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Unimolecular Decomposition Rate Theory at the High Pressure Limit and Its Application to the Dissociations of Methanes and Ethanes

Sukeya Kodama
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591

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A rate theory for the thermal decomposition by a single bond fission at the high pressure limit was derived from the conceptions that the equilibrium between the active molecule and the activated complex is adiabatic and that the zero point energy difference between the molecule and the complex ($\Delta E_z^{\neq}$) participates in the entropy term of the rate constant (k_d^{∞}) and is not related to the enthalpy term. It was also proposed a method calculating k_d^{∞} by replacing the vibrational state sum with the entropy term. The values of k_d^{∞} for methanes and ethanes were calculated using the present theory and the Gorin activated complex model. From good correspondences between the experimental and calculated values, the values of $\Delta H^{\circ}_{f,298}(CH_3(g))=143.2$, $D_0(CH_3-CH_3)=393.0$, and $D_0(CH_3-H)=449.1$ kJ mol^{-1} were obtained for the standard heat of formation and the chemical bond dissociation energy. The apparent activation energy for k_d^{∞} decreases drastically by increasing of the reaction temperature. This fact means that the estimation of thermodynamic values from the apparent activation energy is not adequate. It was also found that the vibrational temperature in the complex is considerably higher than the reaction temperature by the contribution of $\Delta E_z^{\neq}$ mainly. This result denotes that the chemical equilibrium constant cannot be evaluated from the ratio of $k_d^{\infty}/k_c^{\infty}$, where k_c^{∞} means the high pressure limiting rate constant of the radical–radical recombination reaction.

By assuming that the activated complex is in a state of equilibrium with the reactant, Eyring[1] has derived a rate theory using the partition function. The theory of absolute reaction rates has been extensively used for the theoretical calculation of specific rates of many kinds of reaction.[2] On the other hand, Marcus[3] has derived the RRKM theory, by estimating more strictly the state sum on the basis of the RRK theory.[4] The RRKM theory has been widely used for rate calculations of unimolecular decompositions of chemically and thermally activated species.[5]

The propriety of these rate theories must be examined under the following conditions: the physical constants for the activated complex such as the vibrational frequency and the moment of inertia should not be used as a parameter in order to adjust the calculated value to the experimental values; a common activated complex model and the same physical constants should be used when a common species is involved in the activated complexes of reactions of the same kind; when a common product is involved in similar reactions, the same standard heat of formation must be used on the estimation of the chemical bond dissociation energy; the kinetic isotope effect should be explained rationally; the results calculated under these restrictive conditions must be consistent inclusively with the experimental results.

From the theories cited above, however, comprehensive agreements between the calculated and experimental results were not obtained as will be discussed later. In this work, therefore, a new rate theory for unimolecular decompositions at the high pressue limit was derived. In this theory, the entropy term for the estimation of the vibrational state sums of the active molecule and the activated complex was introduced together with the assumption that the transition process from the active molecule to the activated complex is adiabatic. The present theory was applied to thermal decompositions of simple molecules which is adaptable to the Gorin model.[6] Then, a satisfactory agreement between the calculated and experimental results was obtained.

Theoretical

The reaction mechanism for the thermal decomposition by single bond fission of X–Y molecule can be, in general, expressed by

$$\mathrm{X{-}Y} \underset{k_2[\mathrm{M}]}{\overset{k_1[\mathrm{M}]}{\rightleftharpoons}} \mathrm{X{-}Y^*} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (\mathrm{X\cdots Y})_d^{\neq} \xrightarrow{k_5} \mathrm{X} + \mathrm{Y} \qquad (1)$$

from the combination of Lindemann's mechanism[7] and the theory of absolute reaction rates.[1] Here, X–Y*, $(X\cdots Y)_d^{\neq}$, and M mean the active molecule, the activated complex, and the heat bath molecules, respectively.

From the mechanism, the specific rate for the thermal decomposition, k_d, is given by

$$k_d = \frac{k_1 k_3 k_5[\mathrm{M}]}{k_2(k_4 + k_5)[\mathrm{M}] + k_3 k_5}. \qquad (2)$$

The rate constant at the high pressure limit, k_d^{∞}, becomes

$$k_d^{\infty} = \frac{k_1}{k_2}\frac{k_3}{k_4}\frac{k_5}{1 + k_5/k_4}. \qquad (3)$$

According to Boltzmann's distribution law, the existence probability of the active molecules having the vibrational energy of E_v in the isothermal equilibrium state of $\mathrm{X{-}Y} \rightleftharpoons \mathrm{X{-}Y^*}$, $P(E_\mathrm{v})$, can be expressed by

$$P(E_\mathrm{v}) = \exp\Bigl(-\sum_{i=1}^{s}\varepsilon_\mathrm{v}(i)/RT\Bigr)\Big/\prod_{i=1}^{s}q_\mathrm{v}(i)$$
$$= e^{-E_\mathrm{v}/RT}/q_\mathrm{v}. \qquad (4)$$

Here, s, $\varepsilon_\mathrm{v}(i)$, $q_\mathrm{v}(i)$, and q_v mean the vibrational degree of freedom in the X–Y molecule, the energy of i-th vibration, the partition function for i-th vibration, and the total vibrational partition function, respectively. Since E_v distributes over the range from 0 to ∞, the differential form of the vibrational part of k_1/k_2 can be expressed by

$$\frac{\mathrm{d}(k_1/k_2)_\mathrm{vib}}{\mathrm{d}(E_\mathrm{v}/RT)} = P(E_\mathrm{v}). \qquad (5)$$

When the activated complex is in an equilibrium relation with the active molecule, k_3/k_4 can be expressed by

$$\frac{k_3}{k_4} = \frac{[(\mathrm{X\cdots Y})_\mathrm{d}^\ddagger]}{[\mathrm{X{-}Y^*}]} = \mathrm{e}^{-\Delta G^\ddagger/RT} \qquad (6)$$

using the free energy change ($\Delta G^\ddagger$). If it is assumed that process 3 is adiabatic, the total internal energy including the zero point energy in the activated complex is equivalent to that in the active molecule, that is, the enthalpy change ($\Delta H^\ddagger$) is zero. Then, Eq. 6 becomes

$$k_3/k_4 = \mathrm{e}^{\Delta S^\ddagger/R}, \qquad (7)$$

where $\Delta S^\ddagger$ means the entropy change.

