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Application of the RRKM Theory to Energized Ethylene Formed in the Vacuum-ultraviolet Photolysis of *n*-Paraffins

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The Rice-Ramsperger-Kassel-Marcus treatment has been applied to the energized ethylene produced in the vacuum-ultraviolet photolysis of C_2H_6, C_2D_6, C_3H_8, C_3D_8, n-C_4H_{10} and n-C_4D_{10}. The energy spread in the energized ethylene has been evaluated assuming modified statistical distribution of liberated energy among fragment species. The calculated nonequilibrium unimolecular decomposition rate constant for the process $C_2H_4(C_2D_4) \rightarrow C_2H_2(C_2D_2)+H_2(D_2)$ could satisfactorily reproduce the experimental pressure dependence of ethylene to acetylene ratio. Non-statistical kinetic energy E_k seems to appear for the primary decomposition of the *n*-paraffins. Its value ranges from zero for the elimination of methane and ethane from propane and *n*-butane, respectively, at 147.0 nm to about 25 kcal mol^{-1} for the elimination of hydrogen from ethane at 123.6 nm.

In the vacuum-ultraviolet photolysis of *n*-paraffin hydrocarbons in the gas phase, ethylene and acetylene are always among the major products.[1-11] From the analysis of products the following reaction schemes have been proposed[9,12] for the production of ethylene and acetylene in the photolysis of ethane, propane and *n*-butane.

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

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

$$\begin{tikzcd}
n\text{-}C_4H_{10} + h\nu \arrow[r, "\phi_{1a}"] & C_2H_6 + C_2H_4^{**} \arrow[r, "k_d"] \arrow[dr, "k_s{[M]}"'] & C_2H_2 + H_2 & (7) \\
{} \arrow[r, "\phi_{1b}"] & C_2H_6 + C_2H_4^{*} \arrow[r] & C_2H_4 & (8)
\end{tikzcd}$$

$$\xrightarrow{\phi_2} \left(\begin{array}{ll} H + C_2H_4 + C_2H_5 & (9) \\ CH_3 + C_2H_4 + CH_3 & (10) \end{array}\right.$$

Experimental studies[5,12] revealed that two kinds of ethylene should be obtained through the molecular detachment processes; one which undergoes unimolecular decomposition into acetylene and hydrogen competing with collisional stabilization to ethylene and the other which does not decompose even at very low pressure. These two kinds of ethylene are designated as $C_2H_4^{**}$ and $C_2H_4^{*}$, respectively, their relative yields being referred to as ϕ_{1a} and ϕ_{1b}, respectively. The assumption that the ethylene produced in Eqs. (3), (6), (9) and (10) does not decompose is easily justified in terms of the large endothermicity of the reactions.

With respect to energized ethylene the following points should be clarified: (1) How the unimolecular decomposition rate k_d can be correlated to the internal energy retained in the energized ethylene $C_2H_4^{**}$. How the internal energy can be correlated to the maximum energy available in the processes. (2) The nature of $C_2H_4^{*}$. (3) Whether ethylene is originally produced in the form of ethylidene CH_3CH which then isomerizes to C_2H_4, or it is originally formed as C_2H_4.

By means of the classical Kassel formula,[13] Hampson and McNesby[5] first attempted to correlate the experimentally determined unimolecular decomposition rate to the internal energy of ethylene produced in the photolysis of *n*-paraffin hydrocarbons, diazoethane and methylketene. Assuming *a priori* that 80% of the maximum energy available in the process would be retained in ethylene, they succeeded in showing reasonably good correlation in a semi-quantitative manner. Their results suggest that energized ethylene $C_2H_4^{**}$ is vibrationally excited ethylene in its ground electronic state. They also suggested that $C_2H_4^{*}$ is a long-lived triplet ethylene.

Kirk and Tschuikow-Roux[14] applied the Rice-Ramsperger-Kassel-Marcus (RRKM) treatment to the decomposition of ethylene produced in the photolysis of 3-methyldiazirine assuming that ethylene is produced in the photolysis with a wide spread of internal energy, whose distribution was selected arbitrarily to fit the experimental data. According to this model ethylene produced in the photolysis has a continuous distribution of internal energy from zero to maximum value allowed in the process, and both $C_2H_4^{**}$ and $C_2H_4^{*}$

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1) J. R. McNesby and H. Okabe, *Advan. Photochem.*, **3**, 157 (1964).

