BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2422—2425 (1969)

Evaluation of the Activation Energies of Radical Substitution Reactions in the Gaseous Phase. II. An Approximate Formula with Two Constants

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(Received October 31, 1968)

The following approximate formula for evaluating the activation energies of radical substitution reactions has been derived from the formula proposed in a previous paper:

$$E_a = D_i - \varepsilon D_f(1 + \delta D_i)$$

where D_i and D_f are the bond dissociation energies of the initial and the final bonds. The calculated values are in good accordance with the observed values within ± 2.0 kcal/mol. The empirical formulae, proposed by Evans-Polanyi and Semenov *et al.*, between the activation energy and the reaction heat have been derived from this approximate formula. The Hammett-type rule has also been observed to hold in radical substitution reactions, and the substituent constants and the reaction constants have been determined by the use of the formula. A good correlation between the bond dissociation energy of the initial molecule and the radical reactivity index, delocalizability, based on the quantum chemical standpoint, has also been observed.

Evans and Polanyi have made a theoretical investigation of the activation energy of the radical substitution reaction and have obtained, in a homologous reaction, a quantitative relation between the activation energies and the reaction heats.[1] Bagdasaryan,[2] Tikhomirova-Voevodskii,[3] and Semenov[4] indicated that the correlation between the activation energies and the reaction heats is roughly independent of the kind of reaction components.

In a previous paper,[5] the present authors made an empirical study of the energy changes along the radical substitution reaction path, and proposed a theoretical equation for the evaluation of the activation energies employing the Morse potential energy functions. The equation is very useful, but it is rather complicated.

The purpose of this report is to present an approximate formula for the theoretical equation obtained in the previous paper, and to discuss the above empirical rules in connection with this formula.

Derivation of Approximate Formula

The reactions with which we are concerned in this paper are radical substitution reactions of the three-center type, such as

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AB} + \mathrm{C} \tag{1}$$

where A, B, and C are reacting atoms or groups.

As has been described previously,[5] the energy of the transition state and the activation energy of any reaction (1) may, respectively, be given as follows:

$$E^* = \frac{4\alpha(1-\alpha)D_iD_f(D_f-\alpha D_i)}{(D_f-\alpha^2 D_i)^2} \tag{2}$$

$$E_a = \frac{D_i\{(1-2\alpha)D_f + \alpha^2 D_i\}^2}{(D_f-\alpha^2 D_i)^2} \tag{3}$$

where D_i and D_f are the bond dissociation energies of the initial and the final molecules, and where α is related to the reaction heat Q (in kcal/mol) by $\alpha = \exp(\beta Q)$, where β is a constant equal to 0.0190.

For the reaction heats, Q, ranging from -20 to 20 kcal/mol, α and α^2 are approximated as:

$$\left.\begin{aligned} \alpha &= 1 + \beta Q \\ \alpha^2 &= 1 + 2\beta Q \end{aligned}\right\} \tag{4}$$

By substituting Eq. (4) into Eq. (2) and by using the two relations: $Q \simeq D_f - D_i$ and $\beta Q \ll 1$, we obtain:

$$E^* = \varepsilon D_f \times \frac{D_i(\beta D_i - 1)}{(1 - 2\beta D_i)^2} \tag{5}$$

where $\varepsilon = 4\beta = 0.0760$. The second factor on the

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[1] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

[2] Kh. S. Bagdasaryan, *Zh. Fiz. Khim.*, **23**, 1375 (1949).

[3] N. N. Tikhomirova and V. V. Voevodskii, *Dokl. Akad. Nauk, USSR*, **79**, 993 (1951).

[4] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," English Ed., Princeton Univ. Press, Princeton, New Jersey (1958).

