

# Kinetic Isotope Effect of Chemically Activated Vinyl Radicals

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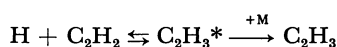
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The apparent decay rates of hydrogen and deuterium atoms in the reactions with acetylene- $d_0$  and - $d_2$  in helium in the pressure range from 100 to 800 Torr (1 Torr = 133.3 Pa) have been measured by the pulse radiolysis-Lyman- $\alpha$  absorption method at  $300 \pm 2$  K. The helium pressure dependence of the rate constants was well interpreted in terms of the RRKM theory including a tunneling effect, using the geometry and force constants of the activated complex and vinyl radical estimated by the *ab initio* calculation. (S. Nagase and C. W. Kern, *J. Am. Chem. Soc.*, **101**, 2544 (1979).)

The reaction of hydrogen atoms with acetylene has been investigated during the last half century.<sup>1–10</sup> The primary reaction mechanism established may be expressed as follows:



Here  $\text{C}_2\text{H}_3^*$  denotes an energized vinyl radical which can re-form reactants or be deactivated to a stable vinyl radical by a collision with a third body.

Recently Keil *et al.* reported two kinds of experiments:<sup>11</sup> one used a mass spectrometer in a flow system for the measurement of the rate constants of the reactions of  $\text{H} + \text{C}_2\text{H}_2$ ,  $\text{H} + \text{C}_2\text{D}_2$ ,  $\text{D} + \text{C}_2\text{H}_2$ , and  $\text{D} + \text{C}_2\text{D}_2$  in the pressure range from 1 to 7 Torr, and the other used a time-resolved Lyman- $\alpha$  photometric method for the measurement of the decay rate of H atoms in the reaction with  $\text{C}_2\text{H}_2$  in flowing helium in the pressure range from 1 to 742 Torr. In order to explain the pressure dependence of these rate constants, they applied the RRKM theory, in which various parameters such as the geometry and vibrational frequencies of an activated complex were estimated by a somewhat arbitrary method.

In a previous investigation,<sup>12</sup> we measured the rate constants of the reactions  $\text{H} + \text{C}_2\text{H}_2$ ,  $\text{H} + \text{C}_2\text{D}_2$ ,  $\text{D} + \text{C}_2\text{H}_2$ , and  $\text{D} + \text{C}_2\text{D}_2$ , by means of the pulse radiolysis-Lyman- $\alpha$  absorption method. In that measurement, the hydrogen pressure was varied from 300 to 1200 Torr and no pressure dependence of the rate constants was observed. In the present study, we used helium as the third body and found the pressure dependence similar to that observed by Keil *et al.*

The recent development of the *ab initio* calculation has been considerable and the potential energy surfaces calculated for some simple reactions are believed to be not far from the real ones. Nagase and Kern have calculated the potential energy surface for the  $\text{H} + \text{C}_2\text{H}_2$  reaction and predicted the geometry and force constants of the activated complex and of the vinyl radical.<sup>13</sup> We tried to use these calculated results to explain the kinetic isotope effects observed in the present experiments in terms of the RRKM theory. In the present calculation, however, there is an important assumption, which should in fairness be stated at the outset. The energy barrier for the reaction of  $\text{H} + \text{C}_2\text{H}_2$  calculated by Nagase and Kern was 6.2 kcal/mol (1 kcal = 4.184 kJ). This value seemed to be too large and was not used in the following calculation.

## Experimental

The apparatus and procedures used in this study are the same as those described in a previous paper,<sup>14</sup> so we mention here only the major features.

Figure 1 shows the apparatus schematically. A mixture of 5 Torr  $\text{H}_2$  or  $\text{D}_2$  and a small amount of  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{D}_2$  (50–130 mTorr) diluted with He (100–800 Torr) was irradiated with an electron pulse (pulse width, 3 ns; upper limit of energy, 600 keV) generated by a Febetron 706 (Hewlett Packard Co.). The time dependence of the concentration of H or D atoms was measured by the absorption of Lyman- $\alpha$  (121.57 nm for H and 121.53 nm for D). The transmitted light was directly detected with a head-on type photomultiplier (Hamamatsu TV Co., R976), which was monitored with an oscilloscope (Tektronix 465). As has been discussed in previous papers,<sup>14,15</sup> the optical density used for the measurement is proportional to the atom concentration in this technique.

