Research on Activation Energy. I. A New Empirical Rule for the Calculation of Activation Energy(1)

By Kiyoteru OTOZAI

(Received May 8, 1951)

Introduction

Because of the difficulty of calculating in a solely theoretical way the activation energy for any sort of reaction, various kinds of empirical or semi-empirical rules have been proposed for the estimation of that energy. The general feature of the purely empirical rules so far proposed is the simplicity of their forms. But at the same time they can be applied only to a specified type of reaction. Moreover, none of these empirical rules provide any information on the geometrical configuration of the activated complex. Compared with these purely empirical methods, the so-called semi-empirical method of Eyring has a marked advance. It can be applied not only to any kind of reaction but it also enables us to presume the geometrical configuration and the

---

(1) Details will be publisled in Scientific Papers from the Osaka University.

dimensions of the activated complex. But unfortunately the estimation of the constant ρ, which represents a fraction of the Coulombic part in the total energy of the bond, and the knowledge of which is always necessary for the calculation of the activation energy according to this method, is at least at present not quite free from ambiguity. For this reason the author has sought a new empirical method of calculation, which makes use only of the experimentally measurable constants but gives us almost as accurate information as the semi-empirical method on the magnitude of the activation energy and the geometrical dimensions of the activated complex. The method reported here is one such which satisfies the above-mentioned requirements, although the theoretical basis for the calculation is not yet quite clear.

Fundamental Assumption

The distance r^*, which corresponds to the inflexion point on the potential-energy curve or the point, where the attractive force between two atoms becomes maximum, (cf. Fig. 1), is assumed to represent the length of the bond in an activated complex. This distance r^* will, therefore, be called the activated internuclear distance. Furthermore we will denote the bond, which appears only in an activated complex (see below) an activated bond. Then the present empirical rule can be summarized as follows: among all the possible structures, which can be constructed by the use of the fixed values of the activated internuclear distances of the bonds to be broken as well as to be formed, such a structure, in which the sum of the energies of the activated bonds becomes minimum, represents the structure of the activated complex and this minimum sum of the energies of the activated bonds gives the activation energy of the reaction, when it proceeds in the exothermic direction. The activation energy of the reaction in the endothermic direction can readily be calculated by the use of the so computed value of the activation energy in the exothermic direction and the heat of the reaction.

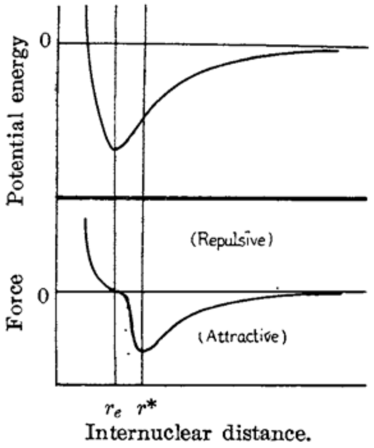
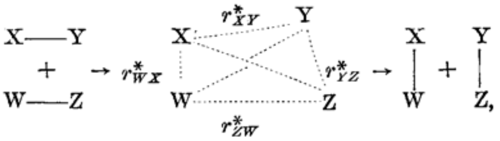


Fig. 1.—The activated internuclear distance.

Thus, for the tetratomic reaction of the type:



the bonds to be broken are X–Y and W–Z, those to be formed are X–W and Y–Z and the activated bonds, which appear only in an activated complex, are X...Z and Y...W. Hence, according to the present rule, among all the possible structures, which can be constructed by the use of the fixed values of the activated internuclear distances r^*_{XY}, r^*_{YZ}, r^*_{ZW}, and r^*_{WX}, such a structure, in which the sum of the energies of the activated bonds X...Z and Y...W becomes minimum, represents the structure of the activated complex, and this minimum sum of the energies gives the activation energy of the reaction, when it proceeds in the exothermic direction.

Carrying out the Calculation

One of the most important parts of the calculation according to the present rule is the determination of the potential-energy $U(r)$ between two atoms as a function of their internuclear distance. But as the ordinarily used Morse's equation was found not accurate enough for this purpose (see below), we have made use of Rydberg's equation:⁽²⁾

$$U(r) = -D_e\{a(r-r_e)+1\}e^{-a(r-r_e)},$$

in which D_e is the equilibrium dissociation energy, a is the characteristic constant for the given pair of atoms and r_e is the equilibrium internuclear distance. All of these constants can be calculated from the spectroscopic data according to the equations:

$$D_e = D + E_0,$$

---

(2) R. Rydberg, *Z. Phys.*, **73**, 381 (1932).

$$E_0=\frac{1}{2}N_A k\nu=1.45\times10^{-3}\omega_e,$$

$$a=9.28\times10^{-3}\omega_e\sqrt{\mu/D_e},$$

where E_0 represents the zero point energy and μ the reduced mass of the pair of atoms. Furthermore, it can readily be shown from Rydberg's equation that the activated distance r^*, which corresponds to the inflexion point on the potential energy curve, is expressed by the equation:

$$r^*=r_e+1/a.$$

The activation energies of some triatomic and tetratomic reactions calculated according to the present method are summarized in Tables 1 and 2 respectively, and compared with the experimental values given in the textbook of Glasstone, Laidler and Eyring⁽³⁾ as well as the values calculated by means of the semiempirical method of Eyring, where the energies are all expressed in kcal. units.

