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Energized Vinyl Radical Formation in the Photolysis of Ethylene

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Synopsis. Energized vinyl radical formation was found in the primary process of the 1634 Å photolysis of ethylene in the pressure region up to about 1 atm. The energized vinyl radical either decomposes unimolecularly to give acetylene and a hydrogen atom, or is deactivated to a stable vinyl radical at collision.

The primary processes in the photolysis of ethylene had been reported to be (1) and (2) in Scheme 1.[1-4] In recent years, however, another process, vinyl radical formation (3) was found on the basis of the formation of 1-butene as a product.[5,6]

$$C_2H_4 + h\nu \begin{cases} \longrightarrow C_2H_2 + H_2 & (1) \\ \longrightarrow C_2H_2 + 2H & (2) \\ \longrightarrow C_2H_3 + H & (3) \end{cases}$$

Scheme 1.

More detailed mechanisms of the primary processes are still open to further investigation. In the present report, the mechanism involving two kinds of vinyl radical is proposed from the photolysis of high pressure ethylene (up to about 1 atom) at 1634 Å.

Experimental

The experimental procedures used in this experiment were almost the same as described previously.[6]

Results and Discussion

Ethylene was photolyzed at 1634 Å with and without nitrogen as a deactivator. The reaction products were the same as reported previously.[6] The ratio of formation rate of 1-butene to that of *n*-butane was plotted as a function of ethylene pressure, and as a function of nitrogen pressure with a fixed ethylene pressure in Figs. 1 and 2, respectively. In each case, the ratio follows a straight line with intercept against ethylene or nitrogen pressure.

As reported previously, 1-butene and *n*-butane are formed through recombination reactions of vinyl and ethyl radicals and of two ethyl radicals, respectively.[6]

It might be also possible that 1-butene is formed through Reaction (4).

$$C_2H_4^* + C_2H_4 \longrightarrow 1\text{-}C_4H_8 \quad (4)$$

But this process is ruled out in this experiment since 1-butene could not be detected in the photolysis of 360 Torr of ethylene with 19 Torr of nitric oxide added as a free radical scavenger. Thus, 1-butene is formed only by the recombination of vinyl and ethyl radicals. The product ratio evidently shows the pressure dependence, and it strongly suggests that the formation of the vibrationally excited vinyl radical, which either

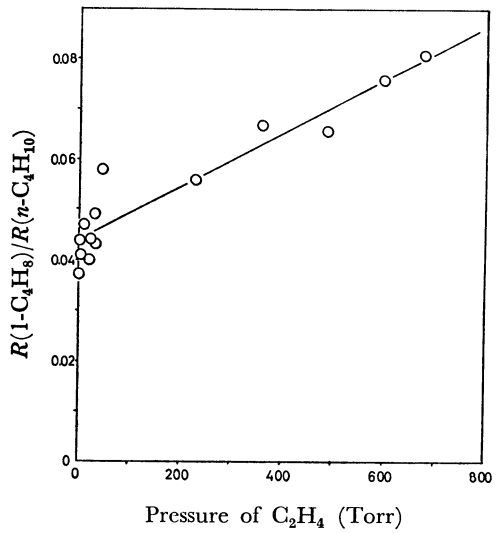

Fig. 1. $R(1\text{-}C_4H_8)/R(n\text{-}C_4H_{10})$ *vs.* the pressure of ethylene (Torr).

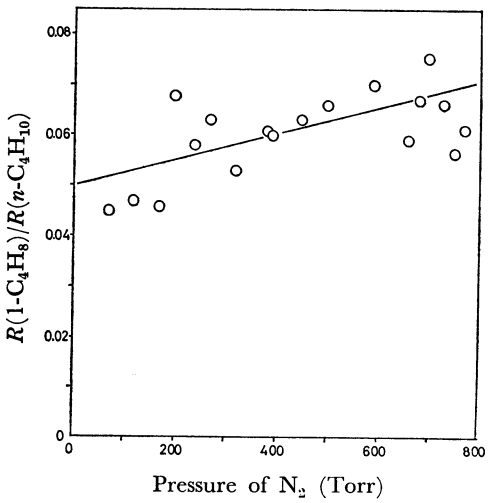

Fig. 2. $R(1\text{-}C_4H_8)/R(n\text{-}C_4H_{10})$ *vs.* the pressure of nitrogen (Torr) (C_2H_4: 25 Torr)

decomposes to give acetylene and a hydrogen atom, or is stabilized at collision to yield a stable vinyl radical. This mechanism has been proposed by Back and Griffith as follows.[4]

$$C_2H_4 + h\nu \longrightarrow H + [C_2H_3^*] \longrightarrow 2H + C_2H_2 \quad (5)$$

The details of the mechanism would be Reaction (6)

$$C_2H_4^* \longrightarrow C_2H_3^{\neq} + H \quad (6)$$

followed quickly by Reaction (7)

$$C_2H_3^{\neq} \longrightarrow C_2H_2 + H \quad (7)$$

provided the lifetime of $C_2H_3^{\neq}$ for dissociation is short enough to preclude any reactions requiring a bimolecu-

lar collision. But they have no direct evidence of the existence of the energized vinyl radicals. If this mechanism were the case, the ratio of 1-butene to *n*-butane would be extrapolated to zero at zero pressure. As seen in Figs. 1 and 2, the intercepts are, however, not zero. Thus, an additional path forming stable vinyl radicals should be considered. Namely two kinds of vinyl radicals must be formed in the primary process; one undergoes the unimolecular decomposition into acetylene and a hydrogen atom competing with collisional deactivation to a stable vinyl radical, and the other does not decompose even at very low pressures.

