The Decomposition of Energized Ethylene Formed in the Photolyses of Alkanes

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The decomposition and the collisional deactivation of energized ethylene formed in the photolyses of ethane, propane, *n*-butane, and cyclobutane at 1470 Å have been studied from the change in ethylene and acetylene yields with varying pressures of alkane or nitrogen added as a deactivator. The rate constants of the collisional deactivation and decomposition of energized ethylene were determined from the experimental data. The unimolecular decomposition theory has been applied to energized ethylene, and the results compared with the experimental rate constants.

In recent years, several studies of the Photolyses of simple alkanes, such as ethane,[1-5] propane,[6-9] *n*-butane,[9-11] and cyclobutane,[12] have been reported in respect of the primary processes. On the other hand, some studies of the photolyses of ethane[13,14] and propane[15] at 1470 Å have been undertaken in order to obtain insight into the nature of intermediate energized ethylene. These works have made it clear that two kinds of energized ethylene should be yielded through the molecular elimination of hydrogen from ethane or that of methane from propane; one undergoes unimolecular decomposition into acetylene and hydrogen, competing with collisional stabilization to ethylene, while the other can not decompose more. In the photolyses of ethane and propane, the following reaction schemes with respect to the ethylene- and acetylene-forming reactions have been proposed:[14,15]

$$\begin{tikzcd} C_2H_6 + h\nu \arrow[r, "\phi_{1a}"] & H_2 + C_2H_4^{**} \arrow[r, "k_d"] \arrow[rd, "k_s^M[M]"'] & C_2H_2 + H_2 & (1) \\ {} \arrow[r, "\phi_{1b}"] & H_2 + C_2H_4^{*} \arrow[r] & C_2H_4 & (2) \\ {} \arrow[r, "\phi_2"] & 2H + C_2H_4 & & (3) \end{tikzcd}$$

$$\begin{tikzcd} C_3H_8 + h\nu \arrow[r, "\phi_{1a}"] & CH_4 + C_2H_4^{**} \arrow[r, "k_d"] \arrow[rd, "k_s^M[M]"'] & C_2H_2 + H_2 & (4) \\ {} \arrow[r, "\phi_{1b}"] & CH_4 + C_2H_4^{*} \arrow[r] & C_2H_4 & (5) \\ {} \arrow[r, "\phi_2"] & H + CH_3 + C_2H_4 & & (6) \end{tikzcd}$$

The k_s^M/k_d values should depend on the energy retained in energized ethylene and the relative deactivation efficiencies of the deactivators. In order to determine the relative deactivation efficiency of energized ethylene, nitrogen was added as a common deactivator to a fixed amount of alkane and the change in the product distribution was studied by means of the change in the pressure of added nitrogen.

Recently, the nonequilibrium decomposition of ethylene has been discussed theoretically using a simple RRKM treatment, especially in the photolysis of 3-methyldiazirine.[16] In this paper, the average rate constants for the decomposition of ethylene produced in the photolyses of several alkanes will be calculated using the unimolecular decomposition theory. The experimental results are compared with the values obtained on a theoretical model for the relative deactivation rates, and a good agreement was found.

Experimental

The experimental procedures used in these experiments were almost the same as have been described previously.[15] A reaction cell with a magnetic circulator was used to prevent the accumulation of the products near the window. C_2H_6, C_3H_8, and *n*-C_4H_{10} were obtained from the Takachiho Chem. Ind. Co., and cyclo-C_4H_8 from Merck, Sharp, & Dohme, Ltd. Samples were purified by means of a gas chromatograph with a silica gel column. A 3 m activated charcoal column was used to detect ethylene and acetylene in a huge amount of unreacted ethane or propane. In the photolysis of *n*-C_4H_{10} or cyclo-C_4H_8, products were analyzed on a 2 m silica gel column with 5% squalane. In order to eliminate radical reactions, experiments were always carried out in the presence of nitric oxide (5—10% of alkanes).