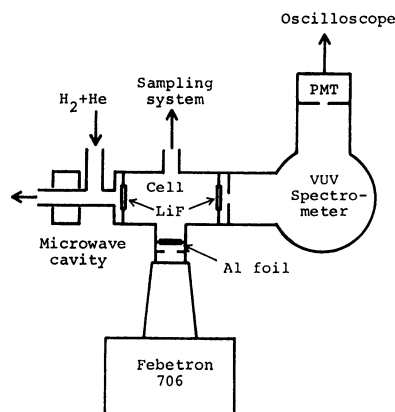


Fig. 1. Schematic diagram of the apparatus.

The high-purity dried He (Nihon Helium Co.) was passed through a trap filled with molecular sieve 4A at 77 K before use. Research grade  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{C}_2\text{H}_2$  (Takachiho Shoji Co.) were used without further purification.  $\text{C}_2\text{D}_2$  was synthesized by the reaction of  $\text{D}_2\text{O}$  (above 99.99%, Merck Co.) with  $\text{CaC}_2$  (Tokyo Kasei Co.), which was heated at about 500 °C for 70 h in vacuum prior to use. The  $\text{C}_2\text{D}_2$  thus obtained was shaken with sulfuric acid for 1 h. The mass and infrared spectra showed that the purity of  $\text{C}_2\text{D}_2$  was better than 99%.

## Results

In the absence of acetylene, practically no change of the atom concentration could be observed in the time

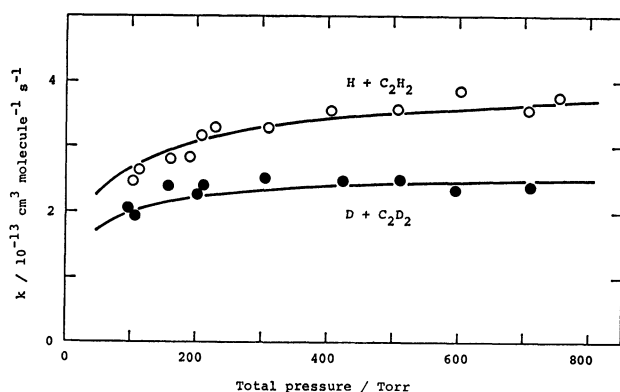


Fig. 2. The apparent decay rates of H atoms in the  $\text{H} + \text{C}_2\text{H}_2$  reaction ( $\circ$ ), and of D atoms in the  $\text{D} + \text{C}_2\text{D}_2$  reaction ( $\bullet$ ) as functions of the total pressure. Solid curves were theoretically calculated.

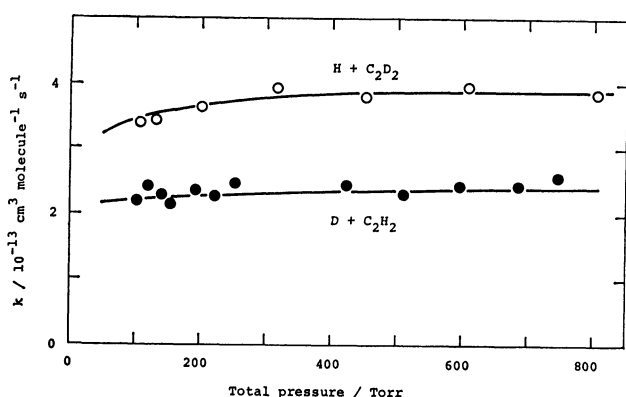


Fig. 3. The apparent decay rates of H atoms in the  $\text{H} + \text{C}_2\text{D}_2$  reaction ( $\circ$ ), and of D atoms in the  $\text{D} + \text{C}_2\text{H}_2$  reaction ( $\bullet$ ) as functions of the total pressure. Solid curves were theoretically calculated.

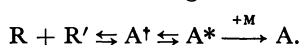
range of 10 ms, while in the presence of 50 mTorr acetylene, the atoms decayed completely within 10 ms. From this first-order decay curve and the concentration of acetylene used, the rate constant of the reaction could be estimated.