Equation 7 can also be derived from the concept of the statistical probability (W)[8] using the relations of

$$k_3/k_4 = W^\ddagger/W^* \qquad (8)$$

and

$$S = k\ln W. \qquad (9)$$

The vibrational portion of k_3/k_4 is given by

$$(k_3/k_4)_\mathrm{vib} = \mathrm{e}^{\Delta S_\mathrm{v}^\ddagger/R}, \qquad (10)$$

and

$$\Delta S_\mathrm{v}^\ddagger = S_\mathrm{v}^\ddagger - S_\mathrm{v}^*. \qquad (11)$$

Here, S_v^* and $S_\mathrm{v}^\ddagger$ mean the entropies for the vibrations of the active molecule and the activated complex, respectively.

The last term of Eq. 3 corresponds to kT/h:

$$\frac{k_5}{1 + k_5/k_4} = \frac{\bar{v}q_\mathrm{t}^\ddagger}{2\delta} = \frac{kT}{h}, \qquad (12)$$

which is derived from the mean velocity passing through the transition state ($\bar{v}=(2kT/\pi m)^{1/2}$), the partition function for the one-dimensional translation in the reaction co-ordinate ($q_\mathrm{t}^\ddagger=(2\pi mkT)^{1/2}\delta/h$), and the relation of $k_5/k_4=1$ by the reason that the forward velocity in the range of the transition state (δ) is equal to the backward velocity.[1]

When the energy corresponding to D_0 of the total vibrational energy (E_v) existing in the s vibtrations was accumulated to the X–Y bond, the transfer of the active molecule to the activated complex becomes possible, where D_0 means the chemical bond dissociation energy of the X–Y bond at 0 K. Since the decomposition is possible when $E_\mathrm{v} \geqslant D_0$, E_e in the relation

$$E_\mathrm{v} = D_0 + E_\mathrm{e} \qquad (13)$$

corresponds to the excess energy carried in the activated complex. Then, $P(E_\mathrm{v})$ can be expressed as

$$P(E_\mathrm{v}) = \mathrm{e}^{-D_0/RT}\,\mathrm{e}^{-E_\mathrm{e}/RT}/q_\mathrm{v}. \qquad (14)$$

By combining Eqs. 3, 5, 10, 12, and 14 and considering the contribution of rotations of $(k_1/k_2)_\mathrm{rot}=q_\mathrm{r}^*/q_\mathrm{r}$ and $(k_3/k_4)_\mathrm{rot}=q_\mathrm{r}^\ddagger q_\mathrm{ir}^\ddagger/q_\mathrm{r}^*$, the differential form of k_d^∞ can be derived as

$$\mathrm{d}k_\mathrm{d}^\infty = \frac{kT}{h}\,\frac{q_\mathrm{r}^\ddagger\, q_\mathrm{ir}^\ddagger}{q_\mathrm{r}q_\mathrm{v}}\,\mathrm{e}^{-D_0/RT}\,\mathrm{e}^{\Delta S_\mathrm{v}^\ddagger/R}\,\mathrm{e}^{-E_\mathrm{e}/RT}\,\mathrm{d}\Bigl(\frac{E_\mathrm{v}}{RT}\Bigr) \qquad (15)$$

Here, q_r and $q_\mathrm{r}^\ddagger$ mean the rotational partition functions of the X–Y molecule and the activated complex. $q_\mathrm{ir}^\ddagger$ denotes the partition function for the internal free rotations in the complex.

The differential of Eq. 13 leads to $\mathrm{d}E_\mathrm{v}=\mathrm{d}E_\mathrm{e}$, because D_0 is constant. Thus, the final form for k_d^∞ can be expressed by

$$k_\mathrm{d}^\infty = \frac{kT}{h}\,\frac{q_\mathrm{r}^\ddagger\, q_\mathrm{ir}^\ddagger}{q_\mathrm{r}q_\mathrm{v}}\,\mathrm{e}^{-D_0/RT}\int_0^\infty \mathrm{e}^{\Delta S_\mathrm{v}^\ddagger/R}\,\mathrm{e}^{-E_\mathrm{e}/RT}\,\mathrm{d}\Bigl(\frac{E_\mathrm{e}}{RT}\Bigr), \qquad (16)$$

when $\Delta S_\mathrm{v}^\ddagger/R$ can be applied as a function of E_e/RT.

Calculations and Results

On the unimolecular decomposition by a single bond fission, the activated complex should be very loose, because it must have the same structure as that for the radical–radical recombination which is a reverse reaction. Thus, the Gorin model[6] was adopted for the activated complex.

Accroding to the Gorin model, the X and Y species in the $(\mathrm{X\cdots Y})_\mathrm{d}^\ddagger$ is in an associated state due to the intermolecular force. Therefore, the activated complex can be treated as the problem of two bodies for the X and Y species. Then, the partition function for the rotation of the complex can be expressed by[9]

$$q_\mathrm{r}^\ddagger = \frac{8\pi^2\Gamma(2/3)\mu kT}{\sigma h^2}\Bigl(\frac{2A}{kT}\Bigr)^{1/3}. \qquad (17)$$

Here, σ, Γ, and μ denote the symmetry number, the gamma function, and the reduced mass, respectively.

The constant of the attractive term in the intermolecular potential, A, can be expressed by

$$A = A_{\mathrm{dis}} + \alpha_{\mathrm{X}}\mu_{\mathrm{D}}(\mathrm{Y})^2 + \alpha_{\mathrm{Y}}\mu_{\mathrm{D}}(\mathrm{X})^2 + 2\mu_{\mathrm{D}}(\mathrm{X})^2\mu_{\mathrm{D}}(\mathrm{Y})^2/3kT, \tag{18}$$

where α and μ_{D} mean the polarizability and the dipole moment of X or Y species. The dispersion term, A_{dis}, can be estimated from the approximation by Slater and Kirkwood.$^{10)}$

$$A_{\mathrm{dis}} = \frac{3he\alpha_{\mathrm{X}}\alpha_{\mathrm{Y}}}{4\pi m_{\mathrm{e}}^{1/2}[(\alpha/N_{\mathrm{e}})_{\mathrm{X}}^{1/2} + (\alpha/N_{\mathrm{e}})_{\mathrm{Y}}^{1/2}]} \tag{19}$$

Here, e and m_{e} mean the charge and mass of an electron. N_{e} is the number of outer-shell electrons.

The vibrational partition function of the molecule exclusive of the zero point energy term is given as

$$q_{\mathrm{v}} = \prod_{i=1}^{s}(1 - e^{-x_i})^{-1} \tag{20}$$

by the harmonic oscilator approximation, where $x_i = h\nu_i/kT$. Here, ν_i is the frequency of the i-th vibration.

The vibrational energy accumulated in the $s-1$ vibrations, except for the stretching vibration of the X–Y bond, E_{e}, can be calculated from

$$E_{\mathrm{e}} = RT\sum_{i=1}^{s-1}\frac{x_i}{e^{x_i} - 1} \tag{21}$$

as a function of temperature. The entropy for the $s-1$ vibrations, S_{v}^*, can be estimated from the equation

$$S_{\mathrm{v}}^* = R\sum_{i=1}^{s-1}\left[\frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i})\right] \tag{22}$$

as a function of temperature. Thus, S_{v}^* can be evaluated as a function of E_{e} from the correlation of S_{v}^* and E_{e} at the same temperature.