2) R. F. Hampson, Jr., J. R. McNesby, H. Akimoto, and I. Tanaka, *J. Chem. Phys.*, **40**, 1099 (1964).

3) H. Akimoto, K. Obi, and I. Tanaka, *ibid.*, **42**, 3864 (1965).

4) R. F. Hampson, Jr. and J. R. McNesby, *ibid.*, **42**, 2200 (1965).

5) R. F. Hampson, Jr. and J. R. McNesby, *ibid.*, **43**, 3592 (1965).

6) S. G. Lias, G. J. Collin, R. E. Robbert, and P. Ausloos, *ibid.*, **52**, 1841 (1970).

7) P. Ausloos and S. G. Lias, *ibid.*, **44**, 521 (1966).

8) P. Ausloos and S. G. Lias, *Ber. Bunsenges. Physik. Chem.*, **72**, 187 (1968).

9) H. Akimoto and I. Tanaka, *ibid.*, **72**, 135 (1968).

10) D. W. L. Griffiths and R. A. Back, *J. Chem. Phys.*. **46**, 3913 (1967).

11) K. Obi, H. Akimoto, Y. Ogata, and I. Tanaka, *ibid.*, **55**, 3822 (1971).

12) H. Akimoto and I. Tanaka, *J. Phys. Chem.*, **71**, 4135 (1967).

13) L. S. Kassel, *ibid.*, **32**, 225 (1928).

14) A. W. Kirk and E. Tschuikow-Roux, *J. Chem. Phys.*, **51**, 2247 (1969).

can be in the ground electronic state with different amounts of internal energy. Energized ethylene $C_2H_4{}^{**}$ can then be interpreted as ethylene whose internal energy is greater than a certain critical value necessary to decomposition, and $C_2H_4{}^{*}$ as that which retains less energy than the critical value.

This model was further developed[15] for ethylene formed in the photolysis of alkanes at 147.0 nm. In order to predict the distribution of internal energy of ethylene more systematically, a statistical model proposed by Campbell and Schlag[16] was employed. Although the RRKM calculation could predict the nonequilibrium unimolecular decomposition rate in fair agreement with experimental data, we had to introduce a correction parameter (A in Eq. (22) of the paper[15]) whose value was hard to reconcile with the statistical model of energy distribution.

This paper presents a modified version of our previous treatment. In the new model a restriction to the statistical calculation for the initial distribution of internal energy of ethylene has been introduced. In order to test the validity of the new model, comparison with experimental data for the photolysis of ethane, propane, and *n*-butane at different excitation wavelengths and also for the photolysis of fully deuterated compounds was made. The new model was found to give good agreement with all sets of data tested and could predict the wavelength effect and isotope effect quantitatively.

Method

Calculation of k_E. Suppose that ethylene with internal energy E is produced through a molecular elimination process in a vacuum-ultraviolet photolysis of *n*-paraffin. A specific rate constant k_E of the decomposition of energized ethylene into acetylene and hydrogen can be given by the RRKM theory[17,18] as follows.

$$k_E = \frac{1}{h}\,\frac{\sigma}{\sigma^+}\,\frac{\sum P(E-E_0)}{N(E)} \tag{11}$$

where σ and σ^+ are the symmetry numbers of the active molecule and the activated complex, respectively. $N(E)$ is the energy level density for the active molecule at energy E, $\sum P(E-E_0)$ the energy-level sum for the activated complex and E_0 the critical energy required for the decomposition of energized ethylene into acetylene and hydrogen. A contribution from the change in moment of inertia between the active molecule and activated complex has been neglected since it is known[15] to be small in the case of a hydrogen elimination process.

