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# Evaluation of the Activation Energies of Radical Substitution Reactions in the Gaseous Phase. I.
## An Empirical Method Employing the Morse Function

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An empirical evaluation of the activation energy has been carried out for the radical substitution reaction involving polyatomic molecules. The potential energy along the reaction path is assumed to be expressed for the initial and the final systems by the two Morse functions with the coefficient "$a'$," which is different from the "$a$" in the usual Morse function of the bond. The difference between the $a'\Delta r^*$ values in the Morse functions of the initial and the final systems in the transition state is empirically determined as a function, $a_f'\Delta r_f^* - a_i'\Delta r_i^* = \beta Q$, of the reaction heat, $Q$. From the Morse function with "$a'$" and the above relation, the activation energy is calculated by using the bond dissociation energies of the initial and the final molecules. The treatment proposed is useful for the evaluation of the activation energies of many types of radical substitution reactions.

Quantitative studies aimed at evaluating the activation energy of the radical substitution reaction in the gaseous phase have been carried out from the latter half of the 1930's. Since Polanyi[1] and Horiuchi[2] found that the difference in the activation energies in a homologous reaction decreased with an increase in the difference in the reaction heats, the activation energy has been considered in relation to the reaction heat. Bagdasaryan,[3] Tikhomirova-Voevodskii,[4] and Semenov[5] have accumulated a number of the experimental data; they have indicated that the activation energies are in regular correlation with the reaction heats. It has also been found[6] that, for the homologous reactions with a similar reaction heat, the activation energy is proportional to the bond dissociation energy of the initial bond.

On the other hand, the theoretical study of the evaluation of the activation energy of the radical reaction has been started by Eyring[7] and followed by Evans and Polanyi.[1]

In the reaction involving a polyatomic molecule, however, the Evans-Polanyi treatment is so complicated that it is very difficult to evaluate theoretically each energetic term along the reaction path.

We have extended the Morse bond-energy function to a polyatomic molecule, as reported by Ogg-Polanyi.[8] The potential energy along the reaction path has been assumed to be approximately expressed by the two functions of the initial and

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

2) J. Horiuchi and M. Polanyi, *Acta Physicochim. U.R.S.S.*, **2**, 505 (1935).

3) Kh. S. Bagdasaryan, *Zh. Fiz. Khim.*, **23**, 1375 (1949).

4) N. N. Tikhomirova and V. V. Voevodskii, *Dokl. Akad. Nauk, U.S.S.R.*, **79**, 993 (1951).

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

6) F. S. Dyachkovskii and A. E. Shilov, *Kinetika i Kataliz*, **4**, 919 (1963).

7) H. Eyring and M. Polanyi, *Z. physik. Chem.*, **B**, **12**, 279 (1931).

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

the final systems. The coefficient "$a'$" is different from the "$a$" in the Morse function[9] of a bond in which the presence of a radical is disregarded. Moreover, the difference between the $a'\Delta r^*$ values in the Morse functions of the initial and the final systems in the transition state was found to be proportional to the reaction heat, where $\Delta r^*$ is an expansion of a bond between the ground state and the transition state.

From the Morse function with the "$a'$" coefficient, the $a_f'\Delta r_f^* - a_i'\Delta r_i^* = \beta Q$ relation, and the bond dissociation energies of the initial and the final bonds, an equation for the evaluation of the activation energies of radical substitution reactions is derived, and its propriety is discussed in connection with the observed values.

## General Considerations

In the evaluation of the activation energy of the radical substitution reaction, we consider such reactions of the three-center type as:

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

where A, B, and C are reacting atoms or groups. As has been proposed by Evans and Polanyi,[1] the energy changes involved in the reaction can be divided into: (i) the repulsion forces between A and BC, (ii) the attraction forces of the BC molecule, (iii) the repulsion forces between C and AB, (iv) the attraction forces of the AB molecule, and (v) the perturbation energy between the states. The quantitative evaluation of each term in the reaction involving a polyatomic molecule is, however, very difficult.

In this paper, the following picture is assumed to give an approximate method for evaluating the activation energy of the reaction (1):

$$\mathrm{A} + \overset{D_i^0}{\mathrm{B{-}C}} \rightarrow \underset{\text{(a)}}{\overset{E_i^*}{(\mathrm{A\ B\cdots C})}} \longleftrightarrow \underset{\text{(b)}}{\overset{E_f^*}{(\mathrm{A\cdots B\ C})}} \rightarrow \overset{D_f^0}{\mathrm{A{-}B}} + \mathrm{C} \tag{2}$$

where (a) or (b) represents the transition state in which the potential energy of the system along the reaction path is localized on the initial B–C bond or on the final A–B bond.

Considering the above speculation in connection with the reaction process, the reaction (1) can be explained by the following three steps. (i) Until the transition state, the A radical approaches from infinity to the initial BC molecule, the BC molecule absorbs the energy of the A radical, and the B–C bond is stretched as the A–B distance decreases. (ii) In the transition state, the energy localized on the B–C bond migrates on the A–B bond. (iii) After the transition state, the energy is concentrated on the A–B bond, and the AB molecule is formed.

