Research on Activation Energy. II.
Some Applications of the Empirical Rule

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Introduction

One of the authors has previously proposed a new empirical rule for the calculation of the activation energy and shown that the rule holds well for triatomic and tetratomic reactions.(1) The present report concerns further applications of the rule for the more complicated reactions. If we denote the distance

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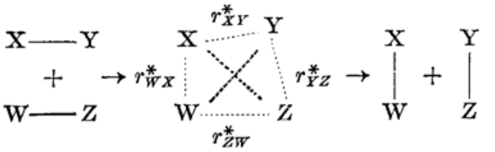
(1) K. Otozai, this Bulletin, **24**, 218 (1951). Details will be published in the Scientific Papers from Osaka University.

corresponding to the inflexion point on the potential-energy curve or to the maximum point on the attractive force curve between two atoms "*the activated internuclear distance*" and the bond, which appears only in the activated complex "*the activated bond*," the present rule can be expressed 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.

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 the activated complex, are X$\cdots$Z and Y$\cdots$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 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$\cdots$Z and Y$\cdots$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.

As the potential-energy function $U(r)$, which is necessary to carry out the calculations according to the present rule, Rydberg's equation:(2)

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

is adopted, where D_e represents the equilibrium dissociation energy, and r_e represents the equilibrium internuclear distance. And the constant a, which is characteristic of the pair of atoms, can be calculated by means of the equation:

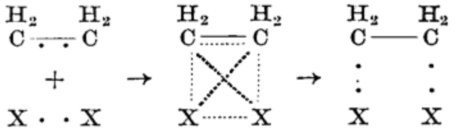
$$a = 9.28\times10^{-3}\times\omega_e\sqrt{\mu/D_e} = 38.3\times\sqrt{k_0/D_e},$$

where ω_e is the frequency of vibration (cm.$^{-1}$), μ the reduced mass per mole, and k_0 the force constant (megadyne/cm.). So it can readily be shown that the activated distance r^* is given by the equation:

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

Addition of Hydrogen and Halogen to Ethylene

The addition reaction of hydrogen or halogen to ethylene:



can be treated by means of the present method, if one of the double bonds of ethylene is assumed to be independent of the reaction. The data necessary for the calculation are tabulated in Table 1, where D_e of $\mathrm{C}\underset{\cdot\,\cdot}{—}\mathrm{C}$ bond was assumed as the difference between that of C═C and C—C, r^* of $\mathrm{C}\underset{\cdot\,\cdot}{—}\mathrm{C}$ bond the arithmetical mean of the internuclear distance of C═C and C—C, and r_e of C–Cl, C–Br and C–I the sum of the covalent radii of respective atoms.

Table 1

Fundamental Data Necessary for the Calculation for the Addition of Hydrogen and Halogen to Ethylene

Bond	$D=D_e$, kcal.	r_e, Å.	ω_e, cm.$^{-1}$	μ	a, Å.$^{-1}$	r^*, Å.
$\mathrm{C}\underset{\cdot\,\cdot}{—}\mathrm{C}$	41					1.44
Cl-Cl(3)	57					2.32
Br-Br(3)	46					2.64
I-I(3)	36					3.04
C-Cl	66.5(4)	1.76	712(5)	8.95	2.42	2.19
C-Br	54.0(4)	1.91	603(5)	10.42	2.46	2.32
C-I	45.5(4)	2.10	534(5)	10.96	2.44	2.51
H-H(3)	103					1.12
C-H	87(4)	1.09(7)	2988(8)	0.923	2.86	1.44
	80(6)				2.98	1.43

The results of the calculation are given in Table 2 and compared with the observed values as well as those calculated by the semi-empirical method of Eyring. From Table 2

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

(3) *Cf.* the preceeding paper.

(4) L. Pauling, "The Nature of Chemical Bonds," Cornell University Press, New York, 1940, p. 53.

(5) R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).

(6) H. Sponer, "Molekülspektren und ihre Anwendungen auf chemische Probleme," Julius Springer, Berlin, 1935.

(7) L. Pauling, "The Nature of Chemical Bonds," p. 168.

(8) I. Nitta, "The Structure of the Molecule," Tokyo, 1942, p. 126.

