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Photolysis of Ethylene at 1634 Å and 1849 Å

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The photolysis of ethylene was carried out at room temperature at 1634 Å and 1849 Å. Products at both wavelengths were hydrogen, acetylene, ethane, *n*-butane and 1-butene. Product analysis and the radical scavenger technique indicate the primary processes to be as follows.

$$C_2H_4 + h\nu \longrightarrow \begin{cases} \longrightarrow C_2H_2 + H_2 \\ \longrightarrow C_2H_2 + 2H \\ \longrightarrow C_2H_3 + H \end{cases}$$

The molecular elimination process in the primary processes varied with wavelengths, and was determined to be 47% and 53% at 1634 Å and 1849 Å, respectively. With reference to the percentage reported at other wavelengths, it is pointed out that molecular elimination is suppressed with the increase in excitation energy.

The photochemistry of ethylene has long been studied[1-6] and the reaction mechanism is proposed from the results of investigations at 1236 Å and 1470 Å,[1-3]

$$C_2H_4 + h\nu \longrightarrow \begin{cases} \longrightarrow C_2H_2 + H_2 & \Phi_1 \\ \longrightarrow C_2H_2 + 2H & \Phi_2 \end{cases}$$

where Φ_1 and Φ_2 stand for the quantum yields of the respective reactions. These are followed by the secondary processes,

$$H + C_2H_4 \longrightarrow C_2H_5$$

$$C_2H_5 + C_2H_5 \longrightarrow \begin{cases} \longrightarrow C_2H_4 + C_2H_6 \\ \longrightarrow n\text{-}C_4H_{10} \end{cases}$$

The quantum yield Φ_1 relative to Φ_2 decreases as the excitation energy increases. Since some molecules such as ethane show a wavelength dependence of the quantum yield of molecular elimination, it seems interesting to study the wavelength dependence of Φ_1 relative to Φ_2 over a wider range.

Ethylene was studied at longer wavelengths. For quantitative treatment, the percentage of the molecular mechanism is expressed by $\Phi_1/(\Phi_1+\Phi_2+\Phi_3)$, where Φ_3 is the quantum yield of the vinyl radical formation process

$$C_2H_4 + h\nu \longrightarrow C_2H_3 + H$$

which was recently found in the photolysis of ethylene at 1470—1931 Å by Potzinger *et al.*[7] In the present study, the primary process of the vinyl radical formation is discussed in detail.

Ethyl radicals were formed in the secondary process of the photolysis of ethylene, and underwent disproportionation reaction or recombination reaction. A number of investigators have determined the ratio of the constants of these two reactions, generating ethyl radicals from different source. The reported ratios show a spread but most values lie in the range 0.10—0.17. The ratio in the photolysis of ethylene is discussed in the present study.

The V–N system beginning near 2650 Å consists of a long progression of broad diffuse bands, starting at 2150 Å and rising rapidly in intensity with decreasing wavelength. At 1744 Å, the V–N bands disappear under the intense bands of the first Rydberg transition, but the V–N system obviously continues, and finally reaches a broad flat maximum at about 1620 Å. At still shorter wavelengths the absorption decreases fairly steadily, down to the next strong Rydberg transition which begins at 1393 Å.[11]

Thus the absorption at 1236 Å corresponds to the second R–N transition, and that at 1470 Å to the mixture of the R–N and V–N transitions. On the other hand, the absorptions at both 1634 Å and 1849 Å in this study correspond to V–N transition.

Experimental

The light source of 1634 Å was an electrodeless discharge bromine lamp, construction of which was reported elsewhere,[12,13] and that of 1849 Å was a conventional low-pressure mercury lamp. The reaction system was a quartz cylinder with quartz windows and a glass-made circulator.

Nitrogen gas was allowed to flow between the lamp and the cell during the photolysis to avoid the absorption of oxygen at 1634 Å.