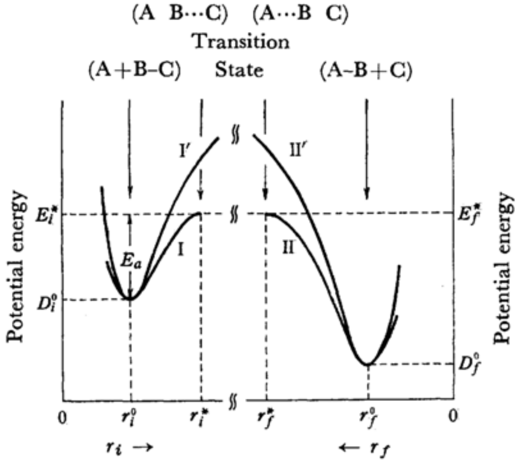

Fig. 1. The potential energy curves of the initial and the final systems along the reaction path.

We may explain the above reaction process with Fig. 1. The potential energy along the reaction path is expressed by the two curves (I and II) of the initial and the final systems, while I′ and II′ are the bond-energy curves neglecting the presence of the A and C radicals, respectively. Then, the curve I can be understood to include not only the curve I′, but also the attraction of the final bond, AB, and the repulsion between A and C.

In order to evaluate the activation energy on the basis of the above scheme, the function of the potential energy curve (I, II) along the reaction path must be determined and the conditions in the transition state must be established.

**The Function of the Potential Energy Curve along the Reaction Path.** As has been described before, the curve I is mainly determined by three energetic terms of the partial dissociation (the attraction) of BC, the partial formation (the attraction) of AB, and the repulsion between A and C. In consideration of these interaction energies, we assumed that the potential energy of the system along the reaction path is expressed by the two Morse functions, (3) for the initial system (curve I) and (4) for the final one (curve II):

$$E_i = D_i^0 - D_i^0(1 - \mathrm{e}^{-a_i'(r_i - r_i^0)})^2 \tag{3}$$

$$E_f = D_f^0 - D_f^0(1 - \mathrm{e}^{-a_f'(r_f - r_f^0)})^2 \tag{4}$$

where the subscripts $i$ and $f$ represent the initial and the final systems; $E$, the potential energy along the reaction path; $r$, the distance between the reacting components, B···C or A···B; $D^0$, the sum of the zero-point energy and the bond dissociation energy; $r^0$, the equilibrium distance of the bond, and $a'$, the Morse constant, depending on the energetic terms described above.

Neglecting the zero-point energy in comparison with the bond dissociation energy, we can obtain, from Eqs. (3) and (4), Eqs. (5) and (6):

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[9] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

$$a_i'\Delta r_i^* = -\ln\left(1-\sqrt{1-\frac{E_i^*}{D_i}}\right) \tag{5}$$

$$a_f'\Delta r_f^* = -\ln\left(1-\sqrt{1-\frac{E_f^*}{D_f}}\right) \tag{6}$$

where $E^*$ is a potential energy in the transition state and $E_i^*=E_f^*=E^*$. Equations (5) and (6) show that the activation energy can be evaluated on the basis of the "$a'$" coefficient and the $\Delta r^*$ values.

In order to evaluate the "$a'$" values in Eqs. (3) and (4), we will consider the reaction (1) as a model of the radical substitution reactions. When the A radical approaches from infinity to the initial BC molecule, the Morse constant, "$a'_i$", of the initial system should change from the original "$a_i$" value to the new "$a_i'$" value. It is considered that this change in the "$a_i'$" value depends on both the attraction of AB and the repulsion between A and C. Taking into account the fact that these energetic terms are expressed as functions of a distance between the components, we postulate the new "$a'$" value by the following formulas:

$$a_i' = a_i(1-\mathrm{e}^{-\gamma\cdot r_f^0}) \tag{7}$$

$$a_f' = a_f(1-\mathrm{e}^{-\gamma\cdot r_i^0}) \tag{8}$$

where "$a$" is a Morse constant in the bond dissociation neglecting the presence of a radical and where $\gamma$ is assumed to be a constant, regardless of the kind of reaction. The Morse constant, "$a$", is equal to $0.1227\omega_0\sqrt{\mu/D}$, where $\omega_0$ is the fundamental vibrational frequency (cm$^{-1}$); $\mu$, the reduced mass, and $D$, the bond dissociation energy (cm$^{-1}$), depending on both terms of the electronic energy and the energy of the repulsion between two nuclei.

In this study, it is assumed that the dissociation energy curve of a bond in a polyatomic molecule is essentially expressed by the Morse function as well as that in a diatomic molecule. For example, in computing the Morse functions of methyl halides, the methyl group is treated as a rigid unit with a mass of 15. The totally symmetric stretching vibrational frequency is used as a fundamental vibrational frequency, $\omega_0$. The Morse constants, "$a$", of a bond in a polyatomic molecule, as calculated with the above characteristic values, are summarized in Table 1.

On the other hand, we can empirically evaluate the "$a'$" value of the exchange reaction of a hydrogen atom with a hydrogen molecule. It is known in this reaction that the activation energy is 6.7 kcal/mol; the normal distance between hydrogen atoms, 0.74 Å; the distance between hydrogen atoms in the transition state, 1.01 Å, and the bond dissociation energy of the hydrogen molecule, 103.0 kcal/mol. By substituting these values into Eq. (5) or (6), the new "$a'$" value along the reaction path is obtained as 1.10 Å$^{-1}$, *i. e.*, $a_i'=a_f'=a'=1.10$ Å$^{-1}$.

