EXPERIMENTALLY VERIFIED RESULTS OF THE PRINCIPLE OF MINIMUM TRANSMITTED IMPULSES FOR SUBSTITUTION REACTIONS

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UDC 541.124.13

In the works of the authors and of V. V. Tolmachev [1, 2], it has been shown that, out of the overall theoretical concepts, there follows the obvious course for a number of the simplest chemical substitution reactions:

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

where R_k are arbitrary fragments (radicals, atoms, or ions). The reacting particles approach each other, overcoming an energy barrier with a height of W_i and reach the reaction region. During the passage through the reaction region, there takes place a rapid rearrangement of the light subsystem (electrons), with a minimum possible change in the state of motion (impulses) of the heavy nuclei. This change must satisfy the laws of the conservation of energy and momentum, taking into account the discrete nature of the energy levels of the internal movement in the corresponding states (a close confirmation has already been given in [3]). The products, forming in the reaction region, are dispersed with an effective potential barrier with a height of W_f and W_f can, in principle, be determined from the elastic scattering of the corresponding fragments. The reaction picture presented differs substantially from the traditional picture, in which there is postulated the formation of an active (collision) complex $R_1 \cdots R_2 \cdots R_3$. As a result, from the overall theory, as has been already demonstrated in [1, 2], there flow the following conclusions.

1. The cross section of reaction (1), with given initial and final quantum numbers, should have characteristic maxima, at energies of the initial relative motion, E_{res}:

$$E_{res} = W_i + {}^1/_2(1 \pm \gamma)(Q_r + \Delta\varepsilon); \quad Q_r = Q - W_i + W_f, \tag{2}$$

where the plus sign corresponds to $(Q_r + \Delta\varepsilon) > 0$ and the minus sign to $(Q_r + \Delta\varepsilon) < 0$; Q is the heat effect of the reaction at absolute zero, and $\Delta\varepsilon = \mathscr{E}_f - \mathscr{E}_i$ is the difference between the internal energies of the fragments before and after the reaction. In the case of monoatomic fragments R_k

$$\mathscr{E}_\alpha = n_\alpha \hbar\omega_\alpha + \hbar^2 l_\alpha (l_\alpha + 1)/2I_\alpha \quad (\alpha = i, f). \tag{3}$$

The value of γ is expressed in terms of the masses, m_k, of the fragments

$$\gamma = \left(1 + 4\,\frac{m_1^2 m_3^2 + m_1 m_2 m_3 (m_1 + m_2 + m_3)}{m_2^2 (m_1 + m_2 + m_3)^2}\right)^{1/2}, \tag{4}$$

only if, simultaneously, the inequalities $m_2 \ll m_1$ and $m_2 \ll m_3$ are not satisfied. In view of the finite dimensions of the reaction region and of the boundary limitations, the values of the cross sections at high l_α (larger than 10-20) and small (in comparison with the fractions of the vibrational quantum number) values of $Q_r + \Delta\varepsilon$, are substantially decreased. The width of the resonance maximum of the cross sections is given by the formula

$$\Gamma_{if} \cong \left\{(Q_r + \Delta\varepsilon)\,\frac{[m_1^2 m_3^2 + m_1 m_2 m_3 (m_1 + m_2 + m_3)]\,(n_i + 1)\hbar\omega_i\,(n_f + 1)\hbar\omega_f}{m_2^2 (m_1 + m_2 + m_3)^2 [(n_i + 1)\hbar\omega_i + (n_f + 1)\hbar\omega_f]}\right\}^{1/2}. \tag{5}$$

2. With exothermic reactions $(Q_r + \Delta\varepsilon < 0)$ the most intensive transitions correspond to the conditions $\mathscr{E}_i \simeq 0$ and $\mathscr{E}_f \simeq |Q_r + \Delta\varepsilon|$ with an accuracy up to fractions of $\hbar\omega_\alpha$. With endothermic reactions $(Q_r + \Delta\varepsilon > 0)$, $\mathscr{E}_f \simeq 0$ and $\mathscr{E}_i \simeq Q_r + \Delta\varepsilon$. Thus, in the exothermic case, almost all of the heat effect of the reaction manifests itself in the form of the excitation of internal movements, and is not distributed uniformly with respect to degrees of en-

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Institute of Electrochemistry, Academy of Sciences of the USSR. Translated from Doklady Akademii Nauk SSSR, Vol. 186, No. 6, pp. 1344-1347, June, 1969. Original article submitted March 21, 1969.

TABLE 1. Calculation of the Activation Energies of the Reactions of Hydrogen Isotopes

Reaction	Source	Activation energy, kcal/mole		Error, %
		experiment (mean value)	calculated	
$H + pH_2$	[4]	8,8	9,1	~3
$H + pD_2$	[5]	7,6	7,4	~3
$D + H_2$	[6]	9,1	8,8	~3
$H + D_2$	[7]	7,3	7,6	~4

Note: The experimental values of the activation energy in Tables 1 and 2 were obtained using formula (9).

ergy, as would be the case in the formation of an activated complex. In the endothermic reaction, there enter preferentially molecules with excited internal movements.