Results and Discussion

A) Experimental Average Rate Constants. The reaction scheme previously established in the photolyses of ethane and propane,[14,15] in which the energized ethylene in two excited states is formed, may be similarly adopted in the photolyses of *n*-butane and cyclobutane:

$$\begin{tikzcd} n\text{-}C_4H_{10} + h\nu \arrow[r, "\phi_{1a}"] & C_2H_6 + C_2H_4^{**} \arrow[r, "k_d"] \arrow[rd, "k_s^M[M]"'] & C_2H_2 + H_2 & (7) \\ {} \arrow[r, "\phi_{1b}"] & C_2H_6 + C_2H_4^{*} \arrow[r] & C_2H_4 & (8) \\ {} \arrow[r, "\phi_2"] & H + C_2H_5 + C_2H_4 & & \\ & & (\text{and/or } 2CH_3 + C_2H_4) & (9) \end{tikzcd}$$

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[12] R. D. Doepker and P. Ausloos, *ibid.*, **43**, 3814 (1965).
[13] R. F. Hampson, Jr., and J. R. McNesby, *ibid.*, **43**, 3592 (1965).
[14] H. Akimoto and I. Tanaka, *J. Phys. Chem.*, **71**, 4135 (1967).
[15] H. Akimoto and I. Tanaka, *Ber. Bunsenges. Physik. Chem.*, **72**, 135 (1968).
[16] A. W. Kirk and E. Tschuikow-Roux, *J. Chem. Phys.*, **51**, 2247 (1969).

$$\begin{array}{ll} \text{cyclo-}C_4H_8 + h\nu \xrightarrow{\phi_{1a}} C_2H_4 + C_2H_4^{**} \xrightarrow{k_d} C_2H_2 + H_2 & (10) \\ \qquad\qquad\qquad \searrow^{k_s^M[M]} & \\ \qquad\;\; \xrightarrow{\phi_{1b}} C_2H_4 + C_2H_4^{*} \longrightarrow C_2H_4 & (11) \end{array}$$

In the case of cyclobutane, the primary process of radical splitting is not observed.[17]

In the presence of nitrogen, the energized ethylene is deactivated upon collision with alkane itself or nitrogen. Thus, assuming the reaction schemes described above, and neglecting the internal scavenging reaction of hydrogen atoms by products at a very low conversion, the following equations are obtained for ethane, propane, and *n*-butane:

$$\frac{\phi(C_2H_4)}{\phi(C_2H_2)} = \frac{\phi_2+\phi_{1b}}{\phi_{1a}} + \frac{k_s^M}{k_d}\left(1+\frac{\phi_2+\phi_{1b}}{\phi_{1a}}\right)[M] + \frac{k_s^{N_2}}{k_d}\left(1+\frac{\phi_2+\phi_{1b}}{\phi_{1a}}\right)[N_2] \qquad (12)$$

and for cyclo-C_4H_8:

$$\frac{\phi(C_2H_4)}{\phi(C_2H_2)} = \frac{\phi_{1a}+2\phi_{1b}}{\phi_{1a}} + \frac{2k_s^M}{k_d}\left(1+\frac{\phi_{1b}}{\phi_{1a}}\right)[M] + \frac{2k_s^{N_2}}{k_d}\left(1+\frac{\phi_{1b}}{\phi_{1a}}\right)[N_2] \qquad (13)$$

where $\phi(C_2H_4)$ and $\phi(C_2H_2)$ are the relative yields of ethylene and acetylene respectively, and M is C_2H_6, C_3H_8, or *n*-C_4H_{10} for Eq. (12) and cyclo-C_4H_8 for Eq. (13).

Figure 1 shows the ratios of C_2H_4 to C_2H_2 in the photolyses of pure C_2H_6, C_3H_8, *n*-C_4H_{10}, and cyclo-C_4H_8 as a function of the alkane pressure. Also, varying amounts of nitrogen were added to a fixed amount of alkane (28 Torr), and the ratios were measured as a function of the N_2 pressure, as is shown in Fig. 2. These results show that Eqs. (12) and (13) are satisfied.