Ethylene was obtained from Takachiho Chem. Ind. Co. Gas chromatographic analysis showed the presence of impurity, 0.1% ethane. After purification by gas chromatography using an active carbon column, the impurity level was below 0.01%. Nitric oxide was also obtained from

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[2] M. C. Sauer, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).

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[5] R. A. Back and D. W. L. Griffiths, *J. Chem. Phys.*, **46**, 4839 (1967).

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[13] K. Obi, Ph, D, Thesis, Tokyo Institute of Technology (1966).

Takachiho Chem. Ind. Co. and was used without further purification. The reaction was followed by freezing out the unreacted ethylene and any condensable products with liquid nitrogen to a sample collection tube. The condensables were analyzed with a Hitachi Model KGL–2A gas chromatograph equipped with a flame ionization detector using a 2 m long column of silica gel-squalane, and with a Hitachi Model 063 gas chromatograph, equipped with a flame ionization detector for hydrocarbon products using a 9 m long column of squalane on Chromosorb P support. For hydrogen, a 1 m long column of active carbon and a thermal conductivity detector were used, a copper oxide furnace being provided between the column and the detector to convert hydrogen into water for higher sensitivity. In order to determine the ratio of hydrogen to ethylene, the reaction system was attached to the Toepler pump system to collect the entire amount of products and the unreacted into the sample collection tube. All experiments were carried out at room temperature.

Results

Photolysis at 1634 Å. The products of photolysis with radiation at 1634 Å were hydrogen, acetylene, ethane, *n*-butane and 1-butene. They are the same as in the photolysis at 1236 Å and 1470 Å except that only traces of 1-butene and hexane were detected and no C–4 compounds other than *n*-butane were observed.[2,3]

In order to see the effect of the secondary photolysis which should be negligibly small, the yields of acetylene, ethane and *n*-butane, were determined for different irradiation times. The relative yields are plotted as a function of irradiation time in Fig. 1. This result provided a linear function of time so that complications due to the secondary photolysis was not significant within one percent of conversion. The following photolysis was conducted within this limit.

Photolysis in the presence of nitric oxide was performed with a constant pressure of ethylene and a fixed time of irradiation. No appreciable decrease in the yield of acetylene was observed in these experiments.

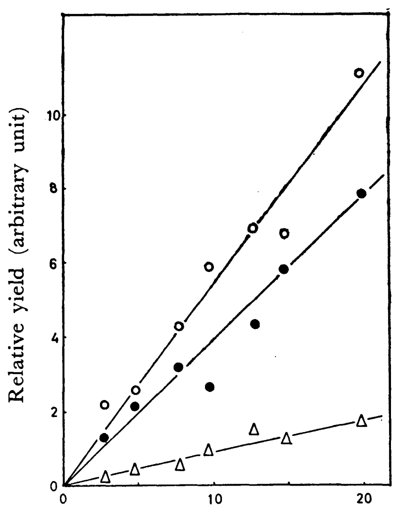

Fig. 1. Relative yields of products *vs.* irradiation time. C_2H_2 (○), *n*-C_4H_{10} (●), and C_2H_6 (△).

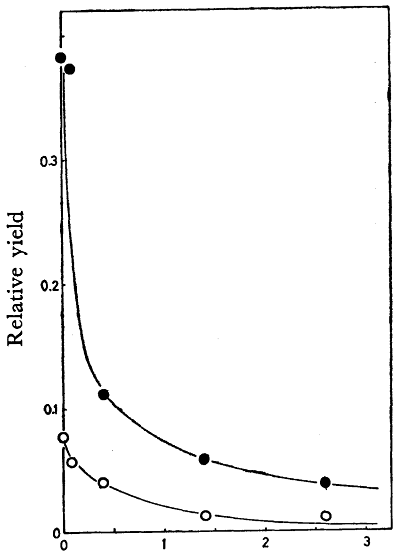

Fig. 2. Relative yields of *n*-C_4H_{10} and C_2H_6 to C_2H_2 *vs.* added NO pressure (C_2H_4; 20 Torr). *n*-C_4H_{10} (●) and C_2H_6 (○).