Figures 2 and 3 show the rate constants obtained for the reactions of  $\text{H} + \text{C}_2\text{H}_2$ ,  $\text{D} + \text{C}_2\text{D}_2$ ,  $\text{D} + \text{C}_2\text{H}_2$ , and  $\text{H} + \text{C}_2\text{D}_2$  as functions of total pressure. Below 100 Torr of helium, the atom concentration was too small for the measurement of the time dependence. It should be noted that the rate constant of the  $\text{H} + \text{C}_2\text{H}_2$  reaction is strongly dependent upon helium pressure, while that for the  $\text{D} + \text{C}_2\text{H}_2$  reaction is almost independent of helium pressure.

### Theoretical Calculation

The treatment of the RRKM theory has been fully discussed in a book by Robinson and Holbrook.<sup>16)</sup> The present experiments correspond to one of the chemical activations discussed in that book.

Let us consider the following reaction:



Here, R and R' denote reactants,  $\text{A}^\ddagger$  an activated

complex,  $\text{A}^*$  an energized product, and A a stabilized product. In the nomenclature used by Robinson and Holbrook, the bimolecular rate constant of the reaction between R and R' may be expressed as follows:

$$k = k_\infty \int_0^\infty \frac{\omega f(E)}{\omega + k_a(E)} dE \quad (1)$$

Here  $\omega$  is the collision frequency between  $\text{A}^*$  and the third body,  $k_a(E)$  the rate constant of the decomposition of  $\text{A}^*$ ,  $f(E)$  the non-equilibrium distribution of energy of  $\text{A}^*$ , and  $k_\infty$  the bimolecular rate constant in the limit of high pressure.

In order to calculate these parameters, we have to use many approximations, which appear in the RRKM theory. Since many different degrees of approximation are introduced in the book of Robinson and Holbrook, the minimum number of equations used in the present calculation will be given below without any detailed interpretations.

$$\omega = \beta_c z p \quad (2)$$

$$z = \sigma_d^2 (8\pi N_A / \mu k T)^{1/2} \quad (3)$$

Here  $\beta_c$  is the collisional efficiency,  $z$  the collision frequency at 1 Torr of the third body,  $p$  the pressure,  $\sigma_d$  the collision radius,  $\mu$  the reduced mass of  $\text{A}^*$  and the third body,  $T$  the temperature,  $N_A$  Avogadro's number, and  $k$  the Boltzmann constant.

$$k_a(E) = L^\ddagger (Q^\ddagger / Q) [1 / h N(E)] \times \sum_{E_{vr}^\ddagger=0}^E \kappa(E - E_{vr}^\ddagger) P(E_{vr}^\ddagger) \quad (4)$$

$L^\ddagger$  is the reaction path degeneracy and  $Q^\ddagger$  and  $Q$  the partition functions for the over-all rotations of  $\text{A}^\ddagger$  and A. The term  $\kappa(E - E_{vr}^\ddagger)$  is the transmission coefficient, which was not discussed in the book of Robinson and Holbrook; however, recent theoretical calculations on the hydrogen atom-molecule reaction revealed that the tunneling effect cannot be ignored even at room temperature, if a hydrogen atom is transferred in the reaction.<sup>17)</sup> There are several ways to estimate the tunneling effect. One of the simplest ways is to use the transmission coefficient for the inverted parabolic potential barrier in one dimension.

$$\kappa(E) = (1 + \exp[2\pi(E - V_0)/h\nu])^{-1} \quad (5)$$

Here  $V_0$  is the barrier height and  $h\nu$  is the magnitude of the imaginary vibrational quanta. This expression has already been discussed by Kato and Morokuma in the unimolecular decomposition of  $\text{CH}_2\text{CH}_2\text{F}$  radicals.<sup>18)</sup>  $P(E_{vr}^\ddagger)$  denotes the number of vibrational-rotational quantum states of  $\text{A}^\ddagger$  with vibrational-rotational non-fixed energy equal to  $E_{vr}^\ddagger$ ,  $h$  the Planck's constant, and  $N(E)$  the density of quantum states of  $\text{A}^*$  with energy between  $E$  and  $E + dE$ . Since in the  $\text{H} + \text{C}_2\text{H}_2$  reaction, no active rotation is involved in  $\text{A}^\ddagger$ , the term  $P(E_{vr}^\ddagger)$  becomes simply  $P(E_v^\ddagger)$ , a value which has been counted directly. The  $N(E)$  has been calculated by using the Whitten-Rabinovitch approximation:

$$N(E) = \frac{Q_r}{(kT)^{r/2}} \frac{(E + aE_2)^{s+r/2-1}}{\Gamma(s + r/2) \Pi h\nu_1} \left[ 1 - \beta \left( \frac{dw}{dE'} \right) \right] \quad (6)$$