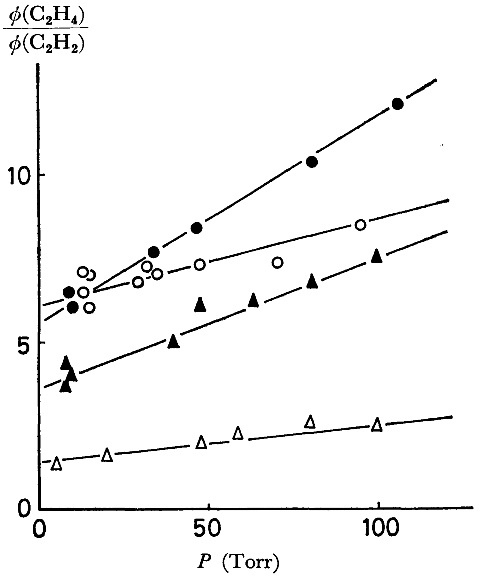

Fig. 1. Ethylene to acetylene ratio *vs.* alkane pressure. C_2H_6 (△), C_3H_8 (▲), *n*-C_4H_{10} (●), and cyclo-C_4H_8 (○)

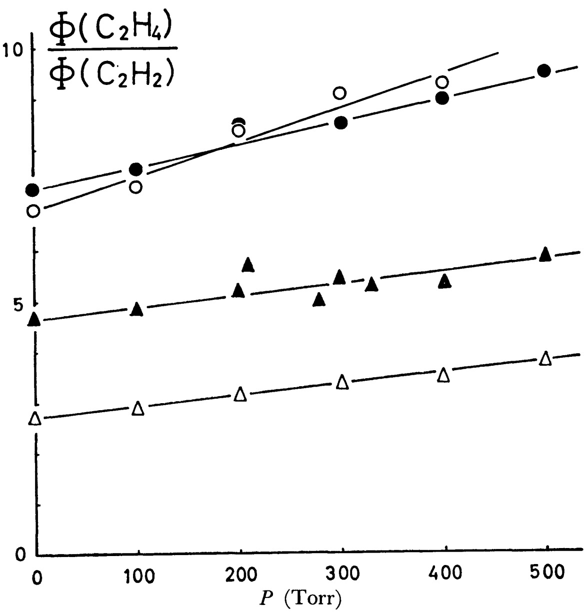

Fig. 2. Ethylene to acetylene ratio *vs.* added nitrogen pressure in the photolyses of alkanes. C_2H_6 (△), C_3H_8 (▲), *n*-C_4H_{10} (●), and cyclo-C_4H_8 (○)

The values of ϕ_2 were determined from the relative yields of methane and ethane in the photolyses of propane and *n*-butane respectively; this will be discussed elsewhere.[17] From the intercepts and the slopes of the plots in Figs. 1 and 2, the values of ϕ_{1a}, ϕ_{1b}, k_s^M/k_d and $k_s^{N_2}/k_d$ can be determined. The results are summarized in Table 1.

TABLE 1. THE RELATIVE YIELDS OF THE PRIMARY PROCESSES AND THE RATIOS OF RATE CONSTANTS IN THE PHOTOLYSES OF ALKANES AT 1470 Å

	ϕ_{1a}	ϕ_{1b}	ϕ_2	k_s^M/k_d (Torr^{-1})	$k_s^{N_2}/k_d$ (Torr^{-1})
C_2H_6	0.39	0.46	0.15	0.0047	0.00088
C_3H_8	0.20	0.20	0.60	0.0089	0.00051
n-C_4H_{10}	0.15	0.19	0.66	0.0095	0.00064
cyclo-C_4H_8	0.28	0.72		0.0039	0.00097

Since the rate of deactivation would not be equal to the strong collision frequency, the rate constant of deactivation, k_s^M, is written as follows:

$$k_s^M = \frac{\beta Z^{C_2H_4-M}}{[M]} \qquad (14)$$

where β is the collisional deactivation probability and $Z^{C_2H_4-M}$ is the collision frequency between the energized ethylene and the deactivator, M. The latter was calculated by means of the gas kinetic theory.

If the unit probability of energy transfer per collision is assumed for propane, the experimental values of k_s^M/k_d and $k_s^{N_2}/k_d$ and the collision frequencies yield values of β for the other deactivators. The values of β and k_s^M are summarized, together with the collision diameters, in Table 2.

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[17] K. Obi, Y. Ogata, H. Akimoto, and I. Tanaka, *J. Chem. Phys.*, in press.