TABLE 1. THE "$a$" CONSTANTS IN THE MORSE FUNCTION

| Bonds | $\omega_0$ (cm$^{-1}$) | $D$ (kcal/mol) | $\mu$ (amu) | $a$ (Å$^{-1}$) |
|---|---|---|---|---|
| HO–H | 3657 | 117 | 0.945 | 2.16 |
| HS–H | 2611 | 90.2 | 0.971 | 1.78 |
| $BF_2$–F | 888 | 151 | 13.7 | 1.87 |
| $NH_2$–H | 3336 | 102 | 0.941 | 2.10 |
| $CH_3$–H | 2915 | 101 | 0.938 | 1.84 |
| $C_2H_5$–H | 2915 | 98 | 0.967 | 1.90 |
| $CH_2Cl$–H | 2968 | 97 | 0.980 | 1.96 |
| $CHCl_2$–H | 2990 | 93 | 0.989 | 2.02 |
| $CCl_3$–H | 3021 | 89 | 0.991 | 2.09 |
| $CH_2Br$–H | 2972 | 95.2 | 0.990 | 1.99 |
| $CHBr_2$–H | 2988 | 87.7 | 0.994 | 2.09 |
| $CF_3$–H | 3062 | 103 | 0.986 | 1.96 |
| $CCl_3$–Cl | 458 | 68.4 | 27.3 | 1.90 |
| $CH_3$–F | 1049 | 108(126)† | 8.38 | 1.92(1.97)† |
| $CH_3$–Cl | 733(712)† | 83.5(73)† | 10.5 | 1.74(1.77)† |
| $CH_3$–Br | 611(603)† | 68.0(59)† | 12.6 | 1.73(1.83)† |
| $CH_3$–I | 534 | 55.0(44)† | 13.4 | 1.73(1.95)† |
| H–Cl | 2990 | 102 | 0.973 | 1.91† |
| H–H | — | 103 | 0.500 | (1.85)†† |
| | | | | Av. 1.92±0.24 |

† Reported in Ref. 8.
†† Reported in Ref. 9.

With the use of the above data, *i. e.*, $a=1.85$ Å$^{-1}$, $a'=1.10$ Å$^{-1}$, and $r^0=0.74$ Å, the coefficient, $\gamma$, is determined to be 1.19 from Eqs. (7) and (8).

**The Conditions in the Transition State.** Taking the difference between Eqs. (5) and (6) and using the relations (7) and (8), we can derive the following equation:

$$a_f'\Delta r_f^* - a_i'\Delta r_i^*$$
$$= -\ln\left(1-\sqrt{1-\frac{E_f^*}{D_f}}\right)\Big/\left(1-\sqrt{1-\frac{E_i^*}{D_i}}\right) \tag{9}$$
$$= a_f(1-\mathrm{e}^{-\gamma\cdot r_i^0})\Delta r_f^* - a_i(1-\mathrm{e}^{-\gamma\cdot r_f^0})\Delta r_i^* \tag{10}$$

As may be seen from Table 1, the "$a$" value turns out to be approximately constant; thus we may put $a_i=a_f=a_m=1.92$ Å$^{-1}$ (the average value of "$a$"). Moreover, since $r_i^0$ is nearly equal to $r_f^0$ in many reactions, the average value, $r_m^0=1/2(r_i^0+r_f^0)$, is employed for the value of $r_i^0$ and $r_f^0$.

$$a_f'\Delta r_f^* - a_i'\Delta r_i^* = a_m(1-\mathrm{e}^{-\gamma\cdot r_m^0})(\Delta r_f^* - \Delta r_i^*) \tag{11}$$

When the following type of reactions is chosen as the standard reactions in computing; R+HR′→RH+R′, the value of $a_m(1-\mathrm{e}^{-\gamma\cdot r_m^0})$ is calculated to be approximately 1.40 Å$^{-1}$.

In the transition state, it is considered that the expansion of the initial bond is equal to that of the final bond in the reaction with the heat $Q=0$,

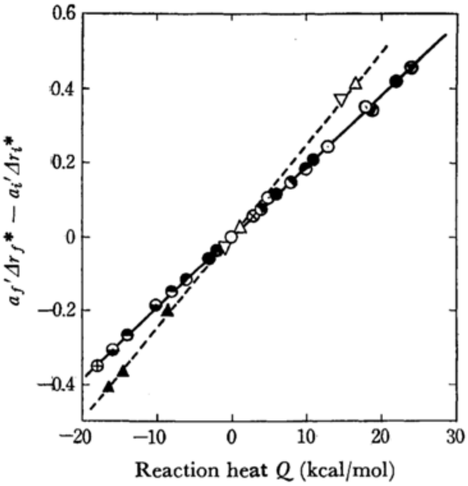

Fig. 2. Plot of the differences, $a_f'\Delta r_f^*-a_i'\Delta r_i^*$, *versus* the reaction heats.