[5] T. Kagiya, Y. Sumida, T. Inoue and F. S. Dyachkovskii, This Bulletin, **42**, 1812 (1969).

right side of Eq. (5), $D_i(\beta D_i-1)/(1-2\beta D_i)^2$, is a function only of the bond dissociation energy, D_i, of the initial molecule. In order to approximate this factor by a simpler expression, let us use:

$$\frac{D_i(\beta D_i-1)}{(1-2\beta D_i)^2} \simeq 1+\delta D_i \tag{6}$$

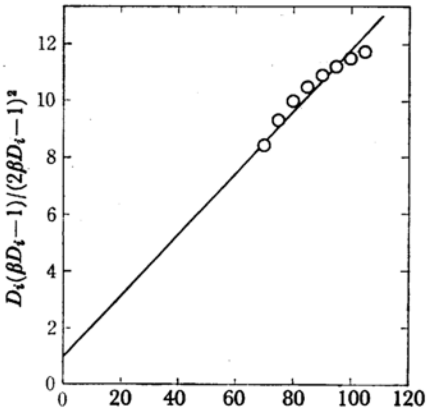

Fig. 1. Plot of $D_i(\beta D_i-1)/(2\beta D_i-1)^2$ *versus* D_i. The straight line represents the equation,
$$\frac{D_i(\beta D_i-1)}{(2\beta D_i-1)^2} = 1+0.108D_i$$

Figure 1 shows that the linear approximation (6) with $\delta=0.108$ holds fairly well in the range of D_i with which we are concerned, *i. e.*, $D_i=70$ to 105 kcal/mol. By substituting Eq. (6) into Eq. (5), we obtain:

$$E^* = \varepsilon D_f(1+\delta D_i) \tag{7}$$

Hence,

$$E_a = D_i - \varepsilon D_f(1+\delta D_i) \tag{8}$$

and

$$\frac{D_i - E_a}{D_f} = \varepsilon + \varepsilon\delta D_i \tag{9}$$

The linear relation (9) between $(D_i-E_a)/D_f$ and D_i has been checked by using the available experimental values of E_a for radical substitution reactions such as those given in the legend of Fig. 2. The results indicate that Eq. (9) works well when the constants ε and δ are chosen to be 0.0850 and 0.0944 respectively. These values are in good agreement with those of $\varepsilon=0.0760$ and $\delta=0.108$ which we have obtained earlier. By using $\varepsilon=0.0850$ and $\delta=0.0944$, we obtain:

$$E_a = D_i - 0.0850D_f(1+0.0944D_i) \tag{10}$$

Results and Discussion

The activation energies of the various types of radical substitution reactions are calculated by means of Eq. (10); they are plotted against the observed values in Fig. 2. For both exothermic and endothermic reactions, the calculated values of the activation energies are in good agreement with the observed values within ±2.0 kcal/mol. It may be concluded from the results that Eq. (10) is a good approximate formula for evaluating the activation energies of radical substitution reactions.

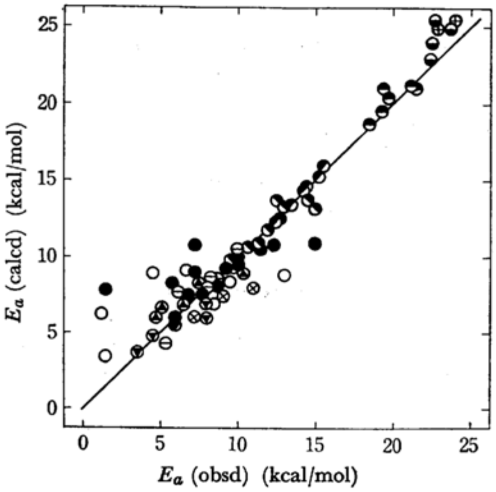

Fig. 2. Comparison of the calculated values of the activation energies of radical substitution reactions with the observed ones.

○ $H+RH\rightarrow H_2+R$, ⊗ $D+RH\rightarrow HD+R$,
● $CH_3+RH\rightarrow CH_4+R$,
◔ $C_2H_5+RH\rightarrow C_2H_6+R$,
◐ $n\text{-}C_3H_7+RH\rightarrow C_3H_8+R$,
◓ $i\text{-}C_3H_7+RH\rightarrow C_3H_8+R$,
◒ $t\text{-}C_4H_9+RH\rightarrow t\text{-}C_4H_{10}+R$,
◭ $CF_3+RH\rightarrow CF_3H+R$,
⊕ $CH_3CO+RH\rightarrow CH_3CHO+R$,
▼ $H+RCl\rightarrow HCl+R$, ⊖ $Na+RCl\rightarrow NaCl+R$

The Evans-Polanyi Rule. Evans and Polanyi have studied the reactions of various alkyl chlorides with a sodium atom:[1]

$$Na + RCl \rightarrow NaCl + R \tag{11}$$

and have found a simple parallelism between the activation energies and the reaction heats; *i. e.*,

$$\Delta E_a = -x\Delta Q \tag{12}$$

where ΔE_a is the increase in the activation energy; ΔQ, the increase in the reaction heat, and x, a constant equal to about 0.25.

