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Abstract

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ON THE RELATION BETWEEN THE ACTIVATION ENERGY AND THE HEAT OF REACTION

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It has long been established empirically ([1]) that for many reactions occurring both in the gas and in the liquid phase there exists a simple relation between the activation energy E and the heat of reaction Q, which for the exothermic direction may be written in the following form:

$$E = a - bQ, \tag{1}$$

where a and b are constants, with $0 < b < 1$. Subsequently, the linear relation between E and Q was observed and discussed by many authors ([2–6]). In the literature, however, there is no sufficiently clear justification of relation (1). The most detailed theoretical analysis of this relation was made by Evans and Polanyi ([7]), but their derivation cannot be considered irreproachable. In order to obtain relation (1), these authors postulate that both the heat of reaction and the activation energy depend linearly on some parameter χ. This parameter, in its meaning, should reflect the features of molecular interaction in a certain series of reactions as a function of the structural characteristics of the reactants. It is, however, very doubtful that in the general case one could find a parameter satisfying this requirement and at the same time having such a simple connection with the heat of reaction and the activation energy. If, for example, the value of the field potential at some point near one of the molecules is chosen as the parameter, then, since in the corresponding wave equation this potential enters as a function of the coordinates, the dependence of the eigenenergy of the system on χ will, generally speaking, prove to be complicated*.

Below we shall attempt to give a justification of relation (1) free from the indicated shortcoming.

For definiteness we shall carry out the reasoning as applied to gas radical exchange reactions. Consider an adiabatic reaction of the form

$$\mathrm{RB} + \mathrm{R}' \to \mathrm{R} + \mathrm{BR}', \tag{2}$$

where B is an atom, and R and R′ are atoms or radicals. As experiment shows, relation (1) is satisfied with sufficient accuracy for a series of reactions in which either R or R′ varies, the varied reactant being a radical. For definiteness we shall suppose that in the series of reactions under consideration R varies, while R′ remains the same. All the arguments can without difficulty be carried out also for the converse case, and also for the case in which the atom B varies.

Let us choose some substituent R_0 as the standard and assume that the change in the potential energy of the system $R + B + R'$ upon passing from R_0 to an arbitrary R is determined by the change of some–

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* To obtain in this way a linear dependence of the energy on χ would be possible only within the framework of perturbation theory. The derivation of relation (1) set out below is essentially equivalent to the application of this method.

second parameter χ, whose magnitude depends on the nature of R. The concrete physical meaning of this parameter may be different and is of no importance in what follows. For example, it may be the effective charge entering the expression for the wave function and acting on the outer electrons of the atom or radical R on the part of the nuclei, or the potential of the electric field near R, etc. On passing from one radical R to another, in the general case, both the depth of the potential wells and the height of the potential barriers, as well as the values of the corresponding internuclear distances, evidently change. However, as will be seen below, the dependence of these distances on χ in the first approximation is not reflected in the positions of the extrema.

Let us denote by x_1, x_2, and x_3 the distances R—B, B—R', and R—R',* respectively, and by l the reaction coordinate. In the initial state $(RB + R')$, $x_1 = x_1^0$ is the equilibrium distance in the molecule R—B; in the final state $(R + BR')$, $x_2 = x_2^0$ is the equilibrium distance in the molecule B—R'; in the activated state $(R \cdot B \cdot R')$, $l = l^*$ represents a definite combination of the corresponding values of the coordinates x_1^*, x_2^*, x_3^*. Near this point, l coincides with one of the normal coordinates of the activated complex; we shall denote its two other normal coordinates by l_1 and l_2 (in the case of a linear activated complex there is also a fourth normal coordinate). In accordance with what has been said, the potential-energy surface for reaction (2), $\varepsilon(x_1, x_2, x_3, \chi)$, has three extrema:

I when $x_2 = x_3 = \infty, \qquad x_1 = x_1^0$ –minimum $(RB + R')$,

II when $x_1 = x_3 = \infty, \qquad x_2 = x_2^0$ –minimum $(R + BR')$,

III when $x_1 = x_1^*,\ x_2 = x_2^*,\ x_3 = x_3^*$ –maximum with respect to l and minimum with respect to l_1 and l_2 $(R \cdot B \cdot R')$.