Table 2

Activation Energies for the Addiiion of Hydrogen and Halogen to Ethylene

Reaction	Activation energy					
	Addition			Reverse reaction		
	obs.	i	ii	obs.	i	ii
$CH_2{:}CH_2+H_2=$ $CH_3{\cdot}CH_3+30$	43	54.8 (46.4) (10)	43 (48) (11)	—	84.8 (62.4) (10)	—
$CH_2{:}CH_2+Cl_2=$ $CH_2Cl{\cdot}CH_2Cl+36$	—	34.8	25.2	—	70.8	80.4
$CH_2{:}CH_2+Br_2=$ $CH_2Br{\cdot}CH_2Br+21$	(30) (9)	31.0	24.4	—	52.0	50.2
$CH_2{:}CH_2+I_2=$ $CH_2I{\cdot}CH_2I+15$	—	20.2	22.4	(36) (9)	35.2	30.0

i. According to the present method.

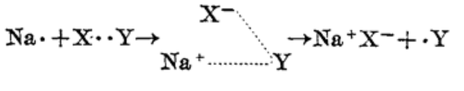
ii. Acccrding to the semi-empirical method of Eyring.

we can see that the present rule holds well for the addition of halogen but somewhat unsatisfactorily for the addition of hydrogen, while just the reverse is the case for the semi-empirical method of Eyring. But it may be worth noting to point out that the difference between the observed and calculated values according to the present method for the addition of hydrogen is remarkably reduced if D_e $=80$ kcal. is used for the C–H bond as is shown in the table.

Atomic Reactions involving Sodium and Halogen Atoms

Since the bond between sodium and halogen atoms can not be expressed in the usual manner by a single potential-energy curve, the present method can not be applied for the reaction involving these atoms without any additional assumptions. Polanyi *et al.*(12) have previously calculated the activation energies of the reactions of the sodium atom with methyl and phenyl halogenides by constructing the so-called potential-energy profile. But according to Eyring *et al.*(13) these calculated values may be in error, because no allowance is made for the resonance at the activated state.

If we assume for the reaction:



$$Na\cdot+X\cdot\cdot Y\rightarrow \begin{matrix} X^- & \\ & \\ Na^+ & Y \end{matrix} \rightarrow Na^+X^-+\cdot Y$$

the energy of the activated bond $Na^+\cdots Y$ in the same way as for the bond $Na\cdots Y$, we can apply the present rule for this type of reaction, where X denotes halogen and Y the hydrogen atom etc. The data necessary for the calculation are tabulated in Table 3, where D_e of Na–H, Na–C, Na–Cl, Na–Br and Na–I were calculated as a geometrical mean of Na–Na and H–H, C–C, Cl–Cl, Br–Br and I–I respectively, r_e of Na–C, Na–Cl, Na–Br and Na–I as the sum of covalent radii of respective atoms, and a of Na–Br as the arithmetical mean of

Table 3

Fundamental Data Necessary for the Calculation for the Reactions Involving Sodium and Halogen Atoms

Bond	$D=D_e$, kcal.	r_e, Å.	ω_e, cm.$^{-1}$	μ	a, Å.$^{-1}$	r^*, Å.
Na^+Cl^-	98(15)					2.88
Na^+Br^-	88(15)					3.03
Na^+I^-	72(15)					3.26
H–Cl(16)	102					1.65
H–Br(16)	87					1.80
H–I(16)	71					2.05
Na–H	44	1.88(6)	1170.8(6)	0.96	1.60	2.50
C–Cl(17)	67					2.17
C–Br(17)	54					2.32
C–I(17)	46					2.51
Na–C	33	2.31			1.63	2.92
Cl–Cl(16)	57					2.32
Br–Br(16)	46					2.64
I–I(16)	36					3.04
Na–Cl	32	2.53			1.60	3.16
Na–Br	28	2.68			1.64	3.29
Na–I	25	2.87			1.68	3.47

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(9) Somewhat uncertain.

(10) $D_e=80$ kcal. was used.

(11) $\rho=10\%$ was used, while for all the other cases $\rho=14\%$.

(12) R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 1375 (1935); M. G. Evans and E. Warhurst, *ibid.*, **35**, 593 (1939).

(13) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company, New York and London, 1941, p. 322.

(14) L. Pauling, *ibid.*, p. 338.

(15) R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).

(16) *Cf.* preceding report.

(17) *Cf.* Table 1.