3. The angular dependence of the cross section of the reaction $\sigma_r \sim \sigma$, where σ is the total differential cross section of the scattering.

The above quantitative data are in agreement with data obtained for substitution reactions in molecular beams and for a number of thermal reactions. For the further comparison of theoretical deductions with the results of the investigation of the most simple thermal reactions, which is the aim of the present work, it is necessary to carry out an averaging of the cross sections with respect to an equilibrium distribution. In a first approximation, leaving only the contributions of the two transition bands, most intense and nearest to the threshold, and sufficiently narrow, we obtain the approximate expression for the rate constant of the reaction k(T)

$$k(T) = Ae^{-E_1/kT} + Be^{-E_2/kT}, \tag{6}$$

where A and B depend relatively weakly on the temperature, and for the exothermic reaction

$$E_1 = W_i + (|Q_r| - n_f^{cr}\hbar\omega_f)\cdot{}^1/_2(\gamma - 1),$$
$$E_2 = W_i + ((n_f^{cr} + 1)\hbar\omega_f - |Q_r|)\cdot{}^1/_2(\gamma + 1), \tag{7}$$

and for the endothermic reaction

$$E_1 = W_i + (Q_r - n_i^{cr}\hbar\omega_i)\cdot{}^1/_2(\gamma + 1) + n_i^{cr}\hbar\omega_i,$$
$$E_2 = W_i + ((n_i^{cr} + 1)\hbar\omega_i - Q_r)\cdot{}^1/_2(\gamma - 1) + (n_i^{cr} + 1)\hbar\omega_i. \tag{7'}$$

Here, for simplicity, we assume that R_k are monoatomic fragments and that the value of $\mathscr{E}_\alpha \cong n_\alpha\hbar\omega_\alpha$ and n_α^{cr} ($\alpha = i, f$) which are of interest to us are determined by the condition

$$0 < |Q_r| - n_\alpha^{cr}\hbar\omega_\alpha \leqslant \hbar\omega_\alpha. \tag{8}$$

In this case, the empirical activation energy, E_a, is equal to

$$E_a = -k\frac{d\ln k(T)}{d(1/T)} = \frac{E_1Ae^{-E_1/kT} + E_2Be^{-E_2/kT}}{Ae^{-E_1/kT} + Be^{-E_2/kT}} = (1-\lambda)E_1 + \lambda E_2, \tag{9}$$

where the parameter λ, lying in the interval from zero to unity, takes into account the ratio of the cross sections for two groups of transitions, and includes effectively also the partial effect of the rotations. Here the Arrhenius law is experimentally observed in the temperature interval, ΔT, satisfying the condition

$$|\Delta T| / T_m < E_a kT_m[\lambda(1-\lambda)]^{-1} / (E_2 - E_1)^2,$$

where T_m is the mean temperature of the experiments. As a result of Eqs. (7) and (8), the allowable interval, ΔT, reaches hundreds of degrees. Thus, for the endothermic reaction*

$$E_a = W_i + [(\lambda\gamma - {}^1/_2(\gamma - 1))\, n_i^{cr} + \lambda\cdot{}^1/_2(\gamma + 1)]\hbar\omega_i - (\lambda\gamma - {}^1/_2(\gamma - 1))Q_r + Q_r \tag{10}$$

and for the exothermic reaction

$$E_a = W_i + [(\lambda\gamma - {}^1/_2(\gamma - 1))\, n_f^{cr} + \lambda\cdot{}^1/_2(\gamma + 1)]\hbar\omega_f - (\lambda\gamma - {}^1/_2(\gamma - 1))|Q_r|. \tag{10'}$$

In this case, as can be verified, taking account of the determination of Q_r, the activation energies of the forward and backward reactions differ by Q.

* In [1, 2] somewhat differing designations and expressions for E_a were used.

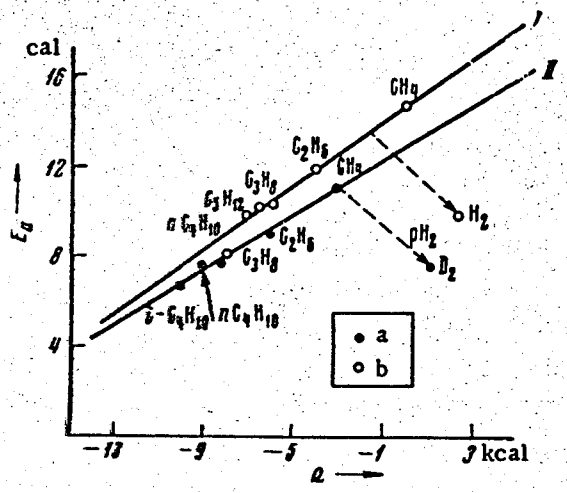

Fig. 1. Dependence of the activation energy E_a on Q for the reactions H + RH (a) and CH_3 + RH(b) according to the data of [11]. The straight lines are Polyani-Semenov formulas. The dotted lines with arrows are deviations from the Polyani-Semenov formula according to the proposed theory for fragments of comparable mass.