At these points the equalities

$$(\partial\varepsilon/\partial x_1)_I = (\partial\varepsilon/\partial x_2)_{II} = (\partial\varepsilon/\partial x_j)_{III} = 0, \quad (j = 1, 2, 3), \tag{3}$$

are fulfilled, where the indices I, II, and III denote the sets of coordinates corresponding to the three indicated extrema. By virtue of these equalities, the values x_1^0, x_1^*, x_2^*, x_3^* are certain functions of χ, whereas x_2^0 obviously does not depend on χ.

Let us now assume that the change in the parameter χ with the change in the nature of R is small, i.e. $\Delta\chi \ll \chi$. This assumption may be satisfied if R is a radical YX and, in the series of reactions considered, only Y changes while X remains unchanged, as, for example, in a homologous series of radicals. We introduce the notation $\xi = \Delta\chi/\chi_0$, where χ_0 is the value of χ in the case of the reaction with the radical R^0, adopted as the standard. Expressing the energy ε and the coordinates x_1^0 and x_i^* $(i = 1, 2, 3)$ as functions of ξ, we expand ε in a series in ξ near each of the indicated extrema and restrict ourselves to the linear terms:**

$$\varepsilon_I = \varepsilon_I^0 + \xi\left(\frac{\partial\varepsilon_I}{\partial\xi}\right)_{\xi=0} + \xi\left(\frac{\partial\varepsilon_I}{\partial x_1^0}\frac{\partial x_1^0}{\partial\xi}\right)_{\xi=0};$$

$$\varepsilon_{II} = \varepsilon_{II}^0;$$

$$\varepsilon_{III} = \varepsilon_{III}^0 + \xi\left(\frac{\partial\varepsilon_{III}}{\partial\xi}\right)_{\xi=0} + \xi\sum_{i=1,2,3}\left(\frac{\partial\varepsilon_{III}}{\partial x_i^*}\frac{\partial x_i^*}{\partial\xi}\right)_{\xi=0}.$$

* As the distance between an atom and a radical (x_1 or x_2) we shall take the distance between B and that atom of the radical with which B is directly bonded in the molecule RB or BR'. The corresponding quantity will be understood as the distance between two radicals (x_3). The normal coordinates of the system $R \cdot B \cdot R'$ will be assumed to depend only on x_1, x_2, and x_3.

** In these equalities, ε_I^0, ε_{II}^0, and ε_{III}^0 are the values of ε_I, ε_{II}, and ε_{III} at $\xi = 0$.

By virtue of conditions (3), in the first and last equalities on the right-hand side only the first two terms are different from zero. Accordingly, for the heat of the (exothermic) reaction and the activation energy (for absolute zero temperature and neglecting the difference in zero-point energies) we find

$$Q \equiv \varepsilon_I - \varepsilon_{II} = Q_0 + \xi G, \tag{4}$$

$$E \equiv \varepsilon_{III} - \varepsilon_I = E_0 - \xi G^*, \tag{5}$$

where $Q_0 = \varepsilon_I^0 - \varepsilon_{II}^0$, $E_0 = \varepsilon_{III}^0 - \varepsilon_I^0$ are the heat of reaction and the activation energy for R^0, taken as the standard;

$$G = \left(\frac{\partial \varepsilon_I}{\partial \xi}\right)_{\xi=0}, \qquad G^* = \left(\frac{\partial \varepsilon_I}{\partial \xi}\right)_{\xi=0} - \left(\frac{\partial \varepsilon_{III}}{\partial \xi}\right)_{\xi=0}. \tag{6}$$