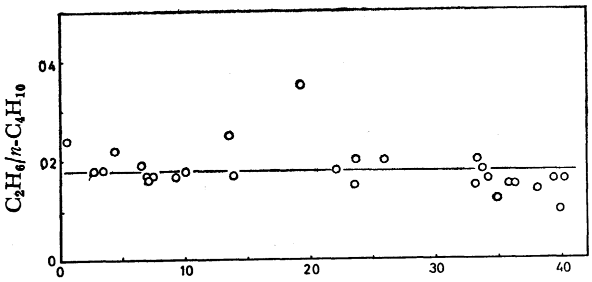

Fig. 3. C_2H_6 to *n*-C_4H_{10} ratio *vs.* C_2H_4 pressure at 1634 Å.

As shown in Fig. 2, ethane and *n*-butane decreased remarkably with increasing concentration of nitric oxide which was an effective free-radical scavenger. These results support the view that acetylene, at least the majority of it, was formed in the primary processes, and that ethane and *n*-butane were formed in the radical reaction.

The ratio of ethane to *n*-butane is plotted as a function of ethylene pressure in the range 0.6—40 Torr in Fig. 3. The ratio calculated to be 0.18±0.04 is independent of ethylene pressure.

The ratio of 1-butene to *n*-butane as products is almost constant, 0.045±0.008 in the pressure range 5—40 Torr.

Photolysis at 1849 Å. The products of the photolysis with light of 1849 Å were hydrogen, acetylene, ethane, *n*-butane and 1-butene as in the case of the photolysis at 1634 Å.

The ratio of ethane to *n*-butane was measured at various pressures of ethylene as shown in Fig. 4. It is independent of ethylene pressure and gives the average value of 0.30±0.06.

The ratio of 1-butene to *n*-butane was determined to be 0.19±0.04, pressure independent in the range 5—35 Torr.

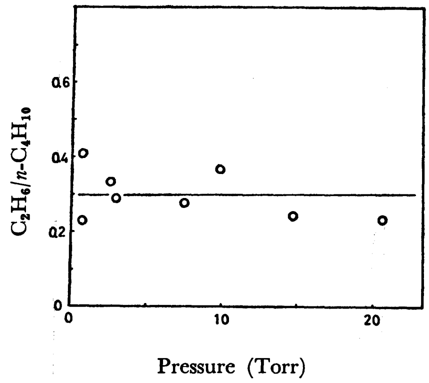

Fig. 4. C_2H_6 to n-C_4H_{10} ratio *vs.* C_2H_4 pressure at 1849 Å.

Discussion

Reaction Mechanism. The formation of a considerable amount of 1-butene at 1634 Å and 1849 Å affords the following processes which account for the products of the present work as well as those of the previous work using shorter wavelengths.

$$
\begin{array}{llr}
C_2H_4 + h\nu & \xrightarrow{\Phi_1} C_2H_2 + H_2 & (1)\\
 & \xrightarrow{\Phi_2} C_2H_2 + 2H & (2)\\
 & \xrightarrow{\Phi_3} C_2H_3 + H & (3)\\
H + C_2H_4 & \xrightarrow{k_4} C_2H_5 & (4)\\
C_2H_5 + C_2H_5 & \xrightarrow{k_5} C_2H_4 + C_2H_6 & (5)\\
 & \xrightarrow{k_6} n\text{-}C_4H_{10} & (6)\\
C_2H_3 + C_2H_5 & \xrightarrow{k_7} 2C_2H_4 & (7)\\
 & \xrightarrow{k_8} C_2H_2 + C_2H_6 & (8)\\
 & \xrightarrow{k_9} 1\text{-}C_4H_8 & (9)
\end{array}
$$