Here,  $Q_r$  is the partition function for the active rotations

in  $A^*$ ,  $r$  and  $s$  the number of active rotations and vibrations,  $E_z$  the sum of zero-point energies,  $\nu_i$  the frequency of the  $i$ -th mode, and  $E' = E/E_z$ . According to Whitten and Rabinovitch,  $a$ ,  $\beta$ , and  $w$  can be expressed as follows:

$$a = 1 - \beta w(E') \quad (7)$$

$$\left. \begin{aligned} (0.1 < E' < 1.0) \, dw/dE' &= - (5.00 + 1.365 E'^{-0.75}) w^2 \\ (1.0 < E' < 8.0) \, dw/dE' &= - (0.60478 E'^{-0.75}) w \end{aligned} \right\} \quad (8)$$

$$\beta = \frac{s-1}{s} \frac{s+\frac{r}{2}}{s} \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2} \quad (9)$$

Here  $\langle \nu \rangle$  and  $\langle \nu^2 \rangle$  are the mean frequency and mean-square frequency of  $A$ . In the present calculation, all vibrations and the rotation around the C-C bond in vinyl radical were taken as active. If the rotation was taken as inactive, we had to assume an extraordinarily large collision radius.

The distribution function  $f(E)$  can be derived by using the principle of detailed balance:

$$f(E) = k_a(E)K(E) / \int_0^\infty k_a(E)K(E)dE \quad (10)$$

Here  $K(E)$  is the Boltzmann distribution function of  $A$ .

$$K(E) = N(E) \exp(-E/kT) / \int_0^\infty N(E) \exp(-E/kT)dE \quad (11)$$

To perform the RRKM calculation, we need the moments of inertia and the vibrational frequencies of the activated complex and the vinyl radical, the barrier height, and the minimum energy of the energized product,  $E_{\min}$ , together with the molecular diameters of He (0.257 nm) and the vinyl radical (0.423 nm); the latter was assumed to be the average of acetylene and ethylene.<sup>19)</sup> The *ad initio* calculation of Nagase and Kern using the 4-31G basis set provides the necessary data. Figure 4 shows the geometry of the activated complex and the vinyl radical. Table 1 summarizes the moments of inertia and the fundamental vibrational frequencies calculated by the GF-matrix method using

the force constants reported. Here it should be noted that the activated complexes  $C_2H_2-D^*$  and  $C_2HD-H^*$  are different. Similarly two vinyl radicals,  $\begin{smallmatrix} D \\ | \\ H \end{smallmatrix} > C = C \begin{smallmatrix} H \\ | \\ H \end{smallmatrix}$

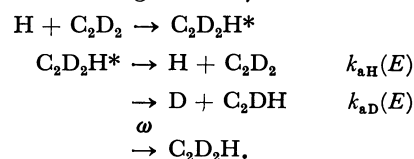
and  $\begin{smallmatrix} D \\ | \\ H \end{smallmatrix} > C = C \begin{smallmatrix} H \\ | \\ H \end{smallmatrix}$ , should be taken as different radicals at the temperature of absolute zero, but, in the present calculation, these two radicals were assumed to be the same, since these two radicals are known to be in equilibrium even at 93 K.<sup>20)</sup> In fact, the partition functions for these two radicals are the same in value within the limits of the calculation.

There is some uncertainty in the value of  $E_{\min}$  because the heat of formation of vinyl radicals and the activation energy for the  $H + C_2H_2$  reaction have not been established. We tentatively adopted 40 kcal/mol for the  $E_{\min}$  of  $C_2H_3^*$ . Since the  $N(E)$  value is not strongly dependent on  $E_{\min}$  around 40 kcal/mol, the adoption of this value does not restrict the conclusions of the following discussion. In the present calculation, the barrier height  $V_0$  was also assumed to be equal to  $E_{\min}$ . Table 1 contains the values of  $E_{\min}$  for other isotopic vinyl radicals, which were calculated by taking into account the zero-point energies of each vinyl radical.