Na–Cl and Na–I. The activated distance r^* of Na^+Cl^-, Na^+Br^- and Na^+I^- was calculated by means of the equation:

$$r^* = 1.04 \times (r_{Na^+} + r_{X^-}),$$

derived as the distance corresponding to the inflexion point on the potential-energy curve of Na^+X^- given by Pauling:(14)

$$U(r) = 331 \times \{-1/r + 296 \times 10^{-4} \times (r_{Na^+} + r_{X^-})^8 / r^9\},$$

where r_{Na^+} and r_{X^-} are the so-called standard radii of sodium and halogen ions respectively. The force constant k_0 for Na–C, Na–Cl and Na–I, which is necessary for the computation of a by means of the above-mentioned equation:

$$a = 38.3 \times \sqrt{k_0 / D_e},$$

was calculated according to the empirical rule of Badger:(18)

$$k_0 = c_{ij} / (r_e - \delta_{ij})^3,$$

where c_{ij} and δ_{ij} are the constants dependent on the rows of the periodic table containing the two atoms.

The results of the calculation for some reactions involving sodium and halogen atoms are tabulated in Table 4 and compared with the experimental results. The observed values enclosed in brackets are the mean for several reactions with varying sorts of organic halides. From Table 4 it may be said that the present rule holds equally well for the reactions involving the heteropolar bonds under the appropriate assumptions as for the ordinary reactions.

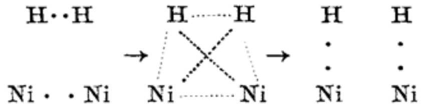
Table 4

Activation Energies for the Atomic Reactions Involving Sodium and Halogen Atoms

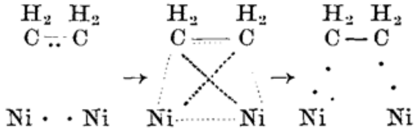
Reaction	Activation energy	
	obs.	calc.
$Na\cdot + Cl\cdot\cdot H \rightarrow Na^+Cl^- + \cdot H - 4$	6	7.3
$Na\cdot + Br\cdot\cdot H \rightarrow Na^+Br^- + \cdot H + 1$	0	2.2
$Na\cdot + I\cdot\cdot H \rightarrow Na^+I^- + \cdot H + 1$	0	1.2
$Na\cdot + Cl\cdot\cdot CR \rightarrow Na^+Cl^- + \cdot CR + 31$	(5.5)	2.1
$Na\cdot + Br\cdot\cdot CR \rightarrow Na^+Br^- + \cdot CR + 34$	(3.0)	1.4
$Na\cdot + I\cdot\cdot CR \rightarrow Na^+I^- + \cdot CR + 26$	(1.2)	0.8
$Na\cdot + Cl\cdot\cdot Cl \rightarrow Na^+Cl^- + \cdot Cl + 41$	0	2.4
$Na\cdot + Br\cdot\cdot Br \rightarrow Na^+Br^- + \cdot Br + 42$	0	1.2
$Na\cdot + I\cdot\cdot I \rightarrow Na^+I^- + \cdot I + 36$	0	0.5

Adsorption of Hydrogen and Ethylene on Nickel

Since the dissociative adsorption of hydrogen on Nickel:



and the so-called associative adsorption of ethylene on Nickel:



are important processes relating to the heterogeneous catalytic reactions, we have applied the present rule for these processes. The data used for the calculation are tabulated in Table 5, where the data for H–H and $C\underset{\cdot\cdot}{-}C$ are the same as in Table 1, and the constant a of Ni–C was computed by means of Badger's rule. The result of the calculation are given in Table 6 and graphically shown in Fig. 1, together with the results of the calculations by other authors. The values of the Ni–Ni distance given in the second column of Table 6 are chosen, taking into consideration the actual structure of the nickel crystal surface as is shown in Fig. 2, where the radii of the two circles, *i. e.*, 4.98 Å. and 6.02 Å. represent the length of the linear form of the activated complexes:

Table 5

Fundamental Data Used for the Calculation of the Adsorption on Nickel

Bond	$D=D_e$, kcal.	r_e, Å.	ω_e, cm.$^{-1}$	μ	a, Å.$^{-1}$	r^*, Å.
H–H	103					1.12
Ni–H	60(19)	1.48(6)	1900(6)	0.983	2.25	1.93
$C\underset{\cdot\cdot}{-}C$	41					1.44
Ni–C	38(20)	1.92(21)			2.74	2.29

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(18) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); *ibid.*, **3**, 710 (1935).

(19) G. Okamoto, J. Horiuchi and K. Hirota, *Scient. Papers Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).

(20) J. Horiuchi, *Catalyst*, **2**, 1 (1947).

(21) A. Sherman, C. E. Sun and H. Eyring, *J. Chem. Phys.*, **3**. 49 (1935).