Steady state treatment led to the relationship

$$\frac{R(C_2H_6) + R(n\text{-}C_4H_{10})}{R(C_2H_2)} = \frac{\Phi_2 + \Phi_3 \cdot \dfrac{k_8}{k_7+k_8+k_9}}{\Phi_1 + \Phi_2 + \Phi_3 \cdot \dfrac{k_8}{k_7+k_8+k_9}} \equiv \alpha \tag{10}$$

$$1 - \frac{R(H_2)}{R(C_2H_2)} = \frac{\Phi_2 + \Phi_3 \cdot \dfrac{k_8}{k_7+k_8+k_9}}{\Phi_1 + \Phi_2 + \Phi_3 \cdot \dfrac{k_8}{k_7+k_8+k_9}} \equiv \beta \tag{11}$$

$$\frac{R(C_2H_6)}{R(n\text{-}C_4H_{10})} = \frac{k_5}{k_6} + \frac{\Phi_3}{\Phi_2} \cdot \frac{k_5+k_6}{k_6} \cdot \frac{k_8}{k_7+k_8+k_9} \equiv \gamma \tag{12}$$

$$\frac{R(1\text{-}C_4H_8)}{R(n\text{-}C_4H_{10})} = \frac{\Phi_3}{\Phi_2} \cdot \frac{k_5+k_6}{k_6} \cdot \frac{k_9}{k_7+k_8+k_9} \equiv \delta \tag{13}$$

where α, β, γ, and δ are the experimentally available values of the product ratios, and R(M) is the formation rate of M.

Reaction (8) is an important process which explains the difference in the ratio of ethane to n-butane at 1634 Å and at 1849 Å. According to a recent work. k_8 is not negligibly small compared with k_7 and k_9, namely $k_7 : k_8 : k_9 = 1.00 : 0.43 : 0.89$.[14] Potzinger *et al.* did not include Reaction (8) on the basis that the addition of oxygen to ethylene had no effect on the quantum yield for acetylene.[7] It might be because the contribution of Reaction (8) at the formation of acetylene was not important. In the present study, however, the Reaction (8) must not be ruled out.

TABLE 1. k_5/k_6 IN THE PHOTOLYSES OF ETHYLENE AT DIFFERENT WAVELENGTHS

Excitation wavelength	k_5/k_6	Ref.
1236 Å[a]	0.18	(3)
1470 Å	0.15	(2)
	0.19	(14)
1634 Å	0.16±0.04	this work
1849 Å	0.21±0.06	this work

a) CH_2CD_2

Disproportionation and Recombination of Ethyl Radicals. Ethyl radical is formed in the photolysis of ethylene. If ethane and n-butane are formed only through ethyl radical reactions, the ratio of the formed amount of ethane to that of n-butane directly leads to k_5/k_6. The photolyses at 1236 Å and 1470 Å are such cases. In the present study, the ratios of ethane to n-butane are 0.18 at 1634 Å and 0.30 at 1849 Å, suggesting the additional amount of ethane from Reaction (8). Thus from Eqs. (12) and (13), we obtain the relation.

$$\frac{k_5}{k_6} = \gamma - \frac{k_8}{k_9} \cdot \delta$$

From our experimental values of γ, δ and reported value of k_8/k_9, 0.48,[14] the value of k_5/k_6 should be obtained.

At 1634 Å, γ is 0.18±0.04 and δ is 0.045±0.008, then k_5/k_6 is 0.16±0.04. At 1849 Å, γ and δ are 0.30±0.06 and 0.19±0.04, respectively, so k_5/k_6 is 0.21±0.06. Comparison of this ratio at different wavelengths is made in Table 1. In consideration of this ratio 0.13+0.02,[8-10] obtained previously from different sources of ethyl radicals, these values in the photolysis of ethylene agree well within the error limit.