The value of β is supposed to be affected by the nature and the degree of internal freedom of the deactivators. It can easily be understood that β increases with the complexity of the molecule from nitrogen to propane. A small decline from propane to n-butane would result from the experimental error. An unexpected lower value is found for cyclobutane. This lower value probably cames from the different character of the internal modes of vibrations compared with those of other paraffins or from the formation of energized ethylene with a different nature. The energized ethylene formed from chain alkanes results from the isomerization of the ethylidene produced in the primary processes, while that from cyclobutane is formed directly. The different nature of the energized ethylene can, therefore, be expected to be formed in the case of cyclobutane. If this is the case, it would be reasonable to obtain the lower value of β.

The experimental average rate constants for the decomposition of energized ethylene can be obtained by using the values of k_s^{M} (in Table 2) and k_s^{M}/k_d (in Table 1).

TABLE 2. THE COLLISIONAL DIAMETERS, THE COLLISIONAL DEACTIVATION PROBABILITIES AND THE RATE CONSTANTS OF DEACTIVATION

	$\sigma_{\mathrm{M-M}}$[a] (A)	β	k_s^{M} ($\mathrm{Torr^{-1}\,sec^{-1}}$)
N_2	3.85	0.063	8.03×10^5
C_2H_6	4.38	0.33	4.77×10^6
C_3H_8	5.24	1	1.58×10^7
n-C_4H_{10}	5.87	0.78	1.34×10^7
cyclo-C_4H_8	5.0	0.25	3.60×10^6
C_2H_4	4.07		

a) Values are taken from J. O. Hirschfelder, C. F. Curtis, and R. P. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York, N. Y. (1964), p. 1214, or are reasonable estimates based on data given in this reference.

B) Calculated Average Rate Constants. It was assumed in this treatment that the energized ethylene molecules decomposing to acetylene and hydrogen were composed of highly vibrational-excited ground-state ethylene.[13] The energized ethylene produced in the photolyses of alkanes may not be monoenergetic. If the energy distribution function of energized ethylene is expressed as $f(E)$, the average rate constant for the decomposition of ethylene is written as follows:[18]

$$k_d = \frac{\displaystyle\int \frac{k_{\mathrm{E}}}{k_{\mathrm{E}}+\omega} f(E)\,\mathrm{d}E}{\displaystyle\int \frac{1}{k_{\mathrm{E}}+\omega} f(E)\,\mathrm{d}E} \tag{15}$$

where k_{E} is the specific rate constant for the decomposition of ethylene at energy E (which can be calculated from the RRKM theory), and ω is the rate of the deactivation of energized ethylene (assumed to be independent of the energy), which is equal to $k_s^{\mathrm{M}}[\mathrm{M}]$.

Calculations of the Specific Rate Constant, k_{E}: The specific rate constant for the decomposition of ethylene at energy E is given by the RRKM theory as follows:[19,20]

$$k_{\mathrm{E}} = \frac{1}{h}\frac{\sigma}{\sigma^+}\left(\frac{I_{\mathrm{A}}{}^+I_{\mathrm{B}}{}^+I_{\mathrm{C}}{}^+}{I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}}}\right)^{1/2}\frac{\sum P(E-E_0)}{N(E)} \tag{16}$$

where σ and σ^+ are the symmetric numbers of the active molecule and the activated complex, I_i and $I_i{}^+$ are the moments of inertia of the active molecule and the activated complex respectively, and E_0 is the critical energy for the decomposition of ethylene to acetylene and hydrogen.

$N(E)$ is the energy level density for the active molecule at energy E. If there is no active internal free rotation for the active molecule, the expression for $N(E)$ is:

$$N(E) = \frac{(E+aE_z)^{s-1}}{\Gamma(s)\prod_i \mathrm{h}\nu_i} \tag{17}$$

which is given by Rabinovitch and Setser,[18] where a is a correcting factor, s is the number of the degrees of freedom for the vibration, and E_z is the zero-point energy (*i.e.* $1/2\sum_i \mathrm{h}\nu_i$).