From Eq. (8) we may calculate the change in the activation energy of a radical substitution reaction (such as those taken up in Fig. 2) caused by changing the alkyl group, R:

$$\Delta E_a = E_a - E_{a_0} = (1-\varepsilon\delta D_f)(D_i - D_{i,0}) \tag{13}$$

where the subscript "0" indicates the value in a certain standard reaction. The $(D_i-D_{i,0})$ factor may be equated to $-(Q-Q_0)$; hence,

$$\Delta E_a = -(1-\varepsilon\delta D_f)\Delta Q \tag{14}$$

which may be brought into the form of Eq. (12) by setting:

$$x = 1 - \varepsilon\delta D_f \tag{15}$$

The x value calculated with $\varepsilon=0.0850$, $\delta=0.0944$, and $D_f=97.5$ kcal/mol,[6] that is the bond dissociation energy of the Na–Cl bond, is 0.22; this is nearly equal to the Evans-Polanyi value, 0.25. It is also found from Eq. (15) that the x value in Eq. (12) does not change with the bond dissociation energy of the initial molecule, while it does with that of the final molecule.

The Semenov Rule. Bagdasaryan,[2] Voevodskii,[3] and Semenov[4] have extended the Evans-Polanyi rule and have found that the activation energy can be calculated from Eq. (16) for exothermic reactions and from Eq. (17) for endothermic reactions:*1

$$E_a = A - yQ \tag{16}$$

$$E_a = A + (1-y)Q \tag{17}$$

where $A=10$ to 18 kcal/mol and $y=0.2$ to 0.4.

By substituting the relation, $D_i \simeq D_f - Q$, into Eq. (8),

$$E_a = (1 - \varepsilon - \varepsilon\delta D_f)D_f - (1 - \varepsilon\delta D_f)Q \tag{18}$$

for both exothermic and endothermic reactions. By comparing Eq. (18) with Eqs. (16) and (17), we obtain:

$$A = (1 - \varepsilon - \varepsilon\delta D_f)D_f \tag{19}$$

$$y = 1 - \varepsilon\delta D_f \text{ (for exothermic reactions)} \tag{20}$$

$$y = 2 - \varepsilon\delta D_f \text{ (for endothermic reactions)} \tag{20$'$}$$

From Eqs. (19) and (20) we find that the calculated values of A and y of exothermic reactions are in the ranges $11 < A < 19$ kcal/mol and $0.20 < y < 0.32$ respectively, provided that $85 < D_f < 100$ kcal/mol. This is in accordance with the Semenov empirical rule.

The Hammett-type Rule. The following is a list of various types of radical substitution reactions (1) changing a reacting radical in three reactions (A, B, and C):

$$A + BC_j \rightarrow AB + C_j \tag{21}$$

$$A_j + BC \rightarrow A_jB + C \tag{22}$$

$$A + B_jC \rightarrow AB_j + C \tag{23}$$

where the subscript j indicates the changing radical.

The increase in the activation energy, ΔE_a, of (21) caused by changing the standard radical, C_0, to C_j is given by:

$$\Delta E_a = (1 - \varepsilon\delta D_f)(D_{i,j} - D_{i,0}) = \dot{\rho}\dot{\sigma} \tag{24}$$

$$\dot{\rho} \equiv k(1 - \varepsilon\delta D_f) \tag{25}$$

$$\dot{\sigma} \equiv (1/k)(D_{i,j} - D_{i,0}) \tag{26}$$

In Eqs. (25) and (26) above, which define $\dot{\rho}$ and $\dot{\sigma}$, k is a constant whose value is chosen so that the value of $\dot{\rho}$ for the $CH_3 + RH \rightarrow CH_4 + R$ reaction is 10.0 (see below and Table 2). Notice that $\dot{\rho}$ and $\dot{\sigma}$ depend only on the final and the initial molecules respectively. We may regard them as analogues of Hammett's ρ and σ; we shall, then, call $\dot{\rho}$ the reaction constant, and $\dot{\sigma}$, the substituent constant.