In the absence of an internal free rotation as is the case here, $N(E)$ and $\sum P(E-E_0)$ can be approximated by

$$N(E) = \frac{(E+aE_z)^{s-1}}{\Gamma(s)\Pi h\nu_i} \tag{12}$$

$$\sum P(E-E_0) = \frac{(E-E+a^\dagger E^\dagger{}_z)^{s\dagger}}{\Gamma(s^\dagger+1)\Pi h\nu_i{}^\dagger} \tag{13}$$

as proposed by Whitten and Rabinovitch.[19] In Eqs. (12) and (13) s and $s^\dagger$ are the numbers of vibrational degrees of freedom, E_z and $E_z{}^+$ are the zero point energy, and ν_i and $\nu_i{}^\dagger$ are vibrational frequencies of active molecule and activated complex, respectively. Energy dependence of parameters a and $a^\dagger$ are calculated using analytical expressions given by Whitten and Rabinovitch[19]

An activated complex having a four-membered ring structure has been considered.[15] The activated complex is assumed to be rigid and the frequencies are taken to be equal to those of ground state ethylene except for one CH stretching mode (B_{2u}) which is taken as a reaction coordinate. All the frequencies used are given in the Appendix. Since the pyrolysis of ethylene proceeds through radical chain mechanism rather than molecular elimination of hydrogen,[20,21] no direct experimental data is available for the value of E_0. Benson and Haugen[22] estimated the activation energy of the reverse reaction, $H_2+C_2H_2 \rightarrow C_2H_4$, to be 40 kcal mol^{-1}. From this value and the heat of reaction of the process 41.7 kcal mol^{-1}, *ca.* 80 kcal mol^{-1} is obtained for the activation energy of decomposition as a first approximation. The E_0 value of 78 kcal mol^{-1} for C_2H_4 is chosen since it was found to give the most consistent results. Taking into account the difference in zero point energy between the active molecule and the activated complex, 1 kcal mol^{-1} should be raised, giving 79 kcal mol^{-1} for the decomposition of C_2D_4.

Calculation of $f(E)$. It is expected that ethylene molecules produced in the photolyses of *n*-paraffins will have certain energy spread rather than monoenergetic energy. However, at present there exists no *a priori* method to determine the energy distribution of the products of the reactions. In the photolysis of ethane, propane and *n*-butane, molecular elimination of hydrogen, methane and ethane would respectively give rise to energized ethylene. In such a system the maximum energy E_t available for the energized ethylene can be given by

$$E_t = E_p - \Delta H \tag{14}$$

where E_p is the energy of photon used in the photolysis of parent *n*-paraffin and ΔH the heat of reaction of each molecular elimination process. The values of ΔH we used are 32.7, 19.4 and 22.5 kcal mol^{-1} for the photolysis of ethane, propane and *n*-butane, respectively. Energy E_t may either be distributed among each degree of freedom of product fragments more or less statistically or appear as non-statistical kinetic energy of fragments.

During the course of molecular elimination the following type of transition state is expected:

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[15] Y. Ogata, K. Obi, H. Akimoto, and I. Tanaka, This Bulletin. **44**, 2671 (1971).

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

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

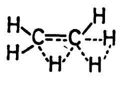
[18] B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

[19] G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963).

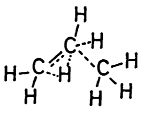
[20] I. D. Gay, R. D. Kern, G. B. Kistiakowsky, and H. Niki, *ibid.*, **45**, 2371 (1966).

[21] S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **71**, 1735 (1967).

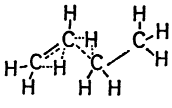
[22] S. W. Benson and G. R. Haugen, *ibid.*, **70**, 3337 (1966).



C_2H_6



C_3H_8



n-C_4H_{10}

It is postulated that one of the hydrogen atoms of the methyl group in the "ethylene" part of parent molecule would start to transfer to the adjacent atom while the molecular elimination of H_2, CH_4, and C_2H_6 starts to occur. We assume that the statistical part of the liberated energy would be distributed among "active" vibrational modes which can be defined as vibrational modes whose associated normal coordinates undergo drastic changes during passage through the transition state. The drastic changes mean those of bond length and bond angle for newly formed bond and those of bond angles accompanying a change of hybridization from sp^3 to sp^2. The following vibrational modes should be taken as inactive; three CH stretching modes of "ethylene" part of all n-paraffins; three CH stretching and three CH_3 deformation modes of "methane" part of propane; and five CH stretching, one CC stretching, three CH_3 deformation, one CH_2 scissors, two CH_3 rocking, one CH_2 wagging, one CH_2 twisting and one CH_3 tortional modes of "ethane" part of n-butane. Using a statistical model proposed by Campbell and Schlag,[16] a fraction of the energized ethylene which retains a vibrational energy E out of the total available energy, E_t, can be written as