In order to calculate the absolute values of  $k$ , we need the values of  $k_\infty$  for each reaction. Table 2 summarizes the  $k_\infty$  values used in the present calculation. Since we have not measured the temperature dependence of the rate constants, we will not discuss the  $k_\infty$  values theoretically.

*Reactions of  $H + C_2H_2$  and  $D + C_2D_2$ .* The calculation of Eq. 1 is now straight-forward for the  $H + C_2H_2$  reaction. An adjustable parameter is the collisional frequency  $\beta_c$  in Eq. 3. The upper solid curve shown in Fig. 2 was drawn by assuming  $\beta_c = 0.078$ . The scattering of the experimental results allowed us to estimate this value only within the error limit of  $\pm 15\%$ . A similar calculation can be carried out for the  $D + C_2D_2$  reaction. The lower solid curve in Fig. 2 was drawn by using the same collisional efficiency.

*Reactions of  $H + C_2D_2$  and  $D + C_2H_2$ .* In these reactions, we have to consider two processes for the decomposition of energized vinyl radicals:



Consequently, the pressure dependence of the decay rate of H atoms should be expressed as follows:

$$k = k_\infty \int_0^\infty \frac{[\omega + k_{aD}(E)]f(E)}{\omega + k_{aH}(E) + k_{aD}(E)} dE \quad (12)$$

A similar equation can easily be constructed for the case of  $D + C_2H_2$ . The solid curves shown in Fig. 3 were calculated by using these equations. The same collisional efficiency was used. Although the scatter of the experimental data precludes any detailed comparison between experiment and theory, the trend of the pressure dependence could be reproduced by the calculation.

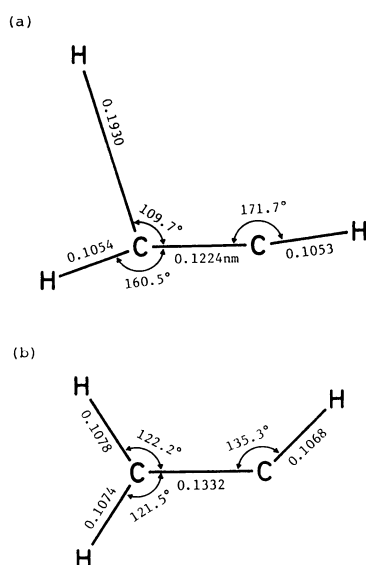


Fig. 4. The geometry of activated complex in the reaction of  $H + C_2H_2$  (a) and of vinyl radical (b).

TABLE 1. PARAMETERS USED FOR CALCULATION

Species	Vibrational frequencies cm <sup>-1</sup>	Moments of inertia kg m <sup>2</sup> × 10 <sup>-47</sup>			Critical energy $E_{\min}$ kcal mol <sup>-1</sup>	Species	Vibrational frequencies cm <sup>-1</sup>	Moments of inertia kg m <sup>2</sup> × 10 <sup>-47</sup>			Critical energy $E_{\min}$ kcal mol <sup>-1</sup>
		$I_a$	$I_b$	$I_c$				$I_a$	$I_b$	$I_c$	
C <sub>2</sub> H <sub>3</sub>	3421	26.25	29.81	3.56*	40.00	C <sub>2</sub> H <sub>2</sub> --D†	3645	30.44	39.33	8.89	38.39
	3348						3578				
	3253						1757				
	1642						824				
	1421						793				
	1209						699				
	981						554				
	893						384				
	843						723i				
C <sub>2</sub> H <sub>3</sub> †	3645	26.63	31.97	5.35	40.00	C <sub>2</sub> HD--H†	3622	30.35	36.16	5.81	36.81
	3578						2707				
	1764						1687				
	884						764				
	793						705				
	703						585				
	577						577				
	479						478				
	890i						858i				
C <sub>2</sub> D <sub>3</sub>	2534	34.91	41.75	6.84*	38.22	C <sub>2</sub> D <sub>2</sub> H	3274	33.14	38.10	4.96*	39.85
	2487						2533				
	2365						2445				
	1457						1523				
	1125						1355				
	981						1002				
	779						894				
	670						674				
	610						644				
C <sub>2</sub> D <sub>3</sub> †	2798	38.40	48.61	10.21	38.22	C <sub>2</sub> D <sub>2</sub> --H†	2799	35.29	41.15	5.86	39.85
	2628						2628				
	1611						1619				
	634						699				
	600						601				
	576						580				
	467						515				
	355						417				
	698i						856i				
C <sub>2</sub> H <sub>2</sub> D	3421	28.43	33.39	4.96*		C <sub>2</sub> DH--D†	3605	34.98	44.23	9.24	41.44
	3332						2724				
	2403						1682				
	1539						809				
	1364						727				
	1109						600				
	937						467				
	827						356				
	763						719i				