TABLE 2. Comparison with Experiment of Calculated Activation Energies for the Reactions H + X_2 at W_i = 1.38 kcal and α = 0

Reaction	Heat effect, kcal	Exptl. mean value of E_a	Source	Cal. value of E_a
H + F_2	−93	2,4	[10]	1,74
H + Cl_2	−44	1,8	[10]	1,42
H + Br_2	−42	~0,9	[11]	1,38
H + J_2	−35	~0,7	[11]	1,38

It is interesting above all to compare the formulas obtained with data, obtained with an accuracy of ~5% from measurements of the activation energy of reactions of the isotopes of hydrogen (see Table 1), when all $W_i \cong W_f$ and $n_\alpha^{cr} = 0$. Here, the method of least squares, taking account of the change in the values of the vibrational quanta, permitted obtaining optimal values of the parameters $W_\alpha \cong 3.2$ kcal/mole and $\lambda = 0.35$. It is characteristic that the overall isotopic course of the change in the activation energy, which is difficult to explain within the framework of the standard concepts, is found to be correct. This course must evidently change with an increase in the temperature, when it is already impossible to limit ourselves to a rough approximation for two systems of levels with constant values of λ. The latter fact explains, in our opinion, the results of measurements at higher temperatures [8]. It is interesting that the main contribution to the activation energy of the hydrogen isotopes in the model under consideration is made not by the repulsion connected with W_i, but by the multi-particle character of the phenomenon.* The correctness of the concepts set forth can, evidently, in principle, be verified qualitatively (separating analytically, from the experiments, the Arrhenius part of the temperature dependence from the possible tunnel effect) in experiments in which, as hydrogen isotopes, there enter thermal μ^- or, in particular, positrons.† In the latter case $\gamma \simeq 1$, since $E_2 >> E_1$ and, consequently, $\lambda \simeq 0$. Thus, for the reactions of a positron, the activation energy should decrease to a few kilocalories, and becomes a measure of the true elastic repulsion, W_i.

It is particularly significant that formulas (10) and (10') explain the empirical Polyani-Semenov rule [9] for activation energies, as well as the divergences observed from this rule. According to this rule, the activation energy of reactions (1) with respect to a homologous series of one of its fragments, varies as a linear function of the

* The conclusion as to the possible role of W_i can change with a more accurate taking into account of the contribution of rotations; in view of the comparatively large value of the rotational quantum number in the first two equations of Table 1, there must be taken into account the effects of symmetry, excluding rotation, and taking I_α into account or not.

† The reasons leading to the principle of minimal transmitted impulses, are retained also for positron substitution reactions. There is a decrease only in the threshold weakening with respect to the inlet channel.

heat effect: $E_a = E_0 + \alpha Q$. In this case, it is not trivial that α is usually less than unity for an endothermic direction of the reactions. From Eqs. (10) and (4), there is actually obtained the Polyani-Semenov rule: the coefficient α depends on the mass m_k. However, with invariable values of m_1 and m_2 ($m_1 < m_3$), for example, the dependence on m_3 will be marked only if the change of m_3 for the homologous series is comparable with m_3. Standard examples of the Polyani-Semenov rule for reactions, to which the theory developed can be extended, are shown in Fig. 1; the characteristic features of the experimental data are explained in a natural fashion with reasonable values of the selected parameters λ and W_i. With comparable masses, m_1, m_2, and m_3, when it is impossible to neglect the dependence of α on the mass, there are obtained divergences from the Polyani-Semenov rule corresponding to the theory. The reason for the above-mentioned fact that, for endothermic reactions usually $\alpha < 1$, is, according to the proposed theory, the change in the contributions of E_1 and E_2 to E_a with a change in Q. At $m_2 \gg m_1$, when $\gamma \simeq 1$, in an exothermic reaction E_2, according to Eq. (7), is substantially greater than E_1 and, correspondingly, it should be true that $\alpha \simeq 0$. In the latter case, for exothermic reactions we should obtain a small negative Polyani coefficient and, correspondingly, a somewhat larger unit of the Polyani coefficient for an endothermic reaction. This has actually been confirmed qualitatively* for the reactions $H + X_2$, where X are halogens, as is evident from Table 2. In the calculation of these reactions, in contrast to the cases shown in Fig. 1, it is essential to take into account the difference in the vibration frequencies of the final products.

In conclusion, we take note of the special characteristics of reactions between charged ions of different signs, and of reactions between ions and dipolar molecules with an ionic bond (in the initial state for endothermic reactions and in the final state for exothermic reactions), as well as of the closely related "harpoon" reactions [12]. Since in this case, the above-mentioned threshold limitations are removed due to the presence of reactions at a distance, contributions are made to the reaction by transitions with large moments and optimal values of the kinetic energy "drift" toward the energy threshold. As a result, the activation energy should decrease substantially and W_i should be determined. This fact is remarked in the experiments of [13]. The excitation of particularly high rotations in exothermic reactions of the latter type can be, in principle, followed experimentally.

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* In comparison of theory with experiment, there must be borne in mind the rather large relative error in the experimental determination of E_a in the given reactions, and the presence of a contribution to the exponential temperature dependence which is substantial at small activation energies.