Similarly, the energy and the entropy for the $s^{\ddagger}$ vibrations of the activated complex, $E_{\mathrm{v}}^{\ddagger}$ and $S_{\mathrm{v}}^{\ddagger}$, can be calculated from the equations

$$E_{\mathrm{v}}^{\ddagger} = RT_{\mathrm{v}}^{\ddagger}\sum_{i=1}^{s^{\ddagger}} x_i^{\ddagger}/(e^{x_i^{\ddagger}} - 1) \tag{23}$$

$$S_{\mathrm{v}}^{\ddagger} = R\sum_{i=1}^{s^{\ddagger}}\left[x_i^{\ddagger}/(e^{x_i^{\ddagger}} - 1) - \ln(1 - e^{-x_i^{\ddagger}})\right] \tag{24}$$

as a function of $T_{\mathrm{v}}^{\ddagger}$, where $x_i^{\ddagger} = h\nu_i^{\ddagger}/kT_{\mathrm{v}}^{\ddagger}$. Here, $\nu_i^{\ddagger}$ and $T_{\mathrm{v}}^{\ddagger}$ mean the frequency of the i-th vibration and the vibrational temperature of the complex. Therefore, $S_{\mathrm{v}}^{\ddagger}$ can be evaluated as a function of $E_{\mathrm{v}}^{\ddagger}$ from the correlation of $S_{\mathrm{v}}^{\ddagger}$ and $E_{\mathrm{v}}^{\ddagger}$ at the same $T_{\mathrm{v}}^{\ddagger}$.

On the other hand, the total energy including the zero point energy for the $s-1$ vibrations of the molecule should be equal to the total sum of the vibrational and zero point energies for the $s^{\ddagger}$ vibrations and the energy for the $p^{\ddagger}$ internal free rotations of the activated complex, because process 3 is adiabatic. Provided that the rotational temperature for the internal free rotations in the complex is equivalent to the reaction temperature (T), the relation

$$E_{\mathrm{e}} + E_{\mathrm{z}} = E_{\mathrm{v}}^{\ddagger} + E_{\mathrm{z}}^{\ddagger} + p^{\ddagger}RT/2 \tag{25}$$

is formed. When the zero point energy difference ($\Delta E_{\mathrm{z}}^{\ddagger}$) is expressed by

$$\Delta E_{\mathrm{z}}^{\ddagger} = E_{\mathrm{z}} - E_{\mathrm{z}}^{\ddagger} = \sum_{i=1}^{s-1} h\nu_i/2 - \sum_{i=1}^{s^{\ddagger}} h\nu_i^{\ddagger}/2, \tag{26}$$

Eq. 25 can be rewritten as

$$E_{\mathrm{v}}^{\ddagger} = \Delta E_{\mathrm{z}}^{\ddagger} - p^{\ddagger}RT/2 + E_{\mathrm{e}}. \tag{27}$$

Thus, $E_{\mathrm{v}}^{\ddagger}$, $S_{\mathrm{v}}^{\ddagger}$, and $\Delta S_{\mathrm{v}}^{\ddagger}$ can be estimated as a function of E_{e} from the relations of Eqs. 13 and 23—27.

In order to ascertain the adequacy of the present theory, the thermal decompositions of $CH_4 \rightarrow CH_3+H$, $CD_4 \rightarrow CD_3+D$, $C_2H_6 \rightarrow 2CH_3$, and $C_2D_6 \rightarrow 2CD_3$ were chosen as the object of the calculations by the following reasons: these decompositions are based on the single bond fission; the Gorin model can be applied for the activated complexes, because X and Y are simplest species such as H and CH_3; the physical constants for the molecules and the complexes are known; in comparison with the calculated results, many experimental results for the decompositions have been reported.

The values used in the calculations of the thermal decomposition rates are shown in Tables 1 and 2 for the wavenumbers of the vibrations of CH_4,$^{11)}$ CD_4,$^{12)}$ C_2H_6,$^{11)}$ C_2D_6,$^{12)}$ CH_3,$^{13)}$ and $CD_3$$^{13)}$ and for the moments of inertia of the rotations of CH_4,$^{14)}$ CD_4,$^{14)}$ C_2H_6,$^{15)}$ C_2D_6,$^{15)}$ CH_3,$^{16)}$ and CD_3.$^{16)}$ Since the free methyl radicals are planar (point group, D_{3h}), the dipole moment is zero. Thus, the value of A estimated from Eq. 19 was 1.89×10^{-78} J m^6 for $(CH_3\cdots H)_{\mathrm{d}}^{\ddagger}$ and $(CD_3\cdots D)_{\mathrm{d}}^{\ddagger}$ and 11.16×10^{-78} J m^6 for $(CH_3\cdots CH_3)_{\mathrm{d}}^{\ddagger}$ and $(CD_3\cdots CD_3)_{\mathrm{d}}^{\ddagger}$, by using the values of $\alpha = 0.401\times10^{-30}$ m^3 $^{17)}$ and $N_{\mathrm{e}}=1$ for H and D and of $\alpha = 2.24\times10^{-30}$ m^3 $^{17)}$ and $N_{\mathrm{e}}=7$ for CH_3 and CD_3.

The values of $S_{\mathrm{v}}^{\ddagger}/R$ on the decompositions of CH_4 and CD_4 are shown in Fig. 1 as a function of $E_{\mathrm{v}}^{\ddagger}$, from the correlation of $E_{\mathrm{v}}^{\ddagger}$ and $S_{\mathrm{v}}^{\ddagger}$ calculated by Eqs. 23 and 24 using the same $T_{\mathrm{v}}^{\ddagger}$. The values of S_{v}^*/R, $S_{\mathrm{v}}^{\ddagger}/R$, and $\Delta S_{\mathrm{v}}^{\ddagger}/R$ on the decompositions of methanes are shown in Fig. 2 as a function of E_{e}. These values were calculated by the following procedures: E_{e} and S_{v}^* at an optional temperature (T) can be calculated from Eqs. 21 and 22; $E_{\mathrm{v}}^{\ddagger}$ can be evaluated from Eq. 27 using the values of E_{e} and T;$^{18)}$ $S_{\mathrm{v}}^{\ddagger}$ corresponding to the $E_{\mathrm{v}}^{\ddagger}$ can

Table 1. Physical Constants for the Molecules and the Activated Complexes on the Thermal Decompositions of CH_4 and CD_4

	Molecule		Complex	
	CH_4	CD_4	$(CH_3\cdots H)^{\ddagger}_{d}$	$(CD_3\cdots D)^{\ddagger}_{d}$
Wavenumber/cm^{-1}	1306(3) 1534(2) 2917(1) 3019(3)$^{a)}$	996(3) 1092(2) 2109(1) 2259(3)$^{a)}$	617(1) 1396(2) 3044(1) 3162(2)	463(1) 1026(2) 2513(1) 2381(2)
Moment of inertia/10^{-47} kg m^2	5.26(3)	10.51(3)	5.85(1) 2.92(2)	11.68(1) 5.84(2)

a) d stretching vibration.