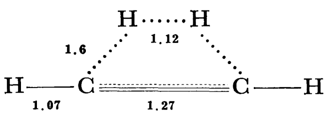
$\sum P(E-E_0)$ is the sum of the energy levels for the activated complex, and in the absence of an active internal free rotation for the activated complex, it is written as follows:[21]

$$\sum P(E-E_0) = \frac{(E-E_0+a^+E_z{}^+)^{s^+}}{\Gamma(s^++1)\prod_i \mathrm{h}\nu_i{}^+} \tag{18}$$

Thus, the expression for k_{E} (*i.e.* Eq. (16)) is:

$$k_{\mathrm{E}} = \frac{1}{h}\frac{\sigma}{\sigma^+}\left(\frac{I_{\mathrm{A}}{}^+I_{\mathrm{B}}{}^+I_{\mathrm{C}}{}^+}{I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}}}\right)^{1/2} \times \frac{\Gamma(s)\prod \mathrm{h}\nu_i}{\Gamma(s^++1)\prod \mathrm{h}\nu_i{}^+}\frac{(E-E_0+a^+E_z{}^+)^{s^+}}{(E+aE_z)^{s-1}} \tag{19}$$

In this paper, the rigid and semirigid models were considered as an activated complex. The structure of the activated complex was assumed to be as follows:



(unit; Å)

The fundamental frequencies and the moments of inertia for the active molecule and activated complexes are given in Table 3. The correlation between the fundamental frequencies is also shown. The frequencies of the fundamental modes of the activated complexes leading to the vibrational modes of products were estimated roughly from the average values of the initial and final systems. The vibrations leading to the free rotation in the final system were taken to have

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[18] B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

[19] R. A. Marcus and O. K. Rice, *J. Phys. Colloid. Chem.*, **55**, 894 (1951).

[20] G. M. Wieder and R. A. Marcus, *J. Chem. Phys.*, **37**, 1835 (1962).

[21] R. A. Marcus, *ibid.*, **20**, 359 (1952).

TABLE 3. STRUCTURE PARAMETERS

	C_2H_4[a]	Model I	Model II	$C_2H_2+H_2$[a]	
frequency (cm^{-1})	3094 (4) (A_{1g}, B_{1g}, B_{2u}, B_{3u})	3200 (2) (A_{1g}, B_{3u})	3200 (2)	4160 (1)	H_2
		3094 (1) (B_{1g})	1500 (1)	3330 (2)	C-H
	1623 (1) (A_{1g})	1800 (1) (A_{1g})	1800 (1)	1974 (1)	C≡C
	1392 (2) (B_{3u}, A_{1g})	2800 (1) (A_{1g})	2800 (1)		
	1024 (3) (B_{1g}, B_{2u}, A_{1u})	850 (4) (B_{3u}, B_{1g}, B_{2u}, B_{2g})	850 (4)	729 (2)	(E_g)
		1024 (1) (A_{1u})	510 (1)	612 (2)	(E_u)
	946 (2) (B_{2g}, B_{1u})	946 (1) (B_{1u})	470 (1)	free rot.	
		trans.	trans.	trans.	
zero-point energy (eV)	1.35	1.21	1.05		
moments of inertia					
$I_A=$	33.7×10^{-40}	33.0×10^{-40}	33.0×10^{-40}		
$I_B=I_C=$ ($g\cdot cm^2$)	16.8×10^{-40}	16.5×10^{-40}	16.5×10^{-40}		
number of symmetry	4	2	2		

a) G. Herzberg "Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra," Van Nostrand, Princeton, N. J. (1945). p. 290 and 326.