In the light of these arguments, the following scheme is proposed with the aid of our previous study.

$$C_2H_4 + h\nu \xrightarrow{\phi_1} C_2H_2 + H_2 \quad (8)$$

$$\xrightarrow{\phi_2} H + C_2H_3^{**} \xrightarrow{k_d} C_2H_2 + H_2 \quad (9)$$

$$\xrightarrow{\phi_3} H + C_2H_3^{*} \xrightarrow{k_s[M]} C_2H_3 \quad (10)$$

$$H + C_2H_4 \longrightarrow C_2H_5 \quad (11)$$

$$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \quad (12)$$

$$\longrightarrow n\text{-}C_4H_{10} \quad (13)$$

$$C_2H_3 + C_2H_5 \longrightarrow 2C_2H_4 \quad (14)$$

$$\longrightarrow C_2H_2 + C_2H_6 \quad (15)$$

$$\longrightarrow 1\text{-}C_4H_8 \quad (16)$$

Scheme 2.

Steady state treatment leads to the relationship

$$\frac{R(1\text{-}C_4H_8)}{R(n\text{-}C_4H_{10})} = A\left\{\frac{\phi_3}{\phi_2} + \left(1+\frac{\phi_3}{\phi_2}\right)\frac{k_s^{C_2H_4}}{k_d}[C_2H_4] + \left(1+\frac{\phi_3}{\phi_2}\right)\frac{k_s^{N_2}}{k_d}[N_2]\right\} \quad (17)$$

where $A=k_9(k_5+k_6)/k_6(k_7+k_8+k_9)$. The value of A was obtained in the previous study as 0.45 at 1634 Å.

From the intercepts and the slopes of the plots in Figs. 1 and 2, the values of ϕ_3/ϕ_2, $k_s^{C_2H_4}/k_d$ and $k_s^{N_2}/k_d$ can be determined. The results are summarized in Table 1.

Table 1. ϕ_3/ϕ_2, k_s^M/k_d, and β

M	ϕ_3/ϕ_2	k_s^M/k_d Torr^{-1}	β
C_2H_4	0.098±0.08	1.1 ±0.1	1.0
N_2	—	0.47±0.1	0.43

It is concluded that at least some portion of acetylene in Scheme 1 may be formed through $C_2H_3^{**}$ from ϕ_2 in Scheme 2.

The rate constant of stabilization, k_s, is written as follows:

$$k_s = \frac{\beta Z^{C_2H_3^{**}-M}}{[M]} \quad (18)$$

where β is the collisional deactivation efficiency and $Z^{C_2H_3^{**}-M}$ is the collision frequency between the energized vinyl radical and the deactivator, M. The latter was calculated by means of the gas kinetic theory on the assumption that the collisional diameter of vinyl radical was the same as that of ethylene. If the unit probability of energy transfer per collision is assumed for ethylene, the experimental value of $k_s^{C_2H_4}/k_d$ and the collisional frequency yield an upper limit of the dissociative rate constant, k_d, 1.0×10^{11} s^{-1}. Using this value of k_d, the collisional deactivation efficiency is obtained. These values are also shown in Table 1.

Calculation using a simple RRKM theory was carried out to compare with the dissociative rate constant obtained experimentally.

It is generally accepted that k_d corresponds to the specific rate constant k_E for the energies ranging from 50 to 80% of the maximum available energy for the decomposition. In this study, the specific rate constant for the decomposition of the vinyl radical was calculated. The computation was carried out for four models of activated complexes by the usage of the program by Akimoto *et al.*[7] The result is shown in Fig. 3. The experimental value of k_d, 1.0×10^{11} s^{-1} corresponds to the k_E at 48—57 kcal mol^{-1}, which is 70—80% of the available energy (70 kcal mol^{-1}). Thus the experimental value and our proposed mechanism are quite reasonable.

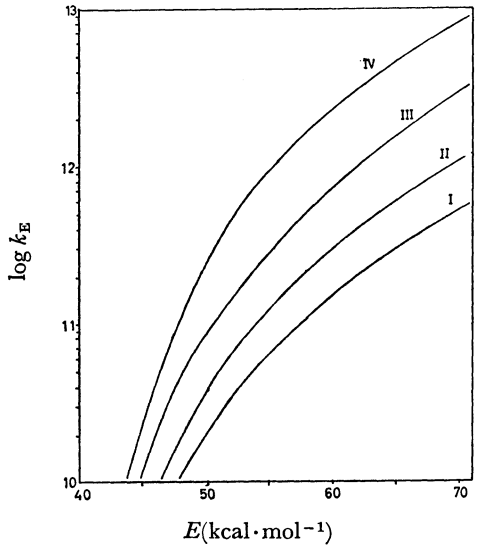

Fig. 3. log k_E *vs.* E. The numbering of the models is taken in order of rigidness.

References

1) M. C. Sauer, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).
2) H. Okabe and J. R. McNesby, *ibid.*, **36**, 601 (1962).
3) J. R. McNesby and H. Okabe, *Advan. Photochem.*, **3**, 157 (1964).
4) R. A. Back and D. W. L. Griffiths, *J. Chem. Phys.*, **46**, 4839 (1967).
5) Y. Inel, A. Siddiqi, and G. G. Meisels, *J. Phys. Chem.*, **75**, 1317 (1971); P. Borrell, A. Cervanka, and J. W. Turner, *J. Chem. Soc., B*, **1971**, 2293; P. Potzinger, L. C. Glasgow, and G. Von Bunau, *Z. Naturforsch., A*, **27**, 628 (1972).
6) H. Hara and I. Tanaka, This Bulletin, **46**, 3012 (1973).
7) H. Akimoto, K. Obi, and I. Tanaka, *ibid.*, **46**, 2267 (1973).