned directly with the product

$$\sigma_i v_i = \pi \sqrt{4\alpha_i b^3 e^2/m_i} = \sqrt{\alpha_i/\mu_i} \cdot 0.92 \cdot 10^{-9} \text{ cm}^3/\text{sec}, \tag{4}$$

where μ_i is the reduced mass in units of the mass of the hydrogen atom.

The condition that classical mechanics be applicable, $m_i v_i a_i/\hbar \gg 1$, and that the interaction

be represented by potential of Eq. (2) (for r > 4b) sets limits on the kinetic energy of relative motion given by Eqs. (2)–(4):

$$\frac{e^2}{8\alpha_i b}\left(\frac{m_e}{m_i}\right)^2 \approx \frac{1}{\alpha_i}\frac{1}{u^2}10^{-6} \text{ eV} \ll \frac{m_i v_i^2}{2} < \frac{\alpha_i e^2}{512b} \approx \alpha_i \cdot 5 \cdot 10^{-2} \text{ eV}.$$

Since usually $\alpha_i \approx 2$–10 and the molecular ions exist at a temperature lower than 0.1 eV, the above kinetic energy limits are not important. For r = 3b and $\alpha_i = 6$ we have U = –1 eV from Eq. (2), and therefore we can take the binding energy of $(AB)^+$ to be of the order of 1–2 eV. Thus the energy of the system $(AB)^+ = (CD)^+$, produced by a collision of A^+ and B, reckoned from its minimum value, is equal to the binding energy of A^+ and B together with a thermal energy, i.e., it is given by $U_0 + T(k-3)/2$, where $U_0 \approx 1$–2 eV, the temperature is T < 0.1 eV and k is the number of the degrees of freedom of the molecules A^+ and B. It is natural to assume that upon collision this energy is distributed among all the degrees of freedom of the $(AB)^+$ molecule. It is unlikely that immediately after the collision, which takes a time $\tau \approx 2b/v_i \approx 10^{-14}$ sec, all the energy $U_0 + \theta T(k-3)/2$ is concentrated in the form of the energy of relative motion of A^+ and B; here $\theta T(k-3)/2$ is the kinetic energy, U_0 is the energy necessary to dissociate $(AB)^+$ into $A^+ + B$, and $(1-\theta)T(k-3)/2$ is the energy retained by the internal degrees of freedom of A^+ and B. We can also assume that after a time on the order of τ the coordinates and momenta of $(AB)^+$ can be found with equal probability at any point in their phase space for a given total energy and angular momentum of $(AB)^+$.

The assumption that the whole phase volume of the composite system is completely filled, independently of all the collisions of the type $A + B^+$ or $C + D^+$, gives the maximum probability of the reaction (1) for a given total energy of the system. This assumption is incorrect if, for example, the phase volumes of $(AB)^+$ and $(CD)^+$ are separated by a potential barrier considerably greater than $U_0/(k-3)$. Like the ergodic hypothesis for large closed systems, this assumption cannot be justified theoretically without solving the equation of motion, but it should be confirmed or rejected by experiment. Support for the assumption is given by the following:

1) all degrees of freedom are excited on collision, since r is no longer a separable variable when $r \approx b$;

2) the vibration and rotation frequencies of $(AB)^+ = (CD)^+$ are incommensurate;

3) nonlinear coupling produces continuous exchange of energy between various degrees of freedom which are separable in the linear approximation.

It follows that, on the average, a time which is long compared with τ should pass before there is a combination of amplitudes and phases corresponding to the decay $(AB)^+ \rightarrow A + B^+$ or $C + D^+$. This is because for a limited volume of $(AB)^+ = (CD)^+$ the decay into $A + B^+$ corresponds to a relatively very small phase volume. The energy of relative motion of $A + B^+$ should become greater than U_0, i.e., it should be of the order of 90% of the energy at the moment of collision. Even in the case of the decay $(AB)^+ \rightarrow C + D^+$ one degree of freedom should contain $\sim 50\%$ of the energy of the system.