Table 2. Physical Constants for the Molecules and the Activated Complexes on the Thermal Decompositions of C_2H_6 and C_2D_6

	Molecule		Complex	
	C_2H_6	C_2D_6	$(CH_3\cdots CH_3)^{\ddagger}_{d}$	$(CD_3\cdots CD_3)^{\ddagger}_{d}$
Wavenumber/cm^{-1}	289(1) 822(2) 995(1)$^{a)}$ 1190(2) 1379(1) 1388(1) 1468(2) 1469(2) 2896(1) 2954(1) 2969(2) 2985(2)	208(1) 594(2) 843(1)$^{a)}$ 970(2) 1077(1) 1155(1) 1041(2) 1081(2) 2083(1) 2087(1) 2226(2) 2235(2)	617(2) 1396(4) 3044(2) 3162(4)	463(2) 1026(4) 2513(2) 2381(4)
Moment of inertia/10^{-47} kg m^2	10.43(1) 42.19(2)	20.84(1) 60.83(2)	5.85(2) 2.92(4)	11.68(2) 5.84(4)

a) Stretching vibration of the C–C bond.

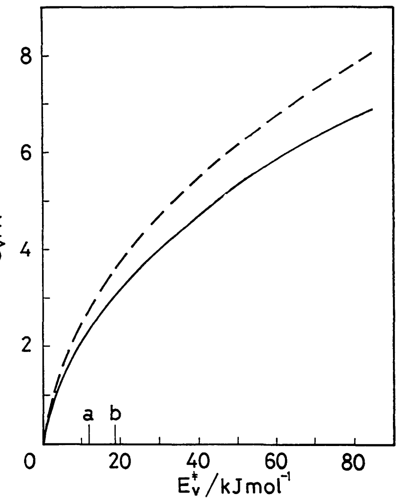

Fig. 1. Relations of $S^{\ddagger}_{v}/R$ versus $E^{\ddagger}_{v}$ on the pyrolyses of methanes. —, CH_4; — —, CD_4; a, $\Delta E^{\ddagger}_{z}(CD_4)$; b, $\Delta E^{\ddagger}_{z}(CH_4)$.

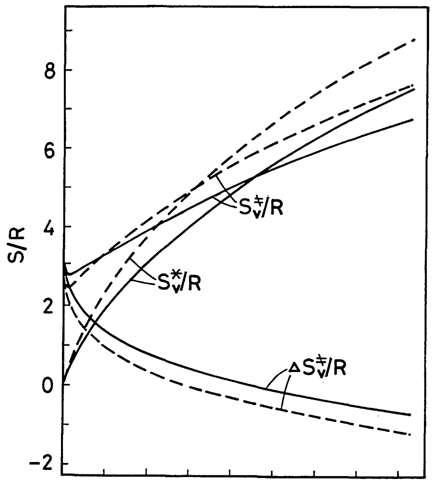

Fig. 2. Plots of S^{*}_{v}/R, $S^{\ddagger}_{v}/R$, and $\Delta S^{\ddagger}_{v}/R$ as a function of E_e on the pyrolyses of methanes. —, CH_4; — —, CD_4.

be estimated from the relation in Fig. 1; $\Delta S^{\ddagger}_{v}$ can be calculated from Eq. 13 using the values of $S^{\ddagger}_{v}$ and S^{*}_{v}.

It is found in Fig. 2 that $\Delta S^{\ddagger}_{v}$ possesses the same positive value as $S^{\ddagger}_{v}$ at $E_e=0$. The facts are due to the following reasons: since both E_e and $p^{\ddagger}RT/2$ in Eq. 27 are zero at $T=0$ K, $E^{\ddagger}_{v}$ at $E_e=0$ is equivalent to $\Delta E^{\ddagger}_{z}$;

since $\Delta E_z^\ddagger$ has a positive value, $S_v^\ddagger$ has also a positive value at $E_v^\ddagger = \Delta E_z^\ddagger$ as is seen in Fig. 1; since S_v^* is zero at $E_e=0$, $\Delta S_v^\ddagger$ is equal to $S_v^\ddagger$ at $E_e=0$. It is also found in Fig. 2 that $\Delta S_v^\ddagger/R$ decreases with an increase of E_e, because S_v^*/R increases more rapidly than $S_v^\ddagger/R$. On the decompositions of C_2H_6 and C_2D_6, the values of S_v^*/R, $S_v^\ddagger/R$, and $\Delta S_v^\ddagger/R$ which were calculated by the same procedures as those mentioned above are shown in Fig. 3 as a function of E_e. The same trends as those in Fig. 2 were also found in Fig. 3.

The calculation of the last term of Eq. 16 was performed by the numerical integration using the values of $\Delta S_v^\ddagger$ in Figs. 2 and 3. The calculated values of the frequency factor

$$A_d^\infty = \frac{kT}{h}\frac{q_r^\ddagger q_{ir}^\ddagger}{q_r q_v}\int_0^\infty e^{\Delta S_v^\ddagger/R}\, e^{-E_e/RT}\, d\left(\frac{E_e}{RT}\right), \tag{28}$$

are shown in Table 3. The values of k_d^∞ were calculated using the values of A_d^∞ listed in Table 3 and $D_0(CH_3\text{-}H)=449.1$ and $D_0(CH_3\text{-}CH_3)=393.0$ kJ mol^{-1} which will be discussed later. The Arrhenius plot of the calculated values of k_d^∞ for the decomposition of CH_4 is shown in Fig. 4 together with those of the experimental values of k_d^∞ obtained by Chen and Back[19] and of k_d which were reported by various workers.[20-27]

On the decomposition of C_2H_6, the values of k_d which were measured as a function of the pressure were reported by several investigators.[28-31] Using these values, the experimental values of k_d^∞ for C_2H_6 were obtained from the intercepts of the plots of $1/k_d$ versus $1/[M]$ or $1/[M]^n$ ($n<1$) on the basis of the relation

$$\frac{1}{k_d} = \frac{1}{k_d^\infty} + \frac{1}{k_1[M]} \tag{29}$$

derived from Eqs. 2 and 3. The experimental values of k_d^∞ for C_2H_6 obtained by this procedure are shown in Table 4. The Arrhenius plot for the calculated values