$$f(E) = \frac{N_{C_2H_4}(E)N_R(E_t-E-E_k)}{\sum N_{C_2H_4}(E_i)N_R(E_t-E_i-E_k)} \qquad (15)$$

where E_k is non-statistical kinetic energy, $N_{C_2H_4}(E)$ the energy-level density of the "active" ethylene part of the n-paraffin and $N_R(E_t-E-E_k)$ that of the "active" remaining part of the n-paraffin. The energy-level densities were calculated by means of Eq. (12). All vibrational frequencies used are given in the Appendix.

Comparison with Experiments. Now that the energy distribution of energized ethylene $f(E)$ and the specific rate constant k_E have been calculated, the apparent rate constant k_d can be given[18] by

$$k_d = \frac{\int \frac{k_E}{k_E+\omega} f(E)\mathrm{d}E}{\int \frac{1}{k_E+\omega} f(E)\mathrm{d}E} \qquad (16)$$

where ω is the rate of deactivation of energized ethylene. Throughout this work a strong collision model is assumed, *viz.*, ω is assumed to be equal to the kinetic collision frequency independent of the energy of ethylene. Kinetic treatment[9] of the reaction schemes in Eqs. (1)—(10) gives the relation

$$\frac{\phi(\text{Ethylene})}{\phi(\text{Acetylene})} = \frac{\phi_2+\phi_{1b}}{\phi_{1a}} + \frac{k_s}{k_d}\left(1+\frac{\phi_2+\phi_{1b}}{\phi_{1a}}\right)P \qquad (17)$$

which allows us to compare the experimentally determined quantity $\phi(\text{Ethylene})/\phi(\text{Acetylene})$ with the calculable quantity of the right hand side of the scheme. In Eq. (17), P is the pressure of n-paraffin, k_s the simple collisional rate constant given by gas kinetics in accordance with the strong collision model ($\omega=k_sP$). The values of k_s we used are 1.43×10^7, 1.58×10^7 and 1.72×10^7 Torr^{-1} s^{-1} for ethane, propane and n-butane, respectively. The ϕ_{1a}, ϕ_{1b} and ϕ_2 are defined in schemes (1)—(10). The values of ϕ_2 were determined[2,3,9,11] experimentally. The values we used are given in Table 1 together with the calculated quantities. The values of ϕ_{1a} and ϕ_{1b} are calculated using the energy distribution function $f(E)$, *i.e.* under the restriction of $\phi_{1a}+\phi_{1b}+\phi_2=1$; ϕ_{1a} is put to be equal to the fraction of energized ethylene with energy greater than E_0 and ϕ_{1b} put to be equal to that of energized ethylene with energy less than E_0.

Under the restrictions of all selected values of parameters, only the value of E_k has been left as an adjustable parameter. Selection of the E_k value to give the best fit of calculated curve to the experimental points has been made for each case.

Results and Discussion

The validity of model has been tested by comparing the calculation with the experimental data of the photo-

TABLE 1. VALUES OF EXCESS ENERGY E_t, RELATIVE YIELDS ϕ_{1a}, ϕ_{1b} AND ϕ_2, AVERAGE ENERGY OF ETHYLENE $\overline{E}$ AND AVERAGE ENERGY OF DECOMPOSING ETHYLENE $\overline{E_d}$ ASSOCIATED WITH NON-STATISTICAL ENERGY PARAMETER E_k

Parent n-Paraffin	Wavelength nm	E_t kcal mol^{-1}	ϕ_{1a}	ϕ_{1b}	ϕ_2[a]	$\overline{E}$ kcal mol^{-1}	$\overline{E_d}$ kcal mol^{-1}	E_k kcal mol^{-1}
C_2H_6	157.7	149	0.60	0.35	0.05	84	97	13
	147.0	162	0.59	0.26	0.15	88	99	20
	123.6	199	0.50	0.07	0.43	107	113	25
C_2D_6	147.0	162	0.62	0.23	0.15	93	103	10
	123.6	199	0.52	0.05	0.43	115	120	10
C_3H_8	147.0	175	0.26	0.14	0.60	87	101	0
	123.6	212	0.33	0.09	0.58	101	110	10
C_3D_8	147.0	175	0.24	0.14	0.62	87	101	0
	123.6	212	0.39	0.10	0.52	103	112	5
n-C_4H_{10}	147.0	172	0.23	0.14	0.63	85	99	0
	123.6	209	0.24	0.06	0.70	101	110	5
n-C_4D_{10}	147.0	172	0.22	0.15	0.63	85	100	0
	123.6	209	0.28	0.07	0.65	104	113	0

a) Experimentally determined. See Ref. 9, 15, 23.