An estimate of the lifetime of the composite system can be obtained only by making the assumption indicated above. The delay time for the process $(AB)^+ \rightarrow C + D^+$ is roughly of the order of

$$\tau \exp\{(U_0 - Q)(k - 3)/U_0\},$$

and the delay time for $(AB)^+ \rightarrow A + B^+$ is $1/\beta$ times greater [Eq. (7)].

On the hypothesis of equal distribution, the probability of the decay of $(AB)^+$ into $A^+ + B$ or $C^+ + D$ depends only on the total energy of the system and the absolute value of the angular momentum and is unaffected by whether the system is in the state $A^+ + B$ or $C^+ + D$ before formation of the $(AB)^+ = (CD)^+$ complex.

This "ergodic hypothesis" is assumed below for the case when the reaction (1) is not connected with an electronic transition, i.e., when the electron states change adiabatically. The same hypothesis can also be used when the reaction is connected with an electronic transition $A^+ + B \rightarrow A + B^+$ if the mean time of the decay $(AB)^+ \rightarrow A^+ + B$ exceeds the mean delay of the electronic transition.

From the above hypothesis and the principle of detailed balancing we obtain

$$\overline{\sigma_{12}v_1}\Delta\Gamma_1 = \overline{\sigma_1 v_1}\,\overline{w}\Delta\Gamma_1 = \overline{\sigma_2 v_2}(1 - \overline{w})\Delta\Gamma_2 = \overline{\sigma_{21}v_2}\Delta\Gamma_2. \quad (5)$$

Here $\overline{w}$ is the probability of the decay $(AB)^+ \rightarrow C^+ + D$ averaged over the total angular momentum. The products $\sigma_i v_i$ are averaged over the momenta of the molecules B or D (if a molecule has a dipole moment then this contributes in practice to α only when the angular momentum of the molecule is zero).

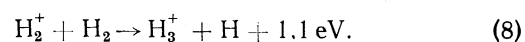From Eq. (5) it follows that the kinetics of the reaction (1) is governed by the quantity

$$\overline{\sigma_1 v_1}\,\overline{w} = \overline{\sigma_1 v_1}/(1 + \beta) \approx \overline{\sigma_1 v_1}. \quad (6)$$

Since $w = 1/(1 + \beta)$, where, from Eqs. (5) and (6),

$$\beta = \sqrt{\overline{\alpha_1 m_2/\alpha_2 m_1}}\,\Delta\Gamma_1/\Delta\Gamma_2, \quad (7)$$

and the phase volume $\Delta\Gamma_1$ for an energy $T(k-3)/2$ is usually much smaller than the phase volume $\Delta\Gamma_2$ corresponding to an energy $T(k-3)/2 + Q$ (Q is the energy of the reaction), β is very small and can be neglected.

2. Let us consider

$$H_2^+ + H_2 \rightarrow H_3^+ + H + 1.1 \text{ eV}. \quad (8)$$

In the ground state we have for H_2 $\alpha = \alpha_1 = 5.4$ and for H we obtain $\alpha = \alpha_2 = 4.5$, $\mu_1 = 1$, $\mu_2 = \frac{3}{4}$. The H_2 molecule has no dipole moment. The vibrational degrees of freedom of H_2 and H_2^+ at the temperature ≈ 0.05 eV are not excited, so that the total energy is $\epsilon_1 \approx T(k-3)/2 = 3.5 T$. Here

$$\Gamma_1 = V\int M\,dM M_+\,dM_+\,p_1^2\,dp_1/2\pi^3\hbar^7,$$

$$M^2/2J + M_+^2/2J_+ + p_1^2/2m_1 \leqslant \epsilon_1 \approx 3{,}5T,$$

$$\Gamma_1 = (8\sqrt{2}/105\pi^3)(VJJ_+ m_1^{3/2}\epsilon_1^{7/2}/\hbar^7),$$

$$\Delta\Gamma_1 = (4\sqrt{2}/15\pi^3)(VJJ_+ m_1^{3/2}\epsilon_1^{5/2}\Delta\epsilon/\hbar^7), \quad (9)$$

where M, M_+, J, and J_+ are the angular momenta and the moments of inertia of H_2 and H_2^+.