Table 1

Activation Energies of Some Triatomic Reactions

No.	Reaction	Activation energy		
		Observed	Calculated	
			i	ii
1	$H+p-H_2\rightarrow$ $o-H_2+H+0$	7	10.1	7.63 (20%)
2	$H+I_2\rightarrow$ $HI+I+35$	0	0.2	2.5 (10%) 1.8 (14%)
3	$I+H_2\rightarrow$ $IH+H-32$	34.2	41.2	43.3 (10%) 40.4 (14%)
4	$H+Br_2\rightarrow$ $HBr+Br+41$	1.2	0.3	3 (10%) 2.1 (14%)
5	$Br+H_2\rightarrow$ $BrH+H-16$	18	23.2	25.5 (20%)
6	$H+Cl_2\rightarrow$ $HCl+Cl+45$	2	0.7	2.7 (14%)
7	$Cl+H_2\rightarrow$ $ClH+H-1$	6	9.0	11.6 (20%)
8	$F+H_2\rightarrow$ $FH+H+45$	8	10.4	10.6 (10%) 6.3 (14%)

i, according to the present method.
ii, according to the semi-empirical method of Eyring, where the number in bracket indicates the value of the constant ρ used for the respective calculation.

Table 2

Activation Energies of Some Tetratomic Reactions

No.	Reaction	Activation energy		
		Observed	Calculated	
			i	ii
1	$H_2+H_2\rightarrow$ H_2+H_2+0	>59	76.4	*ca.* 90 (10%)
2	$H_2+I_2\rightarrow$ $2HI+3$	40	38.2	48.3 (14%)
3	$H_2+Br_2\rightarrow$ $2HBr+25$	>43	41.8	45 (10%) 39 (14%) 26.5 (20%)
4	$H_2+Cl_2\rightarrow$ $2HCl+44$	>36	51.0	54 (10%) 44.5 (14%) 29.5 (20%)
5	$H_2+F_2\rightarrow$ $2HF+129$	>25	92.2	50 (10%)
6	$Br_2+Cl_2\rightarrow$ $2BrCl+1$	14	11.3	—
7	$D_2+HCl\rightarrow$ $HD+DCl+0$	57	*ca.* 58	53 (17%) 43.6 (20%)

Discussion of Errors

When the results shown in Table 1 are compared with those in Table 2, it may be seen that the activation energies calculated according to the present method are generally somewhat too high (in the average about 3 kcal.) in comparison with the experimental values for the triatomic reactions (except for the endothermic reactions), while just the reverse is the case for the tetratomic reactions. However, the same tendency can also be seen for the values calculated by means of the semi-empirical method, although in this case the adequate choice of the constent ρ makes this difference somewhat obscure. Just this tendency seems to betray the difficulty in calculating the activation energy for both sorts of reactions by use of a single relation, as it is the case for the other empirical rules. Although the reason for this discrepancy is not yet clear, the following fact may tell us that at least a part of the inaccuracy attached to the present method is due to the lack of accuracy of the Rydberg's equation for large internuclear distances. Thus, for the activation energy of reaction No. 1 in Table 1:

$$H+p-H_2\rightarrow o-H_2+H,$$

Morse's equation gives 14.6 kcal. and Rydberg's equation gives 10.1 kcal. While from the potential-energy curve directly constructed by the use of the spectroscopic data we obtain 7.5 kcal., which agrees very well with the experimental value 7 kcal.

---

(3) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Company, New York and London, 1941.

Geometrical Dimensions of Activated Complex

According to the present method of calculation the total length of the activated complex of the type X...Y...Z is given by the sum of the activated distances r^*_{XY} and r^*_{YZ}, since the form of this sort of complex must be linear. When we compare the values so calculated of X...Y, Y...Z and X...Y...Z with those calculated by means of the semi-empirical method of Eyring, we find an interesting result, namely, that the total length of the activated complex calculated according to both methods agree very well whereas the respective distances X...Y and Y...Z in the complex sometimes show remarkable differences between two methods, as is shown in Table 3.

Table 3

Dimensions of Activated Complex of Some Triatomic Reactions

Activated complex X...Y...Z	Length of X...Y, Å.		Length of Y...Z, Å.		Length of complex X...Y...Z, Å.	
	i	ii	i	ii	i	ii
H ...H ...H	1.12	0.75	1.12	1.35	2.24	2.10
H ...Br...H	1.80	1.40	1.80	2.10	3.60	3.50
Br...H ...H	1.80	1.42	1.12	1.50	2.92	2.92
H ...Cl...H	1.65	1.33	1.65	2.10	3.30	3.43
Cl ...H ...H	1.65	1.30	1.12	1.40	2.77	2.70
H ...H ...Na	1.12	1.69*	2.55	1.94*	3.67	3.63*
H ...H ...K	1.12	1.84*	2.99	2.29*	4.11	4.13*

i, the present method. ii, the semi-empirical method.