Similarly, the increase in the activation energy, ΔE_a, of (22) caused by changing the attacking radical, A_0 to A_j is given by:

$$\Delta E_a = -\varepsilon(1 + \delta D_i)(D_{f,j} - D_{f,0}) \tag{27}$$

The $-\varepsilon(1+\delta D_i)$ and $(D_{f,j} - D_{f,0})$ are the factors depending only on the initial and the final molecules respectively. It may be considered that the former corresponds to the reaction constant, $\dot{\rho}'$, and the latter, to the substituent constant, $\dot{\sigma}'$.

When changing the parent radical B_0 to B_j, however, the increase in the activation energy, ΔE_a, is represented by a complicated expression and is not given by a simple Hammett-type formula:

$$\Delta E_a = (D_{i,j} - D_{i,0}) - \varepsilon(D_{f,j} - D_{f,0}) - \varepsilon\delta(D_{i,j}D_{f,j} - D_{i,0}D_{f,0}) \tag{28}$$

TABLE 1. THE SUBSTITUENT CONSTANTS IN RADICAL SUBSTITUTION REACTIONS

Substituent	$\dot{\sigma}$	Substituent	$\dot{\sigma}$
CH_3	0	i-C_4H_9	−0.21
C_2H_5	−0.03	t-C_4H_9	−0.26
$C(CH_3)_3CH_2$	−0.04	$CHCl_2$	−0.31
n-C_3H_7	−0.08	CH_3CO	−0.35
n-C_4H_9	−0.10	$CH_2{=}CHCH_2$	−0.38
i-C_3H_7	−0.16	CCl_3	−0.39
CH_2Cl	−0.16		

TABLE 2. THE REACTION CONSTANTS OF RADICAL SUBSTITUTION REACTIONS

Reaction	$\dot{\rho}$
$CH_3 + RH \rightarrow CH_4 + R$	10.0
$C_2H_5 + RH \rightarrow C_2H_6 + R$	11.0
n-$C_3H_7 + RH \rightarrow C_3H_8 + R$	11.8
i-$C_3H_7 + RH \rightarrow C_3H_8 + R$	14.0
t-$C_4H_9 + RH \rightarrow t$-$C_4H_{10} + R$	17.0
$H + RCl \rightarrow HCl + R$	11.5
$Na + RCl \rightarrow NaCl + R$	12.8

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6) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 1st Ed., Dover Publications, N. Y. (1947).

*1 Equation (16) for exothermic reactions holds fairly well, but Eq. (17) for endothermic reactions is not very good. Knox *et al.* have observed that y should be 0.91 for hydrogen abstraction reactions by a chlorine atom (endothermic reaction).[7] This value is in good agreement with the y value, 1.18, calculated by using (20′) and $D_f=102$ kcal/mol,[8] which is the bond dissociation energy of the H–Cl bond.

7) G. C. Fettis and J. H. Knox, "Progress in Reaction Kinetics," Vol. 2, Pergamon Press, p. 1. (The Rate Constants of Halogen Atom Reactions)

8) G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Company, N. Y. (1950).

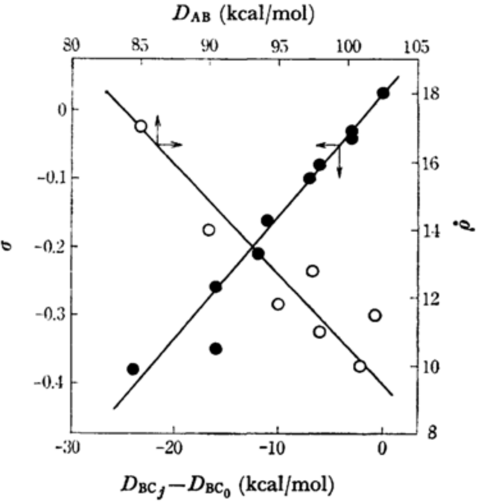

Fig. 3. Relation between the substituent constant $\dot{\sigma}$ or the reaction constant $\dot{\rho}$ and the bond dissociation energy.

$$\Delta E_a=(1-\varepsilon\delta D_{AB})(D_{BC_j}-D_{BC_0})=\dot{\rho}\dot{\sigma}$$

In fact, the increase in the activation energy caused by the change in the radical B_j is not expressed by a simple functional formula of the reaction heat.