\*Active rotation.

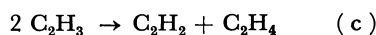
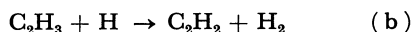
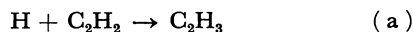
### Discussion

As has been discussed in a previous paper,<sup>12)</sup> the rate constant of the H+C<sub>2</sub>H<sub>2</sub> reaction we obtained in the limit of high pressure is more than twice that reported by Payne and Stief ( $1.56 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).<sup>10)</sup> The result of Keil *et al.* is consistent with theirs. We therefore reconsidered this discrepancy. One possible reason is the participation of the reaction of

TABLE 2.  $k_{\infty}$  USED FOR CALCULATION

Reaction	$k_{\infty}/10^{-13}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
H+C <sub>2</sub> H <sub>2</sub>	4.0
D+C <sub>2</sub> D <sub>2</sub>	2.6
D+C <sub>2</sub> H <sub>2</sub>	2.5
H+C <sub>2</sub> D <sub>2</sub>	4.0

vinyl radicals in the decay of hydrogen atoms in our reaction system.



The apparent decay rate of hydrogen atoms may be expressed as follows:

$$k_{\text{app}} = k_a \left( 1 + \frac{k_b [\text{C}_2\text{H}_3]}{k_a [\text{C}_2\text{H}_2]} \right) = k_a \gamma. \quad (12)$$

The correction factor  $\gamma$  ranges from 1 to 2. The time dependence of  $[\text{C}_2\text{H}_3]$  can be calculated by the Runge-Kutta integration procedure if the ratios of  $k_b/k_a$  and  $k_c/k_a$  and the initial concentration of H and  $\text{C}_2\text{H}_2$  are known. Such calculations have already been made in a previous paper, in which the reaction between hydrogen atoms and ethylene has been discussed.<sup>15)</sup> In the present experiments, we may approximate that  $k_a \approx 4 \times 10^{-13}$ ,  $k_b \approx 6 \times 10^{-11}$ , and  $k_c \approx 10^{-11}$  in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the initial concentration of hydrogen atoms is in the order of  $10^{12} \text{ cm}^{-3}$  and  $[\text{C}_2\text{H}_2]$ , larger than  $2 \times 10^{15} \text{ cm}^{-3}$ . The substitution of these data gives a  $\gamma$  factor of less than 1.1, *i.e.*, no correction seems to be necessary. However, the electron pulse-irradiation might produce an inhomogeneous distribution of atoms in the reaction cell, which cannot easily be estimated. If this occurred, the value of the  $\gamma$  factor would become close to 2. Consequently, it may be safe at present to retain the final conclusion until new evidence can be obtained. The measurement of the activation energy is now being undertaken.

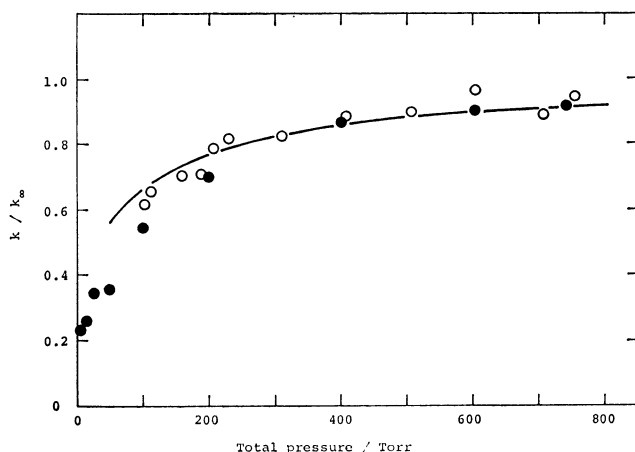


Fig. 5. Comparison of experiments obtained by Keil *et al.* (●) and by the present work (○) with theoretical curve. The value of  $k_\infty$  for the data of Keil *et al.* was assumed to be  $1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