lysis of C_2H_6,[11,12] C_2D_6,[23] C_3H_8,[11] C_3D_8,[23] n-C_4H_{10}[11] and n-C_4H_{10}[23] at two exciting wavelengths, 147.0 and 123.6 nm. The data for the photolysis of C_2H_6 at 157.7 nm are also available[9] for comparison. The results are presented in Figs. 1—4. The best fit curves were obtained by varying the value of E_K after selecting all other parameters. It should be noted that except E_K the best fit curves for all data were obtained with a common activated complex model, a systematic way of calculation for $f(E)$, and common values of E_0. Taking into account the fact that the calculated results are very sensitive to selected parameters, and the range of selection of each parameter is not so wide as regards its physical meaning, successful reproduction of experimental data should not be taken as only fortuitous. Calculated values of relative yields ϕ_{1a} and ϕ_{1b}, average internal energy of ethylene $\overline{E}$ and average energy of decomposing ethylene $\overline{E_d}$ are given in Table I, together with the selected values of E_k. An important feature of the model is the successful reproduction of the curvature of the plots[9] of ϕ(Ethylene)/ϕ(Acetylene) *vs.* P in the photolysis of C_2H_6 at 157.7 nm.

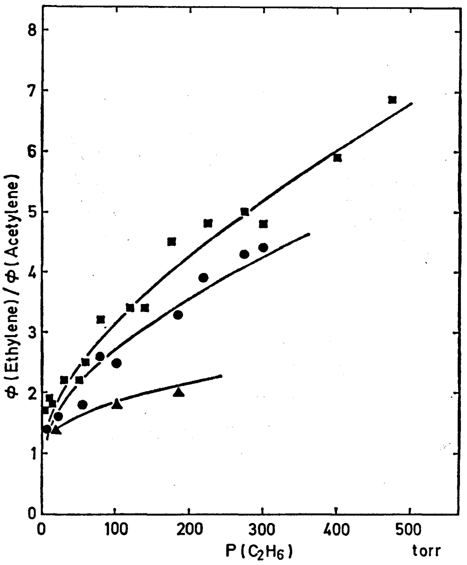


Fig. 1. Calculated ratio of ethylene to acetylene in the photolysis of C_2H_6 (solid lines), compared to experimental results at 157.7 (■), 147.0 (●) and 123.6 nm (▲).

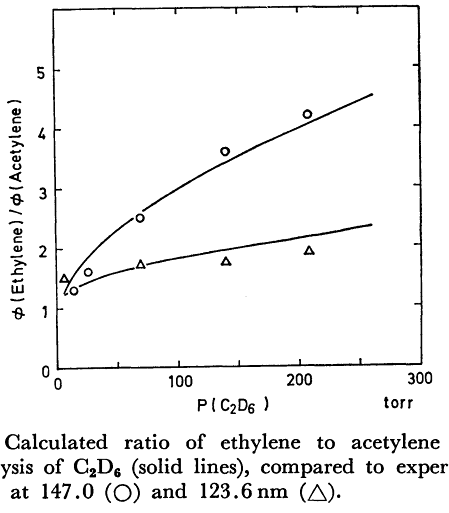


Fig. 2. Calculated ratio of ethylene to acetylene in the photolysis of C_2D_6 (solid lines), compared to experimental results at 147.0 (○) and 123.6 nm (△).