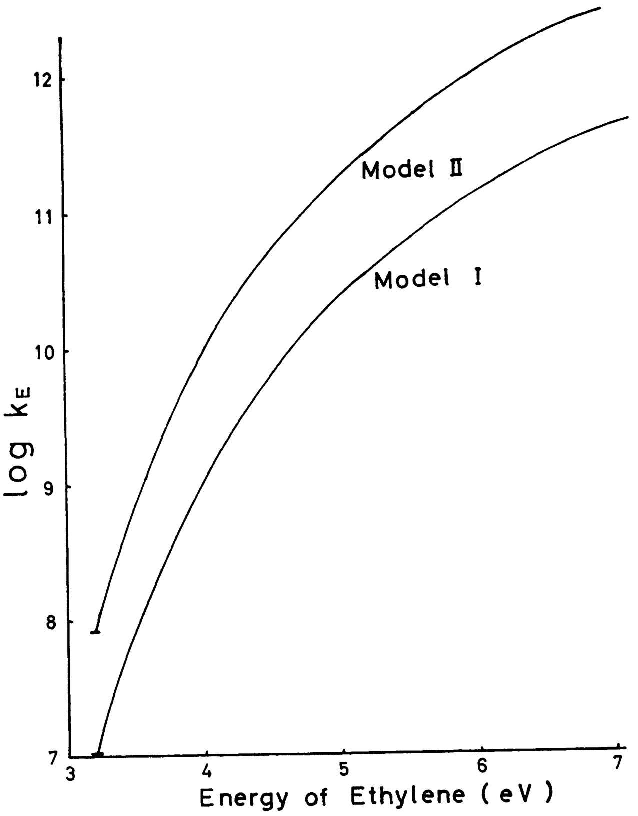

Fig. 3. Variation of the specific rate constant with energy of ethylene.

the same values in the initial system for the rigid model, but were lowered to half those values for the semirigid model.

E_0 was assumed to be 74 kcal/mol (3.2 eV).[22] The correcting factor has a value of 0.7—0.8 when the energy is small, rising to unity at a sufficiently high energy.[18] Since the decomposition reaction would occur near the critical energy, we assumed that $a=1$ and $a^+=0.8$.

Figure 3 shows the plots of log k_E as a function of energy E. The specific rate constant calculated using Model I is rather claser to that obtained by Kirk and Tschuikow-Roux[16] than that calculated using Model II. The difference in the specific rate constants is mainly due to the values of E_0 and the frequencies of the activated complex. These values make it possible to make an arbitrary choice, while there has not previously been any reliable value in the literature.

Calculation of the Energy Distribution Function, f(E): It can be expected that the energized ethylene molecules produced in the photolyses of various alkanes will have energy spreads. However, at present there exists no *a priori* method to determine the energy distribution of the products of the reaction. A simple statistical distribution was used in this paper. If all the internal degrees of freedom for alkane are in an energy equilibrium everwhere on the reaction surface, one can determine the relative concentration of products with energy E simply from the phase-space consideration. The fraction of energized ethylene molecules which have an energy E out of the total available energy, E_t, can be written[23,24] as:

$$f(E)=\frac{N_{C_2H_4}(E)\cdot N_R(E_t-E)}{\sum N_{C_2H_4}(E_i)\cdot N_R(E_t-E_i)} \qquad (20)$$

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22) I. D. Gay, R. D. Kern, G. B. Kistiakowsky, and H. Niki, *J. Chem. Phys.*, **45**, 2371 (1966).

Table 4. The ratios of the yields of primary processes and the experimental and calculated rate constants of decomposition

	$\phi_{1b}/(\phi_{1a}+\phi_{1b})$			A (eV)	$k_d(\text{sec}^{-1})\times 10^{-9}$		
	exp.	calc. from Eq. (20)	calc. (corr.) from Eq. (22)		exp.	Model I	Model II
C_2H_6	0.54	0.08	0.50	2.2	1.01	0.33	1.21
C_3H_8	0.50	0.44	0.50	0.4	1.78	1.00	2.90
n-C_4H_{10}	0.56	0.91	0.55	−3.4	1.41	1.02	2.84
cyclo-C_4H_8	0.72	0.55	0.71	1.0	0.92	0.31	1.05

where $N_{C_2H_4}(E)$ is the energy-level density of the ethylene part of alkane, $N_R(E_t-E)$ is that of the remaining degrees of freedom of alkane, and E_t is the total available energy. The energy-level densities were calculated by means of Eq. (17).

The total available energy is written as follows:

$$E_t = E(h\nu) + E(\text{thermal}) - \Delta H \tag{21}$$

where $E(h\nu)$ is the photon energy of the exciting wavelength, which is equal to 8.4 eV at 1470 Å, E(thermal) is the thermal energy of the active molecule at the initial temperature (neglected in this paper), and ΔH is the heat of the reaction. The total available energies are 6.99, 7.57, 7.44, and 7.60 eV for ethane, propane, n-butane, and cyclobutane respectively.