○ $\mathrm{H+RH\rightarrow H_2+R}$, ⊗ $\mathrm{D+RH\rightarrow HD+R}$, ● $\mathrm{CH_3+RH\rightarrow CH_4+R}$, ◔ $\mathrm{C_2H_5+RH\rightarrow C_2H_6+R}$, ◕ $n$-$\mathrm{C_3H_7+RH\rightarrow}$ $n$-$\mathrm{C_3H_8+R}$, ◓ $i$-$\mathrm{C_3H_7+RH\rightarrow}$ $i$-$\mathrm{C_3H_8+R}$, ◒ $t$-$\mathrm{C_4H_9+RH\rightarrow}$ $t$-$\mathrm{C_4H_{10}+R}$, ⊕ $\mathrm{CH_3CO+RH\rightarrow CH_3CHO+R}$, ⊙ $\mathrm{H+RCl\rightarrow HCl+R}$, △ $\mathrm{H+HX\rightarrow H_2+X}$, ▽ $\mathrm{CH_3+HX\rightarrow CH_4+X}$, ▲ $\mathrm{Br+RH\rightarrow HBr+R}$.

that it is smaller in the exothermic reaction $Q>0$, and that it is larger in the endothermic reaction $Q<0$.

On the basis of these considerations, the right side in Eq. (9) is evaluated from the experimental data and is plotted against the heat of reaction (Fig. 2). The linear relation in Fig. 2 can be expressed by the following formula for the standard reactions:

$$a_f'\Delta r_f^*-a_i'\Delta r_i^* = \beta Q = 0.0190Q \quad (Q\text{: kcal/mol}) \tag{12}$$

Therefore, $(\Delta r_f^*-\Delta r_i^*)$ is equal to $0.0136Q$.

**The Evaluation of the Activation Energy.** As has been described above, the potential energies along the reaction path are expressed by the two following Morse functions:

$$E_i = D_i(2\mathrm{e}^{-a_i'\Delta r_i} - \mathrm{e}^{-2a_i'\Delta r_i}) \tag{13}$$

$$E_f = D_f(2\mathrm{e}^{-a_f'\Delta r_f} - \mathrm{e}^{-2a_f'\Delta r_f}) \tag{14}$$

By substituting the conditions in the transition state, *i. e.*, $E_i^*=E_f^*=E^*$ and $a_f'\Delta r_f^*-a_i'\Delta r_i^*=0.0190Q$, into Eqs. (13) and (14), we can derive the formulas expressing the expansions of the bond lengths and the potential energy of the bond in the transition state:

$$\Delta r_i^* = -\frac{1}{a_i'}\ln\frac{2\alpha(D_f-\alpha D_i)}{D_f-\alpha^2 D_i} \tag{15}$$

$$\Delta r_f^* = -\frac{1}{a_f'}\ln\frac{2(D_f-\alpha D_i)}{D_f-\alpha^2 D_i} \tag{16}$$

$$E^* = \frac{4\alpha(1-\alpha)D_iD_f(D_f-\alpha D_i)}{(D_f-\alpha^2D_i)^2} \tag{17}$$

where $\alpha$ is equal to $\exp(0.0190Q)$. The activation energy can then be expressed by the following equation:

$$E_a = D_i - E^* = \frac{D_i((1-2\alpha)D_f+\alpha^2D_i)^2}{(D_f-\alpha^2D_i)^2} \tag{18}$$

Equation (18) shows that the activation energy can be calculated by using the bond dissociation energies of the initial and the final molecules. In the reaction with the heat $Q=0$, both the denominator and the numerator are zero in Eq. (18). Therefore, the activation energy of this type of reaction can be estimated by interpolating the activation energies of the reactions with $Q\neq 0$.

## Results and Discussion

The expansions ($\Delta r_i^*$, $\Delta r_f^*$) of the bond lengths and the activation energies as calculated by Eqs. (15)—(18), are listed in Table 2, where they are shown in comparison with the observed values.[5,10,11]

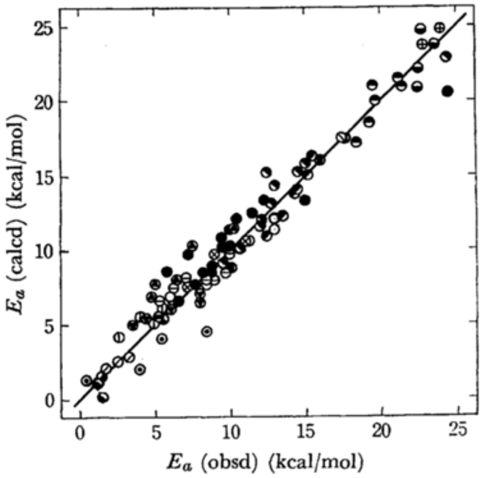

Fig. 3. Comparison of the calculated values with the observed values of the activation energies of the radical substitution reactions.