←1. 93→←1. 12→←1. 93→
Ni······H······H······Ni
←————4. 98————→

←2. 29→←1. 44→←2. 29→
Ni······C······C······Ni
←————6. 02————→

Table 6

Activation Energies for the Adsorption of Hydrogen and Ethylene on Nickel

Ads. of	Ni–Ni distance, Å.	Activation energy i	ii	iii	iv
H_2	2.38				24
	2.49	37.0	34		
	3.52	26.4	16		
	4.32	19.7			
	4.98	16.0			
C_2H_4	2.49	16.1		3.5	
	3.52	10.1		3.3	
	4.32	6.9			
	5.56	3.9			
	6.02	3.2			

i. According to the present method.
ii. Calculated by Okamoto *et al.*(19) according to the semi-empirical method of Eyring, putting $\rho_{HH}=11\%$, $\rho_{NiH}=24\%$, $\rho_{NiNi}=37\%$.
iii. Calculated by Keii(22) according to the semi-empirical method of Eyring, putting $\rho_{CC}=14\%$, $\rho_{NiC}=26\%$, $\rho_{NiNi}=37\%$.
iv. Calculated by Sherman *et al.*(21) according to the semi-empirical method of Eyring, putting $\rho_{HH}=14\%$, $\rho_{NiH}=20\%$, $\rho_{NiNi}=30\%$; the Ni-Ni distance 2.38 Å. is not present on the crystal surface of nickel.

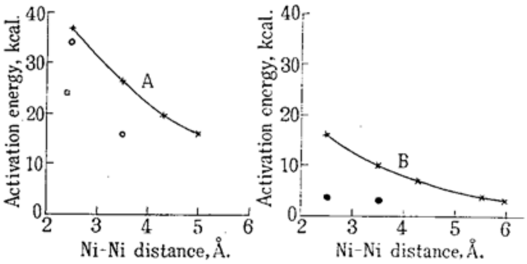

Fig. 1.—Activation energies for the adsorption of hydrogen (curve A) and ethylene (curve B) on nickel: ×, Kume *et al.*; ○, Okamoto *et al.*; □, Sherman *et al.*; ●, Keii.

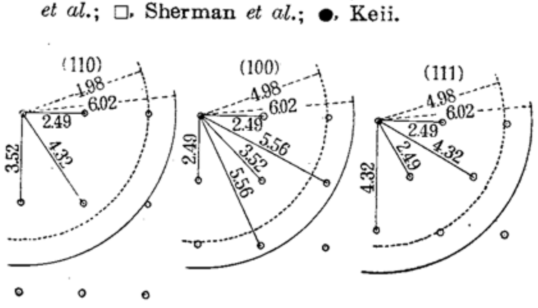

Fig. 2.—Ni-Ni distances on the surface of nickel.

respectively, since according to the present theory no longer forms than these can be considered by the fixed values of each activated internuclear distance. But as the activation energy decreases with the increasing length of the activated complex, the Ni–Ni distance, which is actually present on the crystal surface of nickel and for which the activation energy becomes minimum is 4. 32 Å. for the adsorption of hydrogen and 5. 56 Å. for the adsorption of ethylene.

Although we have no observed value for the activation energy, which are accurate enough to be directly compared with these calculated values, the rate of adsorption of ethylene on nickel has been measured by Steacie and Stovel.(23) By extrapolating the observed values of these authors Keii has obtained the value 3.39×10^{12} sec.$^{-1}$cm.$^{-2}$ as the initial rate at 293°K. and 19. 25 mm. Hg of initial pressure. If we calculate the same rate under the same conditions according to the statistical method presented by Keii by the use of our calculated value of the activation energy, *i. e.*, 3. 9 kcal., we obtain the value 7.73×10^{13} sec.$^{-1}$ cm.$^{-2}$

Summary

1. The empirical rule for the calculation of the activation energy previously proposed has been applied for some more complicated reactions.

2. For the addition reaction of halogen to ethylene the calculated values agree very well with the observed values, but for that of hydrogen the calculated value was somewhat greater than the observed.

3. For the atomic reactions involving sodium and halogen atoms the calculated values agree well with the observed under the appropriate assumptions.

4. The activation energies for the adsorption of hydrogen and ethylene on nickel have been calculated, and the initial rate of adsorption of ethylene calculated by the use of the obtained value of the activation energy was compared with the experimental value of Steacie and Stovel.

The authors wish to express their sincere thanks to Prof. T. Titani for his interest to this research.

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(22) T. Keii, *Catalyst*, **3**, 47 (1948).

(23) Steacie and Stovel, *J. Chem. Phys.*, **2**, 581 (1934).