In the H_3^+ molecule both rotational and vibrational degrees of freedom have to be taken into account. Since $\hbar\nu_1$, $\hbar\nu_2$ and $\hbar\nu_3$ are of the order of several tenths of an electron volt and the total energy is $Q + \epsilon_1 \approx 1.3$ eV, we cannot replace sum-

mation over the quantum numbers $n_i = 0, 1, 2, \ldots$ by integration:

$$\Gamma_2 = V \sum_{n_1, n_2, n_3} \int dM_x dM_y dM_z p_2^2 \, dp_2 / 8\pi^4 \hbar^6,$$

$$\frac{M_x^2}{2J_x} + \frac{M_y^2}{2J_y} + \frac{M_z^2}{2J_z} + \frac{p_2^2}{2m_2}$$

$$\leqslant (Q + \varepsilon - n_1 \hbar \nu_1 - n_2 \hbar \nu_2 - n_3 \hbar \nu_3) \geqslant 0,$$

$$\Delta\Gamma_2 = \frac{V}{8\pi^2\hbar^6} \sum (Q + \varepsilon_1 - n_1 \hbar \nu_1 - n_2 \hbar \nu_2$$

$$- n_3 \hbar \nu_3)^2 \sqrt{J_x J_y J_z}, \; m_2^{3/2} \Delta \varepsilon, \qquad (10)$$

where $M_{x,y,z}$ and $J_{x,y,z}$ are the angular-momentum projections and the moments of inertia along the principal axes of inertia of H_3^+.

From Eqs. (6), (9), and (10) it is found that

$$\beta = \frac{32\sqrt{2}}{15\pi} \sqrt{\frac{\alpha_1}{\alpha_2}} \frac{m_1}{m_2} \frac{JJ_+\varepsilon_1^{1/2}}{\hbar \sqrt{J_x J_y J_z}} \varepsilon_1^2$$

$$\times \left[\sum_{n_1, n_2, n_3} (Q + \varepsilon_1 - n_1 \hbar \nu_1 - n_2 \hbar \nu_2 - n_3 \hbar \nu_3)^2 \right]^{-1}.$$

If the protons in H_3^+ lie at the vertices of an equilateral triangle, then

$$J_x = J_y = J_0, \qquad J_z = 2J_0, \qquad \sqrt{J_x J_y J_z} = \sqrt{2} J_0^{3/2}.$$

Assuming that $\epsilon_1 = 3.5\,T \approx 0.2$ eV and taking only the first term in the sum over n_1, n_2, n_3 ($n_i = 0$) we obtain $\beta = 0.046$ for $Q + \epsilon_1 = 1.3$ eV, $JJ_+ / \sqrt{J_x J_y J_z} \approx 3 \times 10^{-21}$ g$^{1/2}$-cm. When all the terms of the sum are included, the quantity β is about 10 times smaller. Thus obviously we can neglect β in Eq. (6) and we obtain for the reaction (8):

$$\overline{v_1 \sigma_{12}} \approx \sigma_1 v_1 = \sqrt{\alpha_1/\mu_i} \cdot 0.92 \cdot 10^{-9} \text{ cm}^3/\text{sec}$$

$$= 2.1 \cdot 10^{-9} \text{ cm}^3/\text{sec}.$$

This value agrees in order of magnitude with the current of H_3^+ ions in an H_2^+ ion source.[1]

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[1] P. M. Morozov and L. N. Pil'gunov, ZhTF and Soviet Phys. Tech. Phys. (in press).

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