○ $\mathrm{H+RH\rightarrow H_2+R}$, ⊗ $\mathrm{D+RH\rightarrow HD+R}$, ⊙ $\mathrm{OH+RH\rightarrow H_2O+R}$, ● $\mathrm{CH_3+RH\rightarrow CH_4+R}$, ◔ $\mathrm{C_2H_5+RH\rightarrow C_2H_6+R}$, ◕ $n$-$\mathrm{C_3H_7+RH\rightarrow}$ $n$-$\mathrm{C_3H_8+R}$, ◓ $i$-$\mathrm{C_3H_7+RH\rightarrow}$ $i$-$\mathrm{C_3H_8+R}$, ◒ $t$-$\mathrm{C_4H_9+RH\rightarrow}$ $t$-$\mathrm{C_4H_{10}+R}$, ◬ $\mathrm{CF_3+RH\rightarrow CF_3H+R}$, ⊕ $\mathrm{CH_3CO+RH\rightarrow CH_3CHO+R}$, ⊙ $\mathrm{H+RCl\rightarrow HCl+R}$, ⊖ $\mathrm{Na+RCl\rightarrow NaCl+R}$, ⦶ $\mathrm{Na+RBr\rightarrow NaBr+R}$, ⊘ $\mathrm{Na+RI\rightarrow NaI+I}$, ⦸ $\mathrm{Na+RF\rightarrow NaF+R}$, ◔ $\mathrm{H+HX\rightarrow H_2+X}$, ◕ $\mathrm{CH_3+HX\rightarrow CH_4+X}$, ⊖ $\mathrm{Cl+RH\rightarrow HCl+R}$, ⦶ $\mathrm{Br+RH\rightarrow HBr+R}$.

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[10] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Co., New York (1946); *ibid.*, Second Ed. Vol. II (1954).

[11] N. N. Tikhomirova and V. V. Voevodskii, *Chem. Abstr.*, **45**, 9940 (1951).

TABLE 2. THE ACTIVATION ENERGIES OF VARIOUS RADICAL SUBSTITUTION REACTIONS†

| RH or RX | $D_i$ (kcal/mol) | $\Delta r_i^*$ (Å) | $\Delta r_f^*$ (Å) | $E^*$ (kcal/mol) | $E_a$(calcd) (kcal/mol) | $E_a$(obsd)[5,10,11] (kcal/mol) |
|---|---|---|---|---|---|---|
| $H + RH \longrightarrow H_2 + R$ | | | | | | |
| $H_2$ | 103 | (0.27)†† | (0.27)†† | (96.3)†† | (6.7)†† | 6.7 |
| $CH_4$ | 101 | 0.291 | 0.318 | 89.71 | 11.3 | 13.0 |
| $C_2H_6$ | 98.0 | 0.279 | 0.347 | 87.76 | 10.2 | 9.5 |
| $C(CH_3)_4$ | 98.0 | 0.279 | 0.347 | 87.76 | 10.2 | 9.3 |
| $i$-$C_3H_8$ | 90.0 | 0.250 | 0.427 | 82.11 | 7.9 | 8.5 |
| $CH_3CHO$ | 85.0 | 0.236 | 0.481 | 78.24 | 6.8 | 6.0 |
| $D + RH \longrightarrow HD + R$ | | | | | | |
| $CH_4$ | 101 | 0.280 | 0.321 | 90.39 | 10.6 | 11.0 |
| $C_2H_6$ | 98.0 | 0.269 | 0.351 | 88.31 | 9.7 | 9.0 |
| $i$-$C_3H_8$ | 90.0 | 0.243 | 0.433 | 82.54 | 7.5 | 7.2 |
| $OH + RH \longrightarrow H_2O + R$ | | | | | | |
| $CH_4$ | 101 | 0.170 | 0.388 | 96.45 | 4.5 | 8.5 |
| $C_2H_6$ | 98.0 | 0.159 | 0.417 | 94.12 | 3.9 | 5.5 |
| $CH_3CHO$ | 85.0 | 0.118 | 0.553 | 83.04 | 2.0 | 4.0 |
| HCHO | 79.0 | 0.104 | 0.621 | 77.55 | 1.4 | 0.5 |
| $CF_3 + RH \longrightarrow CF_3H + R$ | | | | | | |
| $CH_4$ | 101 | 0.291 | 0.318 | 89.71 | 11.3 | 10.3 |
| $C_2H_6$ | 98.0 | 0.279 | 0.347 | 87.76 | 10.2 | 7.5 |
| $i$-$C_3H_8$ | 90.0 | 0.250 | 0.427 | 82.11 | 7.9 | 6.5 |
| $i$-$C_4H_{10}$ | 89.0 | 0.247 | 0.439 | 81.30 | 7.7 | 5.1 |
| $t$-$C_4H_{10}$ | 85.0 | 0.236 | 0.481 | 78.24 | 6.8 | 4.7 |
| $CH_3 + RH \longrightarrow CH_4 + R$ | | | | | | |
| $H_2O$ | 117 | 0.388 | 0.170 | 96.45 | 20.5 | 24.5 |
| $H_2$ | 103 | 0.318 | 0.291 | 89.71 | 13.3 | 15.0 |
| $CF_3H$ | 103 | 0.318 | 0.291 | 89.71 | 13.3 | 12.3 |
| $CH_4$ | 101 | — | — | — | (12.4)††† | 11.5 |
| $CH_3OH$ | 100 | 0.306 | 0.320 | 87.87 | 12.1 | 10.4 |
| $C_2H_6$ | 98.0 | 0.297 | 0.338 | 86.65 | 11.3 | 10.0 |
| $C(CH_3)_4$ | 98.0 | 0.297 | 0.338 | 86.65 | 11.3 | 10.0 |
| $CH_3Cl$ | 97.0 | 0.293 | 0.348 | 85.99 | 11.0 | 9.4 |
| $n$-$C_3H_8$ | 95.0 | 0.286 | 0.367 | 84.67 | 10.3 | 9.5 |
| $CH_3Br$ | 95.0 | 0.286 | 0.367 | 84.67 | 10.3 | 10.1 |
| $n$-$C_4H_{10}$ | 94.0 | 0.282 | 0.377 | 84.00 | 10.0 | 9.3 |
| $CH_2Cl_2$ | 93.0 | 0.279 | 0.388 | 83.29 | 9.7 | 7.2 |
| $i$-$C_3H_8$ | 90.0 | 0.269 | 0.419 | 81.14 | 8.9 | 8.7 |
| $i$-$C_4H_{10}$ | 89.0 | 0.266 | 0.429 | 80.40 | 8.6 | 8.2 |
| $CHCl_3$ | 89.0 | 0.266 | 0.429 | 80.40 | 8.6 | 5.8 |
| $CH_2Br_2$ | 88.0 | 0.263 | 0.440 | 79.64 | 8.4 | 8.7 |
| $t$-$C_4H_{10}$ | 85.0 | 0.255 | 0.473 | 77.33 | 7.7 | 7.7 |
| $CH_3CHO$ | 85.0 | 0.255 | 0.473 | 77.33 | 7.7 | 7.5 |
| $C_2H_5CHO$ | 85.0 | 0.255 | 0.473 | 77.33 | 7.7 | 7.5 |
| HCHO | 79.0 | 0.243 | 0.542 | 72.43 | 6.6 | 6.6 |
| $C_2H_5 + RH \longrightarrow C_2H_6 + R$ | | | | | | |
| $H_2O$ | 117 | 0.417 | 0.159 | 94.12 | 22.9 | 24.5 |
| HD | 104 | 0.351 | 0.269 | 88.31 | 15.7 | 15.0 |
| $H_2$ | 103 | 0.347 | 0.279 | 87.76 | 15.2 | 14.5 |
| $CF_3H$ | 103 | 0.347 | 0.279 | 87.76 | 15.2 | 12.5 |
| $CH_4$ | 101 | 0.338 | 0.297 | 86.65 | 14.3 | 13.0 |
| $C_2H_6$ | 98.0 | — | — | — | (13.1)††† | 12.8 |
| $n$-$C_3H_8$ | 95.0 | 0.314 | 0.355 | 82.97 | 12.0 | 12.2 |