* S. Shida and K. Nakata, the 2nd meeting of the Chemical Society of Japan, April 2, 1949.

Furthermore, as the constant a in Rydberg's equation does not vary so much from bond to bond and its mean value becomes 2.69 Å.$^{-1}$, we can roughly put

$$\begin{aligned} r^* &= r_e + 1/a \\ &= r_e + 0.37 \text{ Å.} \end{aligned}$$

So it may be said that the average length of a bond in an activated complex is about 0.37 Å. longer than the equlibrium bond-distance.

Length of Hydrogen Bond

The present method of calculation gives us some interesting information on the length of the hydrogen bond. If we assume, namely, the hydrogen bond of the type R—X...H...Y—R′ as a sort of an activated complex of the reaction

$$\text{R-X-H} + \text{Y-R}' \rightarrow \text{R-X} + \text{H-Y-R}'$$

the length of the activated complex X...H...Y of the reaction

$$\text{X-H} + \text{Y} \rightarrow \text{X} + \text{H-Y}$$

may give at least the lower limit of the distance between X and Y in the above-mentioned hydrogen bond, because the bond energies of the diatomic molecules X—H and H—Y will appreciably be greater than those of RX—H and H—YR, so that the activated distances of the former will be shorter than those of the latter. This expectation was found actually the case as shown in Fig. 2, except for F...H...F, in which, however, our calculated value 2.38 Å. agrees fairly well with the value 2.32 Å. calculated by Pauling.(4)

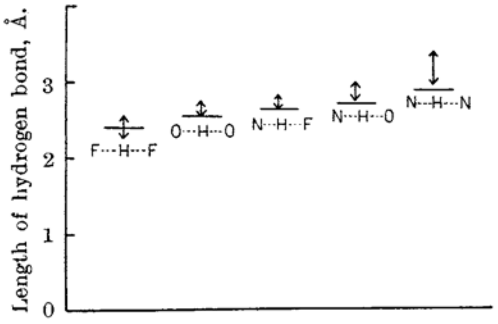
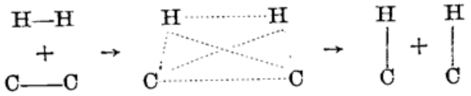


Fig. 2.—Length of the hydrogen bond.

Dissociated Adsorption of Hydrogen on Charcoal

As an example for the application of the present method to the heterogeneous reaction, we may cite the calculation of the activation energy for the dissociated adsorption of hydrogen on the surface of charcoal:



The activation energy calculated by means of the present method as a function of the C—C distance is plotted in Fig. 3 and compared with that of Sherman and Eyring,(5) who

---

(4) L. Pauling, "The Nature of Chemical Bonds", Cornell University Press, New York, 1940, p. 297.

(5) A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

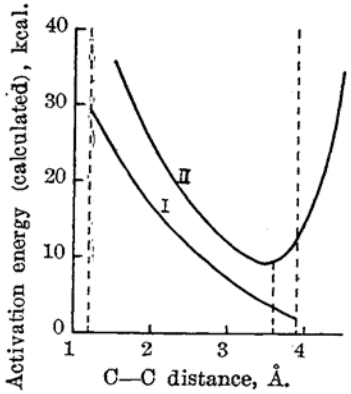


Fig. 3.—Activation energy of the dissociated adsorption of hydrogen on charcoal: I, by the present author; II, by Sherman and Eyring.

calculated the same energy by the use of the semiempirical method of Eyring putting $\rho=10$ %. The most favorable C—C distance for the adsorption, that is the distance, where the activation energy becomes mininum according to the present method, is 3. 92 Å. corresponding to the structure of the linear form. of the activated complex C...H...H...C, while this energy becomes minimum at the distance 3. 6 Å. according to the semi-empirical method. But it may be worth while to mention that both curves in Fig. 3 coincide completely if the value of ρ in the calculations according to the semi-empirical method is taken somewhat larger than 10%.

Summary

1. It has been assumed that the bond-distance in an activated complex is equal to the bond-distance corresponding to the inflexion point on the potential-energy curve of the pair of atoms.

2. According to this fundemental assumption, a new simple method of calculation of activation energy of reactions has been devised.

3. The method has been applied to some kinds of triatomic reactions and the double decompositions between two diatomic molecules with satisfactory results.

4. For the triatomic reactions, the geometrical length of the activated complexes computed by means of the present method agrees well with those calculated by means of the semi-empirical method of Eyring.

5. It has been shown that the present method of calculation gives some information on the lower limit of the length of the hydrogen bond.

6. The activation energy for the dissociated adsorption of hydrogen on the surface of charcoal has been calculated as a function of the distance between two carbon atoms. The result obtained agrees well with that obtained by Sherman and Eyring according to the semi-empirical method.

The author wishes to express his sincere thanks to Prof. T. Titani for his interest in this research. The author is also indebted to Dr. T. Horie for his kind information on the spectroscopic data.

Faculty of Science, Osaka University, Osaka