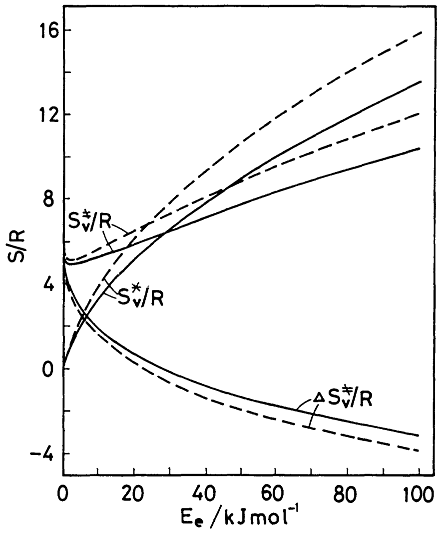

Fig. 3. Plots of S_v^*/R, $S_v^\ddagger/R$, and $\Delta S_v^\ddagger/R$ versus E_e on the pyrolyses of ethanes. —, C_2H_6; — —, C_2D_6.

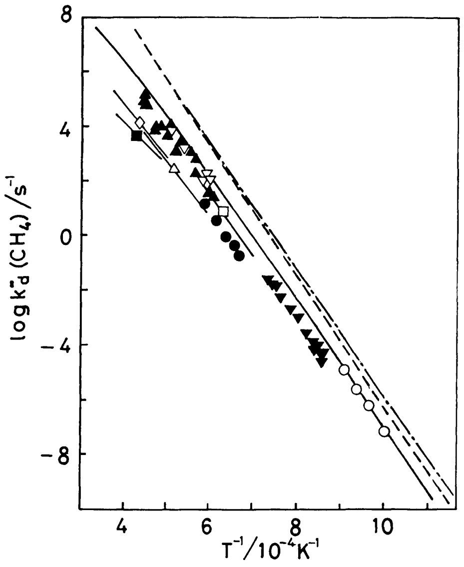

Fig. 4. Arrhenius plots of k_d^∞ on the pyrolysis of CH_4. Calculated value: —, the present theory; – – –, the RRKM theory; —·—, the theory of absolute reaction rates. Experimental value: ○, Ref. 19; ▲, Ref. 20; –□–, Ref. 21; ▽, Ref. 22; ▼, Ref. 23; –△–, Ref. 24; –◇–, Ref. 25; –■–, Ref. 26; ●, Ref. 27. The experimental values other than Ref. 19 (○) are not the high pressure limiting rate constant.

Table 3. Calculated Values of A_d^∞ for the Thermal Decompositions of Methanes and Ethanes

T/K	$A_d^\infty/10^{15}$ s^{-1}		T/K	$A_d^\infty/10^{17}$ s^{-1}	
	CH_4	CD_4		C_2H_6	C_2D_6
800	27.3	21.5	800	11.59	14.34
1000	25.6	16.6	900	9.34	9.52
1200	21.9	11.9	1000	7.20	6.12
1400	17.7	8.19	1200	3.93	2.41
1600	13.8	5.55	1400	2.00	0.929
1800	10.4	3.74	1600	0.987	0.361
2200	5.78	1.71	1800	0.482	0.144
2600	3.24	0.83	2000	0.236	0.059

Table 4. Experimental Values of k_d^∞ on the Thermal Decomposition of C_2H_6

T/K	k_d^∞/s^{-1}	Ref.	T/K	k_d^∞/s^{-1}	Ref.
822.9	1.5×10^{-7}	28	873.2	2.0×10^{-6}	30
838	4.3×10^{-7}	31	893.5	9.5×10^{-6}	28
839.2	2.5×10^{-7}	30	913.2	3.3×10^{-5}	29
840.2	3.1×10^{-7}	29	933.2	7.1×10^{-5}	29
843.7	5.5×10^{-7}	28	958.7	2.4×10^{-4}	29
843.7	5.6×10^{-7}	29	978.0	6.3×10^{-4}	29
857.9	1.3×10^{-6}	28	999.5	1.3×10^{-3}	29
872.9	3.1×10^{-6}	28			

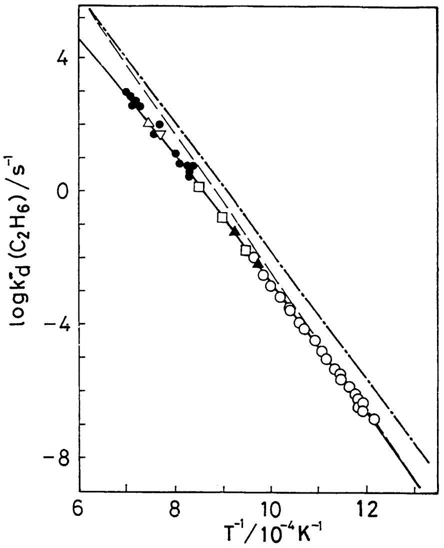

Fig. 5. Plots of $\log k_d^{\infty}$ versus $1/T$ on the thermal decomposition of C_2H_6. Calculated value: ——, the present theory; – – –, the RRKM theory; —·—, the theory of absolute reaction rates. Experimental value: ○, the values listed in Table IV; ▲, Ref. 27; ▽, Ref. 32 (average of five values of k_d^{∞} at 1300 K); ●, Ref. 33; △, Ref. 34; □, Ref. 36.

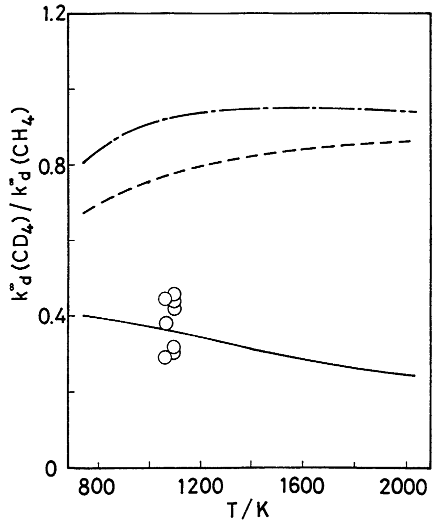

Fig. 6. Plots of $k_d^{\infty}(CD_4)/k_d^{\infty}(CH_4)$ versus T. Calculated value: ——, the present theory; —·—, the RRKM theory; – – –, the theory of absolute reaction rates. Experimental value: ○, Ref. 39. The experimental values are not the rate constant ratio at the high pressure limit.