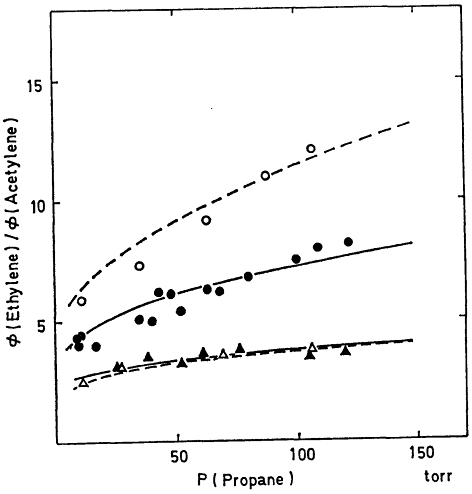


Fig. 3. Calculated ratio of ethylene to acetylene in the photolysis of C_3H_8 (solid lines) and C_3D_8 (dashed lines), compared to experimental results for C_3H_8 at 147.0 (●) and 123.6 nm (▲), and C_3D_8 at 147.0 (○) and 123.6 nm (△).

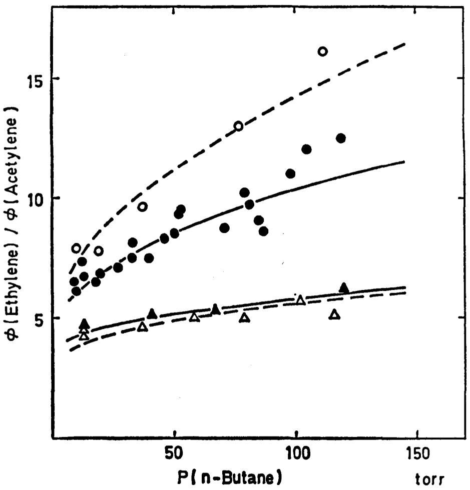


Fig. 4. Calculated ratio of ethyiene to acetylene in the photolysis of n-C_4H_{10} (solid lines) and n-C_4D_{10} (dashed lines), compared to experimental results for n-C_4H_{10} at 147.0 (●) and 123.6 nm (▲) and n-C_4D_{10} at 147.0 (○) and 123.6 nm (△).

According to the present model the curvature results from a very wide spread of internal energy of the energized ethylene formed in the photolysis. Although in all other cases the scatter of experimental points does not allow us to make a clear preference, the non-linear correlation seems to fit the experimental results better than the linear one. The values of ϕ_{1a} and ϕ_{1b} given in Table 1 differ somewhat from those obtained from linear correlation of ϕ(Ethylene)/ϕ(Acetylene) *vs.* pressure plots.[9,12,15] We believe that the linear correlation is true only in appearance and that the k_s/k_d and ϕ_{1a}/ϕ_{1b} values thus obtained are no more than those in a zero approximation. The latter situation has been pointed out by Campbell

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[23] H. Akimoto and I. Tanaka, unpublished data.

et al.[24] who stated linear plots may not be a sufficient guarantee against a simple two step mechanism.

Production of vibrationally excited polyatomic species in photodissociative processes has been reported in several species. These include the photolysis of cyclobutanone,[16,25] cyclopentanone,[25] methylketene,[26] tetrahydrofuran,[27] 2,3-diazabicyclo[2,2,1]hept-2-ene,[28] *t*-pentyl nitrite,[29] 1-pyrazoline,[30] diazoethane,[31] and 3-methyl diazirine.[32] Generally the excess photon energy has been found to be distributed over the products so that the species formed have a spread of energy. For the case of energized cyclopropane formation, the statistical model which assumes the microscopic equilibration of liberated energy among all degrees of freedom of products, was found[16,30] to be inappropriate to predict the energy partitioning for cyclopropane. Thus the assigned energy for cyclopropane was an underestimate in the case of cyclobutanone and an overestimate in the case of 1-pyrazoline. For the energized ethylene formation in the photolysis of *n*-paraffins,[15] such simple statistical model also failed to predict the energy partition particularly in the case of *n*-butane, where a large negative correction factor was required to reproduce the experimental data. In this work the modified statistical model which introduced an "active" model of energy partitioning was found to be satisfactory at least for the reproduction of experimental data. Although clear justification cannot be made without more information on the potential surface of photodissociation, the assumption we employed is consistent with the general view[29] that a change in an equilibrium bond distance or bond angle during the course of dissociation may lead to preferential excitation of vibrational modes involving the affected bond.