TABLE 2. Continued

| RH or RX | $D_i$ (kcal/mol) | $\Delta r_i^*$ (Å) | $\Delta r_f^*$ (Å) | $E^*$ (kcal/mol) | $E_a$(calcd) (kcal/mol) | $E_a$(obsd)[5,10,11] (kcal/mol) |
|---|---|---|---|---|---|---|
| $n$-$C_4H_{10}$ | 94.0 | 0.310 | 0.364 | 82.38 | 11.6 | 11.9 |
| $i$-$C_3H_8$ | 90.0 | 0.298 | 0.407 | 79.53 | 10.5 | 11.3 |
| $i$-$C_4H_{10}$ | 89.0 | 0.295 | 0.417 | 78.85 | 10.1 | 10.7 |
| $t$-$C_4H_{10}$ | 85.0 | 0.284 | 0.461 | 75.85 | 9.1 | 9.6 |
| $n\text{-}C_3H_7 + RH \longrightarrow n\text{-}C_3H_8 + R$ | | | | | | |
| $CH_4$ | 101 | 0.367 | 0.286 | 84.67 | 16.3 | 15.5 |
| $C_2H_6$ | 98.0 | 0.355 | 0.314 | 82.97 | 15.0 | 15.2 |
| $n$-$C_3H_8$ | 95.0 | — | — | — | (14.1)††† | 14.5 |
| $n$-$C_4H_{10}$ | 94.0 | 0.343 | 0.357 | 80.29 | 13.7 | 14.3 |
| $i$-$C_3H_8$ | 90.0 | 0.327 | 0.395 | 77.83 | 12.2 | 13.5 |
| $i$-$C_4H_{10}$ | 89.0 | 0.324 | 0.406 | 77.13 | 11.9 | 13.1 |
| $t$-$C_4H_{10}$ | 85.0 | 0.314 | 0.450 | 74.25 | 10.8 | 12.4 |
| $i\text{-}C_3H_7 + RH \longrightarrow i\text{-}C_3H_8 + R$ | | | | | | |
| HD | 104 | 0.433 | 0.243 | 82.54 | 21.5 | 21.2 |
| $H_2$ | 103 | 0.427 | 0.250 | 82.11 | 20.9 | 21.5 |
| $CF_3H$ | 103 | 0.427 | 0.250 | 82.11 | 20.9 | 19.5 |
| $CH_4$ | 101 | 0.419 | 0.269 | 81.14 | 19.9 | 19.7 |
| $C_2H_6$ | 98.0 | 0.407 | 0.298 | 79.53 | 18.5 | 19.3 |
| $n$-$C_3H_8$ | 95.0 | 0.395 | 0.327 | 77.83 | 17.2 | 18.5 |
| $t\text{-}C_4H_9 + RH \longrightarrow t\text{-}C_4H_{10} + R$ | | | | | | |
| $CF_3H$ | 103 | 0.481 | 0.236 | 78.24 | 24.8 | 22.7 |
| $CH_4$ | 101 | 0.473 | 0.255 | 77.33 | 23.7 | 23.7 |
| $C_2H_6$ | 98.0 | 0.461 | 0.284 | 75.85 | 22.1 | 22.6 |
| $n$-$C_3H_8$ | 95.0 | 0.450 | 0.314 | 74.25 | 20.7 | 22.4 |
| $CH_3CO + RH \longrightarrow CH_3CHO + R$ | | | | | | |
| $H_2O$ | 117 | 0.553 | 0.118 | 83.04 | 34.0 | 36.0 |
| $H_2$ | 103 | 0.481 | 0.236 | 78.24 | 24.8 | 24.0 |
| $CH_4$ | 101 | 0.473 | 0.255 | 77.33 | 23.7 | 22.8 |
| $H + RCl \longrightarrow HCl + R$ | | | | | | |
| $CH_3Cl$ | 83.5 | 0.242 | 0.494 | 76.57 | 6.9 | 8.0 |
| $C_2H_5Cl$ | 80.5 | 0.236 | 0.528 | 74.13 | 6.4 | 8.0 |
| $CH_2Cl_2$ | 78.0 | 0.232 | 0.558 | 72.03 | 6.0 | 6.0 |
| $CHCl_3$ | 73.5 | 0.226 | 0.614 | 68.08 | 5.4 | 4.5 |
| $CCl_4$ | 68.4 | 0.225 | 0.682 | 63.41 | 5.0 | 3.5 |