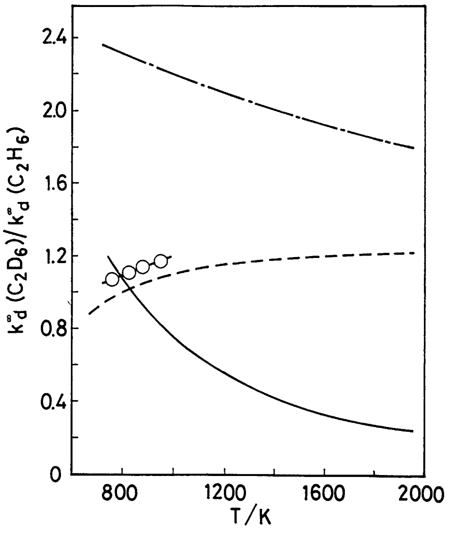

Fig. 7. Temperature dependences of $k_d^{\infty}(C_2D_6)/k_d^{\infty}(C_2H_6)$. Calculated value: ——, the present theory; —·—, the RRKM theory; – – –, the theory of absolute reaction rates. Experimental value: ○, Ref. 31. The experimental values are not the rate constant ratio at the high pressure limit.

of k_d^{∞} on the decomposition of C_2H_6 is shown in Fig. 5 together with the plots for the values of k_d^{∞} listed in Table 4 and the experimental values of k_d^{∞} which were reported by various investigators.[27,32-38]

On the kinetic isotope effect, the rate constant ratio for the decompositions of CH_4 and CD_4 can be calculated from the equation.

$$k_d^{\infty}(CD_4)/k_d^{\infty}(CH_4) = A_d^{\infty}(CD_4)\,e^{-\Delta D_0/RT}/A_d^{\infty}(CH_4) \qquad (30)$$

The difference between the chemical bond dissociation energies, ΔD_0, is equivalent to the zero point energy difference which can be estimated from the frequencies of stretching vibration for the breaking bond (ν_{st}).

$$\begin{aligned}\Delta D_0 &= D_0(CD_3\text{-}D) - D_0(CH_3\text{-}H)\\ &= (h/2)[\nu_{st}(CH_4) - \nu_{st}(CD_4)] \qquad (31)\end{aligned}$$

The ratios of $k_d^{\infty}(CD_4)/k_d^{\infty}(CH_4)$ calculated using the values of $A_d^{\infty}(CD_4)$ and $A_d^{\infty}(CH_4)$ listed in Table 3 and ΔD_0=4.83 kJ mol^{-1} obtained from the wavenumbers in Table 1 are shown in Fig. 6 together with the experimental values obtained by Chen and Back,[39] although none of these are the ratios at the high pressure limit. Similarly, the ratios of $k_d^{\infty}(C_2D_6)/k_d^{\infty}(C_2H_6)$ calculated using the values of $A_d^{\infty}(C_2D_6)$ and $A_d^{\infty}(C_2H_6)$ in Table 3 and ΔD_0=0.91 kJ mol^{-1} are shown in Fig. 7 together with the ratios observed by Clark and Quinn,[31] though their values are also not the ratios at the high pressure limit.

Discussion

Thermodynamic Considerations. The enthalpy per mole of a gaseous substance at T/K and 1 atm, H_T°, can be, in general, expressed as

$$H_T^{\circ} = E_0 + \langle E_t\rangle + \langle E_r\rangle + \langle E_v\rangle + RT, \qquad (32)$$

where E_0 denotes the internal energy at 0 K. $\langle E_t\rangle$,

$<E_r>$, and $<E_v>$ indicate the average energies for the translational, rotational, and vibrational motions at T/K, respectively. Therefore, the energy change at 0 K for the reaction of $CH_4(g) \rightarrow CH_3(g)+H(g)$, $\Delta E_0(CH_4)$, can be expressed by

$$\Delta E_0(CH_4) = E_0(CH_3) + E_0(H) - E_0(CH_4)$$
$$= \Delta H^\circ_T(CH_4) - RT\left[\frac{5}{2} + \left(\sum_{i=1}^{6}\frac{x_i}{e^{x_i}-1}\right)_{CH_3} - \left(\sum_{i=1}^{9}\frac{x_i}{e^{x_i}-1}\right)_{CH_4}\right] \tag{33}$$

from the following relations: $<E_t>=3RT/2$ for H, CH_3, and CH_4; $<E_r>=3RT/2$ for CH_3 and CH_4; $<E_r>=<E_v>=0$ for H; $<E_v>=RT\sum x_i/[\exp(x_i)-1]$ for CH_3 and CH_4. The enthalpy change of the reaction, $\Delta H^\circ_T(CH_4)$, can be calculated from the heats of formation of H, CH_3, and CH_4 at T/K and 1 atm. Similarly, the energy change at 0 K for the reaction of $C_2H_6(g) \rightarrow 2CH_3(g)$, $\Delta E_0(C_2H_6)$, is given by

$$\Delta E_0(C_2H_6) = 2E_0(CH_3) - E_0(C_2H_6)$$
$$= \Delta H^\circ_T(C_2H_6) - RT\left[4 + 2\left(\sum_{i=1}^{6}\frac{x_i}{e^{x_i}-1}\right)_{CH_3} - \left(\sum_{i=1}^{18}\frac{x_i}{e^{x_i}-1}\right)_{C_2H_6}\right] \tag{34}$$

because of $<E_t>=<E_r>=3RT/2$ for CH_3 and C_2H_6. $\Delta H^\circ_T(C_2H_6)$ means the enthalpy change of the reaction at T/K and 1 atm.

The chemical bond dissociation energy (D_0) can be calculated from

$$D_0 = \Delta E_0 + \Delta E_z^{\ddagger} \tag{35}$$

by using Eqs. 26, 33, and 34. The electronic bond dissociation energy (D_e) is given by

$$D_e = D_0 + h\nu_{st}/2, \tag{36}$$

where $h\nu_{st}/2$ is the zero point energy for the stretching vibration of the breaking bond.

The values of D_0, D_e, $\Delta E_z^{\ddagger}$, ΔE_0, and ΔH°_{298} for the decompositions of CH_4 and C_2H_6 were calculated from Eqs. 26 and 33 to 36 by using the wavenumbers in Tables 1 and 2 and the standard heats of formation of 218.0 for H(g),[40] 143.2 for $CH_3(g)$, −74.8 for $CH_4(g)$,[41] and −84.7 kJ mol^{-1} for C_2H_6.[41] These values are shown in Table 5 together with the values calculated for the decomposition of $CH_3I(g) \rightarrow CH_3(g)+I(g)$.[42]

The values listed in Table 5 appear to be reasonable by the following reasons: the values of k_d^∞ calculated using the present theory and the values in Table 5 are in excellently accord with the experimental values of k_d^∞ for the decompositions as are seen in Figs. 4 and 5; the value of $\Delta H^\circ_{f,298}(CH_3)=143.2$ kJ mol^{-1} (34.2 kcal mol^{-1}) which was used commonly for the three decompositions are appropriate, judging from the previously reported values of 33.0,[43] 33.2,[44] 33.9,[45] 34.0,[46] 34.1,[47] 34.4,[48] 34.7,[49] 34.8,[50] 34.9,[51] and 35.1[52] kcal mol^{-1}. The values in Table 5 suggest that D_0, D_e, ΔE_0, and ΔH°_{298} should not be used confusedly, because these have different definitions and values with one another.