As shown in Table 1 the average energy of decomposing ethylene $\overline{E}_d$ ranges from 97 to 120 kcal mol^{-1}, which is roughly 20—40 kcal mol^{-1} higher than the critical energy E_0. Thus, if an energy quanta transferred by a single collision between *n*-paraffin is as much as 40 kcal mol^{-1}, the strong collision model we used can be justified. Data on an amount of energy transferred by a single collision for deactivation of highly vibrationally excited species are still scarce. Setser *et al.*[33] have shown that ethylene and cyclopropane remove energy from vibrationally excited cyclopropane and methylcyclopropane, respectively, in average steps of at least about 30 kcal mol^{-1} at room temperature. Taking into account the similarity of molecular complexity and the average energy of around 110 kcal mol^{-1} contained in energized cyclopropane and methylcyclopropane in their system, our present system may be analogous to theirs. Thus their conclusion would be applicable to our case and the strong collision assumption may be justified. On the other hand, the photolysis of paraffins in the presence of nitrogen indicates[15] that the collision efficiency of ethane against energized ethylene would be smaller than unity. If this is the case, the best fit of the data is obtained at higher values of E_k, and those given in Table 1 should be taken as a lower limit.

An activated complex model which has the same frequencies as in the ground state molecule except for the reaction coordinate is of course a conventional one. But the selection of the "rigid" model is in accord with the results of quasi-equilibrium theory of ion fragmentation where molecular elimination of hydrogen from a hydrocarbon parent ion is assumed to proceed through a "rigid" activated complex.[34] An activated complex with lower frequencies naturally yields a higher decomposition rate and could not reproduce the experimental data even if other parameters were adjusted.

As shown in Table 1, 13, 20 and 25 kcal mol^{-1} are assigned as suitable values of the non-statistical energy E_k in the photolysis of ethane at 157.7, 147.0 and 123.6 nm respectively. While it is indicated to be close to zero at 147.0 nm in the photolysis of propane and *n*-butane, E_k appears to increase with excitation energy in the case of C_2H_6, and E_k for C_2D_6 appears to be smaller than that for C_2H_6. In the photolysis at 123.6 nm an appreciable amount of E_k may be implied for the elimination of methane from propane and less amount for the elimination of ethane from *n*-butane. Although the assignment of specific values of E_k is difficult for these cases due to the insensitivity of the calculated results to the value of E_k, the trend may be noted that the E_k is smaller for the deuterated compound. Since the reduction of the value of E_0 can be compensated to some extent by the increase of the value of E_k to reproduce experimental data, the value of E_k can not be defined unambiguously. Nevertheless the set of values of E_k would be correct at least relatively (Table 1) since a common value of E_0 was used throughout the calculation.

Non-statistical kinetic energy has been observed in some ion fragmentation processes.[34] Taubert[35] determined experimentally translational energies of some fragment ions after the ionization of paraffins by electron impact. His data suggested that in the elimination of neutral methane from $C_3H_8^+$, the excess energy remains mostly as internal energy of the fragments while in the elimination of a hydrogen molecule from $C_3H_8^+$ and $C_2H_6^+$, part of the excess energy appears as non-statistical kinetic energy to the amount *ca.* 13 and

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[24] R. J. Campbell, E. W. Schlag, and B. W. Ristow, *J. Amer. Chem. Soc.*, **89**, 5098 (1967).

[25] R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, **43**, 1934 (1965).

[26] D. P. Chong and G. B. Kistiakowsky, *J. Phys. Chem.*, **68**, 1793 (1964).

[27] B. C. Roquitte, *ibid.*, **70**, 1334 (1966).

[28] D. Durant and G. R. McMillan, *ibid.*, **70**, 2709 (1966).

[29] T. F. Thomas, C. I. Sutin, and C. Steel, *J. Amer. Chem. Soc.*, **89**, 5107 (1967).

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

[31] C. L. Kibby and G. B. Kistiakowsky, *J. Phys. Chem.*. **70**, 126 (1966).

[32] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, **1965**, 1700.

[33] D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *J. Chem. Phys.*, **40**, 1751 (1964).

[34] M. L. Vestal, "Ionic Fragmentation Processes," Fundamental Processes in Radiation Chemistry, P. Ausloos ed., Interscience Publishers, New York, N. Y. (1968), p. 59.

[35] R. Taubert, *Z. Naturforsch.*, **199**, 911 (1964).