**Comparison with the Data of Keil *et al.*** In Fig. 5, we plotted the pressure dependence of the  $k/k_\infty$  ratios for the  $\text{H} + \text{C}_2\text{H}_2$  reaction obtained by Keil *et al.* and by us. Both experiments are in fair agreement with theoretical curve. According to Keil *et al.*, their RRKM calculation well explained this pressure dependence.<sup>11)</sup>

This fact probably means that the differences between the parameters of the moments of inertia and of the vibrational frequencies for the activated complex and vinyl radicals are not large enough to cause any difference in the pressure dependence of the rate constant. Since there is an adjustable parameter,  $\beta_c$ , in the theory, we cannot make a definite comparison. Incidentally, Keil *et al.* took the value of 0.25 for  $\beta_c$ .

**Tunneling Effect.** In the above treatment, we introduced a tunneling effect into the RRKM calculation. The calculation without a tunneling effect has also been carried out, and similar agreement between experiment and theory could be obtained, although the adjustable parameter,  $\beta_c$ , increased to 0.21. As far as the consistency between experiment and theoretical calculation is concerned, no substantial difference could be found between including and excluding the tunneling effect. Probably this effect will become a crucial problem when  $k_\infty$  is discussed theoretically.

## References

- 1) K. F. Bonhoeffer and P. Harteck, *Z. Phys. Chem.*, **139**, 64 (1928).
- 2) E. W. R. Steacie, "Atomic and Free Radical Reactions," Renhold, New York (1954), Vol. 1. Early studies are reviewed.
- 3) E. L. Tollefson and D. J. LeRoy, *J. Chem. Phys.*, **16**, 1057 (1948).
- 4) J. R. Dingle and D. J. LeRoy, *J. Chem. Phys.*, **18**, 1632 (1950).
- 5) H. Girouard, F. M. Graber, and B. F. Mayers, General Dynamics-Astronautical Rept. No. N64-13061, San Diego (1963) NASA CR 52376.
- 6) G. G. Volpi and F. Zocchi, *J. Chem. Phys.*, **44**, 4010 (1966).
- 7) J. V. Michael and R. E. Weston, Jr., *J. Chem. Phys.*, **45**, 3632 (1966).
- 8) J. V. Michael and H. Niki, *J. Chem. Phys.*, **46**, 4969 (1967).
- 9) K. Hoyermann, H. G. Wagner, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*, **75**, 22 (1971).
- 10) W. A. Payne and L. J. Stief, *J. Chem. Phys.*, **64**, 1150 (1976).
- 11) D. G. Keil, K. P. Lynch, J. A. Cowfer, and J. V. Michael, *Int. J. Chem. Kinet.*, **8**, 825 (1976).
- 12) Y. Ishikawa, K. Sugawara, and S. Sato, *Bull. Chem. Soc. Jpn.*, **52**, 3503 (1979).
- 13) S. Nagase and C. W. Kern, *J. Am. Chem. Soc.*, **101**, 2544 (1979).
- 14) K. Sugawara, Y. Ishikawa, and S. Sato, *Bull. Chem. Soc. Jpn.*, **53**, 1344 (1980).
- 15) Y. Ishikawa, M. Yamabe, A. Noda, and S. Sato, *Bull. Chem. Soc. Jpn.*, **51**, 2488 (1978).
- 16) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," John Wiley and Sons, Inc., New York (1972).
- 17) B. C. Garrett and D. G. Truhlar, *J. Chem. Phys.*, **72**, 3460 (1980).
- 18) S. Kato and K. Morokuma, *J. Chem. Phys.*, **72**, 206 (1980).
- 19) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York (1964).
- 20) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **30**, 2147 (1963).