The apparent activation energy for the unimolecular decomposition of C_2H_6 at the high pressure limit, E_{app}, was calculatd from the relation

$$E_{app} = \frac{RT_1T_2}{T_2 - T_1}\ln\frac{(k_d^\infty)_{T_2}}{(k_d^\infty)_{T_1}} \tag{37}$$

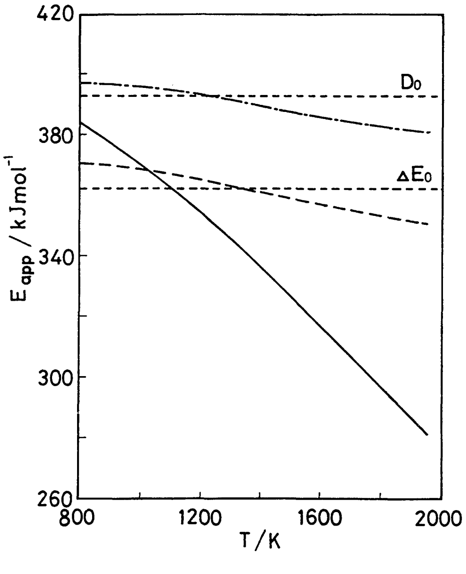

Fig. 8. Temperature dependences of the apparent activation energy on the thermal decomposition of C_2H_6 at the high pressure limit. Calculated value: —, the present theory; -·-, the RRKM theory; ---, the theory of absolute reaction rates.

Table 5. Thermodynamic Values for the Thermal Decompositions of C_2H_6, CH_4, and CH_3I

Reaction	D_0	D_e	$\Delta E_z^{\ddagger}$	ΔE_0	ΔH°_{298}
	kJ mol^{-1}				
$C_2H_6 \rightarrow CH_3+CH_3$	393.0	399.0	30.9	362.1	371.1
$CH_4 \rightarrow CH_3+H$	448.4	466.5	18.9	429.5	436.0
$CH_3I \rightarrow CH_3+I$	243.7	246.9	13.1	230.6	236.3

using the values of A_{d}^{∞} in Table 3 and $D_0=393.0$ kJ mol^{-1} which were supported experimentally as seen in Fig. 5. It is found in Fig. 8 that E_{app} calculated at intervals of $T_2-T_1=200$ K decreases drastically with an increase of the reaction temperature. This fact suggests that the estimations of the thermodynamic quantities of D_0, ΔE_0, ΔH°, and others from the apparent activation energy are not suitable.

Comparisons of k_{d}^{∞}. In order to compare the results calculated by the present theory with those by the theories which were proposed previously, the calculations on the basis of the theory of absolute reaction rates[1] and the RRKM theory[3] were performed using the same activated complex model and physical constants as the case of the present theory.

The specific rate by the theory of absolute reaction rates,[1] k_{d}^{∞}(ARR), can be expressed by the equation

$$k_{\mathrm{d}}^{\infty}(\mathrm{ARR}) = \frac{kT}{h}\,\frac{q_{\mathrm{r}}^{\neq}\,q_{\mathrm{ir}}^{\neq}q_{\mathrm{v}}^{\neq}}{q_{\mathrm{r}}q_{\mathrm{v}}}\,\mathrm{e}^{-\Delta E_0/RT} \tag{38}$$

as is well known. Using $q_{\mathrm{v}}^{\neq}=\Pi\{1-\exp(-h\nu_{\mathrm{i}}^{\neq}/kT)\}^{-1}$ and $\Delta E_0(\mathrm{CH_4})=429.5$ and $\Delta E_0(\mathrm{C_2H_6})=362.1$ kJ mol^{-1} in Table 5, the values calculated from Eq. 38 are shown in Figs. 4—8. It is found in Figs. 4 and 5 that the values of k_{d}^{∞}(ARR) are too high as compared with the experimental values.

A main reason for the high specific rates originates in the fact that ΔE_0 was applied in place of D_0 because of the assumption that the equilibrium between the molecule and the activated complex is isothermal. The fact suggests that $\Delta E_{\mathrm{z}}^{\neq}$ is not used to reduce the enthalpy term from D_0 to ΔE_0 in very short time as a vibrational period of the X–Y stretching vibration in the reaction coordinate and that $\Delta E_{\mathrm{z}}^{\neq}$ participates in the entropy term of the activated complex.

The specific rate at the high pressure limit by the RRKM theory, k_{d}^{∞}(RRKM), is given by[53]

$$k_{\mathrm{d}}^{\infty}(\mathrm{RRKM}) = \frac{kT}{h}\,\frac{q_{\mathrm{r}}^{\neq}\,q_{\mathrm{ir}}^{\neq}}{q_{\mathrm{r}}q_{\mathrm{v}}}\,\frac{\mathrm{e}^{-D_0/RT}}{\Gamma(1+p^{\neq}/2)} \times\int_0^{\infty}\Sigma P(E_{\mathrm{v}}^{\neq})\left(\frac{E^{\neq}-E_{\mathrm{v}}^{\neq}}{kT}\right)^{p^{\neq}/2}\mathrm{e}^{-E^{\neq}/kT}\,\mathrm{d}(E^{\neq}/kT). \tag{39}$$

The values of k_{d}^{∞}(RRKM) calculated using the approximation for vibrational energy-level sums[54] are also shown in Figs. 4—8.

It is found in Figs. 4 and 5 that the apparent temperature dependence of k_{d}^{∞}(RRKM) is high as compared with that of the present theory, that is, E_{app} by k_{d}^{∞}(RRKM) little decreases with an increase of the reaction temperature as is seen in Fig. 8. Hence, the deviation from the experimental values enlarges with an increase of the reaction temperature as is seen in Fig. 5. The kinetic isotope ratios of $k_{\mathrm{d}}^{\infty}(\mathrm{CD_4})/k_{\mathrm{d}}^{\infty}(\mathrm{CH_4})$ and $k_{\mathrm{d}}^{\infty}(\mathrm{C_2D_6})/k_{\mathrm{d}}^{\infty}(\mathrm{C_2H_6})$ calculated by the RRKM theory are very high as compared with the experimental ratios as are seen in Figs. 6 and 7. These results suggest that the integration term in Eq. 39 or the approximation for vibrational energy-level sums[54] does not correspond to the real behavior.