The energy distribution function of the energized ethylene calculated from Eq. (20) is shown in Fig. 4(a), with ethane as the example. As C_2H_4* is thought to have a smaller energy than the critical energy,[16,25] the fraction of C_2H_4* can be estimated from Fig. 4(a). As may be seen in Table 4, the estimated values differ from the experimental values. Therefore, the correcting parameter, A, was introduced into Eq. (20) as follows:

$$f(E) = \frac{N_{C_2H_4}(E)N_R(E_t-A-E)}{\sum N_{C_2H_4}(E_i)N_R(E_t-A-E_i)} \tag{22}$$

The correcting parameter was determined so that the fractions of C_2H_4* calculated from the energy distribution functions of Eq. (22) were nearly equal to the experimental fractions of C_2H_4*. The experimental fractions, the calculated fractions, and the correcting parameter are summarized in Table 4. The corrected energy distribution of energized ethylene is shown in Fig. 4(b), with ethane as the example.

The correcting parameter expresses the difference between the simple statistical distribution as calculated by Eq. (20), and the real energy distribution of energized ethylene. The correcting parameter is larger than zero in the photolysis of ethane, propane, or cyclobutane, while it is negative for n-butane. It is interpreted that energized ethylene would have a smaller vibrational energy than that to be expected from the simple statistical distribution for the positive A value, in other words, that the relative translation or rotation of the products would take away a larger energy than that to be expected from Eq. (20). In particular, the correcting parameter is fairly large in the case of ethane. According to the Monte Carlo calculations,[26] this may be explained by the large energy transfer into the relative translational mode, since the hydrogen molecule in the products is quite light.

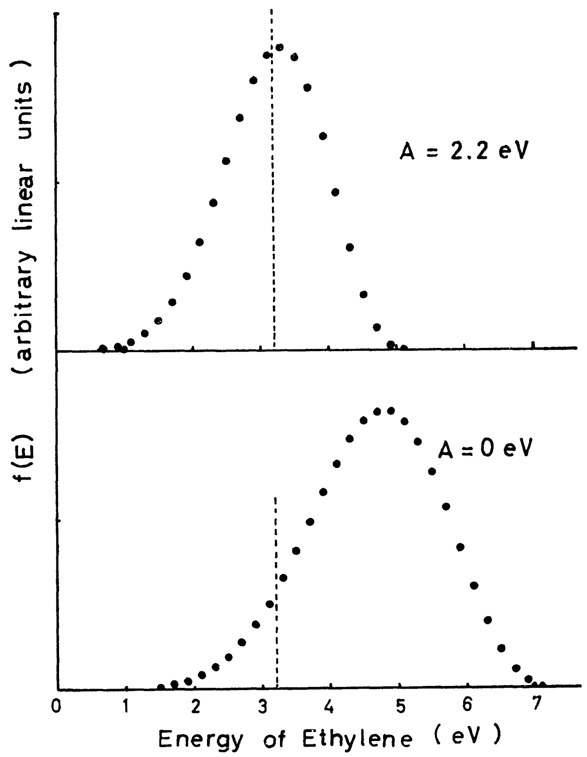

Fig. 4. Energy distributions of ethylene formed in the photolysis of ethane. (a) is calculated without a correcting parameter A; (b) is calculated with a correcting parameter A=2.2 eV.

Calculation of the Average Rate Constants, k_d: A graphical integration procedure consists of approximating the energy distribution above E_0 to a histogram of regular energy intervals (ΔE=0.2 eV). The average rate constants for the decomposition can be calculated by means of Eq. (15) using the values of k_E, $f(E)$ and k_s^M. When the pressure of alkane is 100 Torr, the experimental rate constants and the calculated

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[23] R. J. Campbell and E. W. Schlag, *J. Amer. Chem. Soc.*, **89**, 5103 (1967).

[24] P. Cadman, H. M. Meunier, and A. F. Trotman-Dickenson, *ibid.*, **91**, 7640 (1969).

[25] A. Mele and H. Okabe, *J. Chem. Phys.*, **51**, 4798 (1969).

[26] P. J. Kuntz E. M. Hemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, *J. Chem. Phys.*, **44**, 1168 (1966).

ones for the two kinds of the activated complex are summarized in Table 4.

In spite of the fairly simple estimation of the vibrational frequencies of the activated complexes, the calculated rate constants show good agreement with the experimental ones. Although it is not possible to choose between the two model, these simple models yield satisfactory results.