8 kcal mol^{-1}, respectively.[34] Our results agree with this observation, and the parameter E_k would be justified as non-statistical kinetic energy.

Following the present scheme, C_2H_4* has been interpreted to be an electronic ground state ethylene which contains less vibrational energy than a critical value necessary for decomposition. Since experimental data have been reproduced successfully according to this scheme, it seems unnecessary to invoke another long-lived electronic state of ethylene unless direct evidence indicates the presence of such species.

Energized ethylene formed in Eqs. (1), (2), (4), (5),(7) and (8) has been sometimes quoted[12] as "ethylidene". However, so far there is no experimental evidence that ethylidene is produced in a primary process in the photolysis of *n*-paraffins. We could exclude primary processes such as

$$C_2H_6 + h\nu \longrightarrow H_2 + CH_3CH: \qquad (18)$$

$$CH_3CH: \longrightarrow C_2H_4^{**} \qquad (19)$$

According to an extended Hückel MO calculation,[36] ground state ethylidene CH_3CH: lies 81 kcal mol^{-1} above the ground state of ethylene. Thus ethylene produced through the isomerization of ethylidene should have at least 81 kcal mol^{-1} of internal energy even if ethylidene formed in Eq. (18) is in the lowest vibrational state. Since E_0 is about 80 kcal mol^{-1}, all of the ethylene thus formed should be able to decompose at low enough pressure and should be interpreted as $C_2H_4^{**}$. Thus there should be another process which forms exclusively ethylene whose internal energy is lower than 80 kcal mol^{-1}, which would hardly be accepted. Formation of ethylidene in the primary step of the photolysis of *n*-paraffin seems improbable.

Appendix

The vibrational frequencies of C_2H_4 (C_2D_4) are taken[37] to be 3000(2250), 1600(1500), 1350(1000), 1000(800), 3100(2300), 1250(900), 950(700), 950(800), 3100(2350), 800(600), 3000(2200), 1450(1100) cm^{-1} for ν_1 to ν_{12} in order. Exactly the same frequencies were used in activated complex, except for ν_9 which was taken as reaction coordinate.

For normal mode frequencies[37] of *n*-paraffin the average values were assigned to the same type of mode. They are given below, where numbers in parentheses are the number of modes, the two successive numbers being the frequencies in cm^{-1} for hydrogenated and deuterated compounds, respectively. For C_2H_6 and C_2D_6: CH strecthing (6), 3000, 2200; CC stretching (1), 1000, 850; CH_3 deformation (6), 1450, 1100; CH_3 rocking (4), 1000, 800; and CH_3 torsion (1), 300, 200. Three CH stretching modes which correlate to ethylene part were taken as inactive for the calculation of $f(E)$. For C_3H_8 and C_3D_8: CH stretching (8), 3000, 2200; CC stretching (2), 1000, 950; CH_3 deformation and CH_2 scissors (7), 1450, 1100; CH_3 rocking (4), 1100, 800; CH_2 rocking (1), 700, 550; CH_2 twisting and wagging (2), 1300, 950; CCC bending (1), 400; 300; and CH_3 torsion (2), 200, 150. Three CH stretching modes which correlate to ethylene part, and three CH stretching and three CH_3 deformation modes which correlate to methane part were taken as inactive for the calculation of $f(E)$. For *n*-C_4H_{10} and *n*-C_4D_{10}: CH stretching (10), 3000, 2200; CC stretching (3), 1000, 950; CH_3 deformation and CH_2 scissors (8), 1450, 1100; CH_3 rocking (4), 1100, 800; CH_2 rocking (2), 700, 550; CH_2 twisting and wagging (4), 1300, 950; CCC bending (2), 400, 300; CH_3 torsion (2) 200, 150; and CH_2CH_2 torsion (1), 100, 90. Three CH stretching modes which correlate to ethylene part and five CH stretching, one CC stretching, four CH_3 deformation and CH_2 scissors, two CH_3 rocking, two CH_2 twisting and wagging and one CH_3 torsion modes which correlate to ethane part were taken as inactive for the calculation of $f(E)$.

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[36] O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **92**, 6395 (1970).

[37] T. Shimanouchi, "Table of Molecular Vibrational Frequencies," Part 1, U. S. Department of Commerce, National Bureau of Standards (1967).