In order to evaluate the substituent constants and the reaction constants of the type (21) of reactions, we choose the hydrogen abstraction reactions ($\dot{\rho}=10.0$) by a methyl radical as the standard reactions and a methyl group ($\dot{\sigma}=0$) as a standard substituent, C_0. By substituting the differences in the observed activation energies of the standard reactions into the relation, $\dot{\sigma}=\Delta E_a/\dot{\rho}$, where $\Delta E_a=E_{a(CH_3-H)}-E_{a(R-H)}$, we can evaluate the substituent constants, $\dot{\sigma}$ (Table 1). Moreover, the reaction constants, $\dot{\rho}$, of the other reactions are evaluated by the use of the substituent constants determined by such operations (Table 2).

As has been defined above, the substituent constants, $\dot{\sigma}$, and the reaction constants, $\dot{\rho}$, are, respectively, proportional to the $(D_{i,j}-D_{i,0})$ and $(1-\varepsilon\delta D_f)$ factors. As Fig. 3 shows, each constant can be expressed as a function of the bond dissociation energy.

The Radical Reactivity Index, D_r^R. Fukui *et al.*,⁽⁹⁾ from the quantum chemical point of view, have proposed the delocalizability, D_r^R, as a radical reactivity index of radical substitution reactions (1):

$$D_r^R=\sum_j^{occ}\frac{(C_r^j)^2}{\lambda_j}+\sum_j^{unocc}\frac{(C_r^j)^2}{-\lambda_j} \tag{29}$$

where C_r^j is the coefficient of the rth atomic orbital in the jth molecular orbital of the BC molecule, and λ_j, the coefficient of β in the energy of the jth molecular orbital of the BC molecule. Using this index, it has been assumed that the activation energy is written in the form:⁽¹⁰⁾

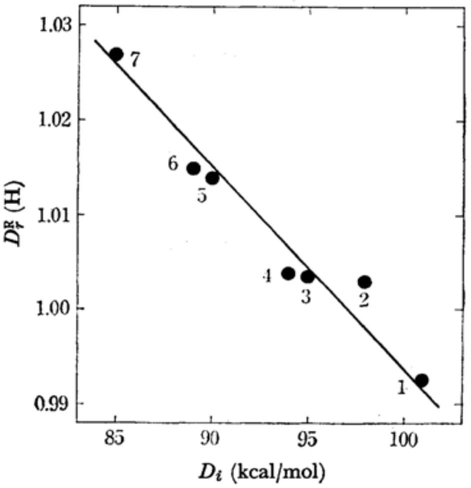

Fig. 4. Relation between the delocalizability of hydrogen abstraction reaction and the bond dissociaion energy. B=hydrogen atom

$E_a=(1-\varepsilon\delta D_f)D_i-\varepsilon D_f$

$E_a=c_1-c_2D_r^R$

1 Me–H, 2 Et–H, 3 *n*-Pr–H, 4 *n*-Bu–H, 5 *i*-Pr–H, 6 *s*-Bu–H, 7 *t*-Bu–H

$$E_a=c_1-c_2D_r^R \tag{30}$$

where it has been assumed that c_1 is a constant for a definite type of reactions and that c_2 is a constant depending only on the radical A.⁽¹⁰⁾

Equation (8) is rewritten as:

$$E_a=(1-\varepsilon\delta D_f)D_i-\varepsilon D_f \tag{31}$$

For the hydrogen abstraction reactions by a methyl radical, $CH_3+RH\rightarrow CH_4+R$, the final bond dissociation energy, D_f, in Eq. (31) is constant, and the coefficient, c_2, in Eq. (30) should not change if the above assumption is satisfied. Therefore, the values of D_r^R(H) should be expressed as a linear function of $D_{i(RH)}$, with a negative slope. This linear relation between D_r^R(H) and $D_{i(RH)}$ has been checked in Fig. 4.

On the basis of the above considerations, it may be concluded that Eq. (8) is not only a good approximate formula for the evaluation of the activation energies of radical substitution reactions, but also corresponds well with the empirical rules described previously.

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9) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34,** 1111 (1961).

10) K. Fukui, H. Kato and T. Yonezawa, *ibid.*, **35,** 1475 (1962).