† Calculated by Eq. (18) with $\beta=0.0190$
†† An experimental value
††† Evaluated by interpolation

The calculated values of the activation energies are in good accordance with the observed values for many, though not all, types of reactions within ±2.0 kcal/mol. It should be noted that Eq. (18) holds not only in the homopolar reactions, but also in the reactions with some ionic character.

In the reaction, $R+HR' \rightarrow RH+R'$, with the same reaction heat and the same $\beta$ value (0.0190), it is also found that the activation energy decreases with an increase in the value of $D_i$ (or $D_f$). This relation may be due to the increase in the expansion, $\Delta r_i^*$, with a decrease in the dissociation energy of the initial molecule.

On the other hand, in the following reaction, in which the hydrogen atom pulls the hydrogen of hydrogen halides:

$$H + HX \rightarrow H_2 + X \qquad (19)$$

the values calculated by Eq. (18) with the standard $\beta$ value are considerably larger than the observed values. This disagreement may be explained as follows. On the basis of the facts that $r^0_{H-X}$ (1.22—1.47 Å) and $r^0_{H-H}$ (0.74 Å) are not equal to each other and both differ from $r^0_{R-H}$ (1.09 Å), Eqs. (11) and (12) do not hold for the reaction (19).

In our treatment, the difference in the equilibrium distances results in changes in both the Morse constant "$a'$" and the $\beta$ value. We assume that the value of $(a_f'\Delta r_f^* - a_i'\Delta r_i^*)$ is expressed by Eq. (12), which has a new $\beta$ ($\beta'$) value which is different from 0.0190 (Fig. 2):

$$a_f'\Delta r_f^* - a_i'\Delta r_i^* = \beta' Q \quad (Q\text{: kcal/mol}) \qquad (20)$$

The $\beta'$ value is calculated with the use of the experimental data, *i. e.*, $\beta'=0.0260$ for the reaction (19).

Moreover, in the following reaction, it is well known that the activation energy generally decreases in the order RF > RCl > RBr > RI and cannot be evaluated by Eq. (18) using the standard $\beta$ value:

TABLE 3. THE ACTIVATION ENERGIES OF VARIOUS RADICAL SUBSTITUTION REACTIONS

| RH or RF | $D_i$ (kcal/mol) | $Q$ (kcal/mol) | $\beta'$ | $E_a$(calcd) (kcal/mol) | $E_a$(obsd)[5,10] (kcal/mol) |
|---|---|---|---|---|---|
| $Na + RF \longrightarrow NaF + R$ | | | | | |
| $CH_3F$ | 108 | 1.0 | 0.0133 | 29.7 | >25.0 |
| $Na + RCl \longrightarrow NaCl + R$ | | | | | |
| $C_6H_5Cl$ | 87.0 | 10.5 | 0.0190 | 10.0 | 10.2 |
| $CH_2{=}CHCl$ | 86.5 | 11.0 | 0.0190 | 9.8 | 10.0 |
| $CH_3Cl$ | 83.5 | 14.0 | 0.0190 | 9.0 | 9.7 |
| $C_2H_5Cl$ | 80.5 | 17.0 | 0.0190 | 8.4 | 9.7 |
| $n$-$C_5H_{11}Cl$ | 80.0 | 17.5 | 0.0190 | 8.4 | 8.4 |
| $n$-$C_4H_9Cl$ | 79.5 | 18.0 | 0.0190 | 8.4 | 8.8 |
| $i$-$C_5H_{11}Cl$ | 79.0 | 18.5 | 0.0190 | 8.3 | 8.3 |
| $CH_2Cl_2$ | 78.0 | 19.5 | 0.0190 | 8.1 | 8.2 |
| $CH_3CHCl_2$ | 77.9 | 19.6 | 0.0190 | 8.1 | 7.2 |
| $n$-$C_3H_7Cl$ | 77.5 | 20.0 | 0.0190 | 8.0 | 9.0 |
| $t$-$C_4H_9Cl$ | 75.0 | 22.5 | 0.0190 | 7.7 | 8.0 |
| $CHCl_3$ | 73.5 | 24.0 | 0.0190 | 7.4 | 6.2 |
| $CCl_4$ | 68.4 | 29.1 | 0.0190 | 6.9 | 5.0 |
| $CH_2{=}CHCH_2Cl$ | 58.0 | 39.5 | 0.0190 | 6.6 | 5.3 |
| $Na + RBr \longrightarrow NaBr + R$ | | | | | |
| $CH_2{=}CHBr$ | 73.4 | 14.3 | 0.0224 | 5.9 | 5.4 |
| $C_6H_5Br$ | 71.0 | 16.7 | 0.0224 | 5.4 | 4.0 |
| $CH_3Br$ | 68.0 | 19.7 | 0.0224 | 4.9 | 5.0 |
| $C_2H_5Br$ | 67.0 | 20.7 | 0.0224 | 4.8 | 4.9 |
| $CH_2Br_2$ | 61.0 | 26.7 | 0.0224 | 4.1 | 2.6 |
| $Na + RI \longrightarrow NaI + R$ | | | | | |
| $CH_2{=}CHI$ | 58.0 | 12.7 | 0.0301 | 2.7 | 3.2 |
| $CH_3I$ | 56.3 | 14.4 | 0.0301 | 2.5 | 2.5 |
| $C_2H_5I$ | 53.0 | 17.7 | 0.0301 | 2.1 | 1.7 |
| $H + HX \longrightarrow H_2 + X$ | | | | | |
| HCl | 102 | 1.0 | 0.0260 | 5.4 | 5.6 |
| HBr | 86.5 | 16.5 | 0.0260 | 1.0 | 1.2 |
| HI | 70.0 | 33.0 | 0.0260 | 0.0 | 1.5 |
| $CH_3 + HX \longrightarrow CH_4 + X$ | | | | | |
| HCl | 102 | − 1.0 | 0.0260 | 6.5 | 6.2 |
| HBr | 86.5 | 14.5 | 0.0260 | 1.5 | 1.4 |
| $Cl + RH \longrightarrow HCl + R$ | | | | | |
| $H_2$ | 103 | − 1.0 | 0.0260 | 6.4 | 6.6 |
| $CH_4$ | 101 | 1.0 | 0.0260 | 5.5 | 5.2 |
| $Br + RH \longrightarrow HBr + R$ | | | | | |
| $H_2$ | 103 | −16.5 | 0.0260 | 17.5 | 17.7 |
| $CH_4$ | 101 | −14.5 | 0.0260 | 16.0 | 15.9 |
| $CH_3Br$ | 95.0 | − 8.5 | 0.0260 | 12.0 | 13.4 |
| $CHCl_3$ | 89.0 | − 2.5 | 0.0260 | 8.7 | 10.0 |

$$\mathrm{Na} + \mathrm{XR} \rightarrow \mathrm{NaX} + \mathrm{R} \quad (\mathrm{X}{=}\text{a halogen atom}) \quad (21)$$

On the basis of the similar considerations described above, the new $\beta$ values can be empirically evaluated. The following empirical relation can be obtained between $\beta'_{\mathrm{R-X}}$ and $r^0_{\mathrm{R-X}}$:

$$\beta'_{\mathrm{R-X}} = \beta'_{\mathrm{R-F}} + 5.0 \times 10^{-5}((r^0_{\mathrm{R-X}})^6 - (r^0_{\mathrm{R-F}})^6) \quad (22)$$

where $\beta'_{\mathrm{R-F}}=0.0133$ and $r^0_{\mathrm{R-F}}=1.96$ Å. The activation energies of the reaction (21), calculated with the new $\beta$ value obtained from Eq. (22), are listed in Table 3. It may also be found in Table 3 that, in the reaction (21) with the same reaction heat and a different $\beta$ value, the acitvation energy decreases with a decrease in the dissociation energy of the initial bond. If the relation, $\Delta r_f^* - \Delta r_i^* =$ constant$\times Q$, holds for the reaction (21) as well as for the standard reaction, a decrease in the dissociation energy may result in a remarkable decrease in the slope of the Morse function curve and, consequently, in that of the activation energy.

These results lead to the following conclusions. The activation energy of the radical substitution reactions can be evaluated by the method based on the Morse function. In reactions of the $\mathrm{R} + \mathrm{HR}' \rightarrow \mathrm{RH} + \mathrm{R}'$ type, with the same reaction heat, the activation energy depends on the expansion of the bond, while in reactions of the $\mathrm{Na} + \mathrm{XR} \rightarrow \mathrm{NaX} + \mathrm{R}$ type, with the same reaction heat, the change in the activation energy depends mostly on the difference in the slope of the Morse function curve.

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