Eliminating ξ from (4) and (5), we obtain relation (1)

$$E = a - bQ,$$

in which

$$a = E_0 + Q_0 \frac{G^*}{G}, \qquad b = \frac{G^*}{G}. \tag{7}$$

Let us now suppose that the transition from the standard R^0 to an arbitrary R shifts all points of the potential surface in one and the same direction, at least in the region from the initial well to the barrier*. This assumption is quite natural in the case when, in a series of radicals $\dot{R} \equiv Y\dot{X}$, the individual members differ only in the nature of the substituent Y. Under the stated assumption the derivatives $\left(\frac{\partial \varepsilon_I}{\partial \xi}\right)_{\xi=0}$ and $\left(\frac{\partial \varepsilon_{III}}{\partial \xi}\right)_{\xi=0}$ have the same signs. Further, since the influence of a change in R on the potential-energy surface is transmitted mainly owing to the direct interaction of R with atom B, and since $x_1^0 < x_1^*$, it is not difficult to see that $\left|(\partial \varepsilon_I/\partial \xi)_{\xi=0}\right| > \left|\partial \varepsilon_{III}/\partial \xi)_{\xi=0}\right|$. Taking (6) and (7) into account, it follows from what has been said that $0 < b < 1$, which agrees with the experimental data.

For the derivation of relation (1) given above, the essential assumption is that the influence of R on the potential-energy surface is determined by the change of only one parameter, and that its change is sufficiently small. This assumption, as noted above, is permissible for a series of reactions

$$RB + R' \to R + BR',$$

in which the radicals $R \equiv Y\dot{X}$ differ from one another only in the nature of Y. To a lesser degree the stated assumption is permissible for a series in which the radicals R differ in the nature of atom X, or in which the nature of atom B changes, since in this case the changes of the parameter χ cannot be sufficiently small. It also follows from the derivation that relation (1) cannot hold for a series of reactions in which the nature of two components changes (for example, R and B, or R and R'), or in which some of its members have so branched a substituent Y that a direct strong interaction ("steric repulsion") arises between B and Y. Under these conditions, in the general case, the change of the potential surface will be determined by the change of more than one parameter.

The experimental data confirm these conclusions. When the experimental values of the activation energy and heat of reaction ([6]) are plotted, the points lie sufficiently close to one and the same straight line in those cases where, in fact, only the substituent Y varies in the radical R (or R'). This regularity is obeyed less well if, in a series of reactions,

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* In other words, it is assumed that the potential curves corresponding to different reactants do not intersect in the indicated region. For a discussion of this question see, for example, ([8]).

varied atom X or B.* If, however, the values of E and Q are plotted for reactions of the type $RB + R' \to R + BR'$, differing in the nature of two or, still more, all three components (R, B, R'), then the points do not fall on a straight line, but mainly lie within a band of width ~ 3.5 kcal and in some cases fall outside this band ([6]).

From the theoretical point of view, one should expect that, with further refinement of the experimental data for E and Q, it will turn out that, for reactions differing, for example, in the nature of two radicals, the values of a and b in equation (1) will be somewhat different.

This consideration is confirmed, for example, by the study of V. V. Voevodsky ([5]). He found that for a series of reactions

$$RH + R' \to R + HR',$$

in which R varies (R and R' are aliphatic radicals), the following relation may be written:

$$E = a - 0.27Q.$$

It turned out that the quantity a, which has the meaning of the activation energy at $Q = 0$, is related to the structure of R' and can be found for a series of radicals.

The dependence of a and b on the nature of the reacting molecules or ions is also well known for ionic, in particular protolytic, reactions (see the reviews in ([3])). However, so far only in some cases has it been possible to relate the value of b to the structural characteristics of the molecules (see ([9])).

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* Relation (1) is not fulfilled when one halogen atom, playing the role of atom B, is replaced by another; this is connected with the crossing of potential curves corresponding to different reactants ([2]) (see the footnote on p. 712).

Note: Figure translations are in progress. See original paper for figures.