On the other hand, the present theory and the calculation procedure seem to be proper judging from the following reasons: the parameters to adjust to the experimental values were not used totally; the common activated complex model and physical constants were used for three decomposition reactions; the calculated values of k_{d}^{∞} and $k_{\mathrm{d}}^{\infty}(\mathrm{CD_3I})/k_{\mathrm{d}}^{\infty}(\mathrm{CH_3I})$[42] were in excellently accord with the experimental values.

Reverse Reaction and Chemical Equilibrium. The reverse reaction of the X–Y bond dissociation reaction, that is, the recombination reaction of X and Y species can be expressed by the scheme

$$\mathrm{X}+\mathrm{Y} \underset{k_5}{\overset{k_6}{\rightleftharpoons}} (\mathrm{X}\cdots\mathrm{Y})_{\mathrm{c}}^{\neq} \underset{k_3}{\overset{k_4}{\rightleftharpoons}} \mathrm{X{-}Y}^{*} \xrightarrow{k_2[\mathrm{M}]} \mathrm{X{-}Y} \tag{40}$$

from the same concept as that for the decomposition expressed in Eq. 1. From the scheme, the specific recombination rate at the high pressure limit, k_{c}^{∞}, is given by

$$k_{\mathrm{c}}^{\infty} = k_6/(1+k_5/k_4). \tag{41}$$

The specific rate by the theory of absolute reaction rates, k_{c}^{∞}(ARR), is given as[55]

$$k_{\mathrm{c}}^{\infty}(\mathrm{ARR}) = \xi\,\frac{2\Gamma(2/3)N_{\mathrm{A}}}{\sigma}\left(\frac{2\pi kT}{\mu}\right)^{1/2}\left(\frac{2A}{kT}\right)^{1/3}\frac{q_{\mathrm{e}}((\mathrm{X}\cdots\mathrm{Y})_{\mathrm{c}}^{\neq})}{q_{\mathrm{e}}(\mathrm{X})\,q_{\mathrm{e}}(\mathrm{Y})} \tag{42}$$

by using Eq. 17 based on the Gorin model, where q_{e} denotes the electronic partition function. It is well-known that the calculated values by Eq. 42 are accord with the experimental values within the limits of the depression by the steric hindrance factor (ξ).[56] For example, ξ for the recombination of methyl radicals is abount one half.[57] However, the equilibrium constant for the chemical equilibrium $\mathrm{XY(g)} \rightleftharpoons \mathrm{X(g)}+\mathrm{Y(g)}$, K_{p}, can not be evaluated from the ratio of $k_{\mathrm{d}}^{\infty}(\mathrm{ARR})/k_{\mathrm{c}}^{\infty}(\mathrm{ARR})$ although both were derived on the basis of the same conception, because k_{d}^{∞}(ARR) are not consistent with the experimental values of k_{d}^{∞} as are seen in Figs. 4 and 5.

According to the Gorin model, the vibrational temperature in $(\mathrm{X}\cdots\mathrm{Y})_{\mathrm{c}}^{\neq}$ is almost the same as the reaction temperature (T), because the interaction between X and Y in $(\mathrm{X}\cdots\mathrm{Y})_{\mathrm{c}}^{\neq}$ is very weak. On the other hand, $T_{\mathrm{v}}^{\neq}$ in $(\mathrm{X}\cdots\mathrm{Y})_{\mathrm{d}}^{\neq}$ is calculable by the following procedures: the values of $E_{\mathrm{v}}^{\neq}$ at designated T and $T_{\mathrm{v}}^{\neq}$ can be evaluated from Eqs. 21, 23, and 27; $T_{\mathrm{v}}^{\neq}$ corresponding to T can be estimated from the plots of

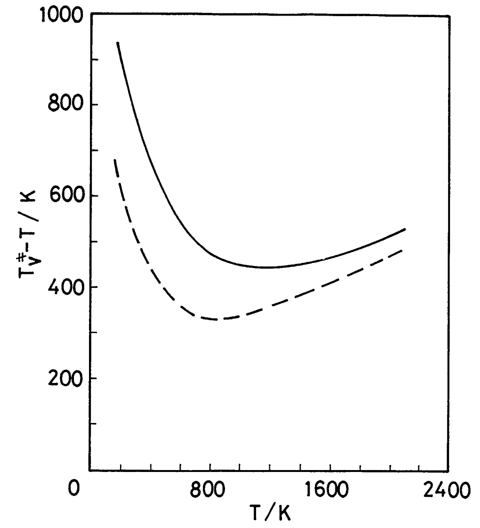

Fig. 9. Relations of the vibrational temperature in the activated complex ($T_v^{\ddagger}$) and the reaction temperature (T) on the pyrolyses of ethanes. —, C_2H_6; – –, C_2D_6.

T and $T_v^{\ddagger}$ against $E_v^{\ddagger}$. It is found in Fig. 9 that $T_v^{\ddagger}$ on the thermal decompositions of C_2H_6 and C_2D_6 are considerably high as compared with the experimental temperature. The main contributions to $T_v^{\ddagger}$ in the lower and higher temperature ranges are due to $\Delta E_z^{\ddagger}$ and E_e, respectively. The similar diagram as Fig. 9 was also found on the decompositions of CH_4 and CD_4.

These results obtained on the basis of the present theory exhibit which the vibrational temperature in $(X\cdots Y)_d^{\ddagger}$ is higher than that in $(X\cdots Y)_c^{\ddagger}$, although the same Gorin model was applied for both activated complexes. Therefore, the X and Y species formed by Eq. 1 are in more vibrationally excited states than those in the thermal equilibrium state. Thus, these findings suggest generally that the ratio of $k_d^{\infty}/k_c^{\infty}$ is different from K_p in the thermal equilibrium state, that is, the equilibrium constant can not be evaluated from k_d^{∞} and k_c^{∞} which were obtained separately.

$$K_p \neq k_d^{\infty}/k_c^{\infty} \tag{43}$$

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17) Estimated from $\alpha(H_2)=0.802$, $\alpha(CH_4)=2.63$, and $\alpha(C_2H_6)=4.49\times10^{-30}\,\mathrm{m}^3$.

18) The values of $p^{\ddagger}$ in Eq. 27 are 2 and 5 for the decompositions of methanes and ethanes, respectively. Meanwhile, the rotational degrees of freedom for $q_{ir}^{\ddagger}$ in Eq. 16 become $p^{\ddagger}+1$, when $q_r^{\ddagger}$ is calculated by Eq. 17 which was derived by handling as the problem of two bodies for X and Y.

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