Molecular Mechanism of the Primary Processes at 1634 Å *and* 1849 Å. Substitution of our values of k_5/k_6 and the reported relative values, $k_7 : k_8 : k_9 = 1.00 : 0.43 : 0.89$,[14] into Eqs. (12) and (13) gives the following.

$$\frac{R(C_2H_6) + R(n\text{-}C_4H_{10})}{R(C_2H_2)} = \frac{\Phi_2 + 0.19\Phi_3}{\Phi_1 + \Phi_2 + 0.19\Phi_3} \equiv \alpha \tag{15}$$

$$1 - \frac{R(H_2)}{R(C_2H_2)} = \frac{\Phi_2 + 0.19\Phi_3}{\Phi_1 + \Phi_2 + 0.19\Phi_3} \equiv \beta \tag{16}$$

$$\frac{R(C_2H_6)}{R(n\text{-}C_4H_{10})} = 0.16 + 0.22\frac{\Phi_3}{\Phi_2} \equiv \gamma \quad (\text{for } 1634\,\text{Å}) \tag{17-8}$$

$$= 0.21 + 0.22\frac{\Phi_3}{\Phi_2} \equiv \gamma \quad (\text{for } 1849\,\text{Å}) \tag{17-2}$$

$$\frac{R(1\text{-}C_4H_8)}{R(n\text{-}C_4H_{10})} = 0.44\frac{\Phi_3}{\Phi_2} \equiv \delta \quad (\text{for } 1634\,\text{Å}) \tag{18-1}$$

$$= 0.46\frac{\Phi_3}{\Phi_2} \equiv \delta \quad (\text{for } 1849\,\text{Å}) \tag{18-2}$$

Relative quantum yields of the primary processes can

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14) T. Ibuki and Y. Takezaki, private communication.

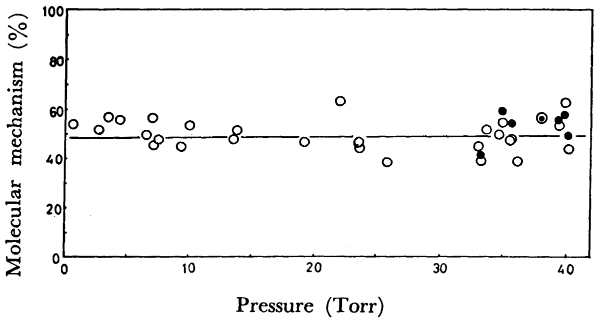

Fig. 5. Molecular mechanism (%) *vs.* C_2H_4 pressure at 1634 Å.
(○) from Eqs. (15) and (17—1); (●) from Eqs. (16) and (17—1).

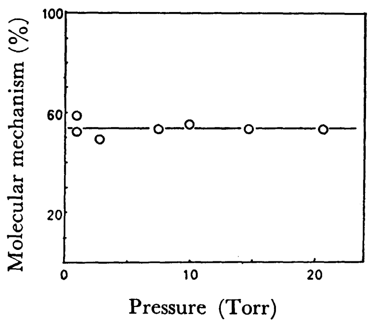

Fig. 6. Molecular mechanism (%) *vs.* C_2H_4 pressure at 1849 Å.

be obtained using Eqs. (15)—(18) with the values of α, β, γ, and δ.

In most experiments, α and γ values were used to obtain the percentage of the molecular elimination process, which is shown in Fig. 5 as a function of ethylene pressure at 1634 Å and in Fig. 6 at 1849 Å. It is pressure independent at both wavelengths. The average values of molecular mechanism, Φ_1, are 47% at 1634 Å and 53% at 1849 Å.

Φ_1 at 1634 Å calculated from β and γ values is also shown in Fig. 5, giving the average value 51%.

The value of δ from the ratio of 1-butene and n-butane is 0.045 at 1634 Å and 0.19 at 1849 Å. The relative quantum yields of the primary processes also can be calculated at 1634 Å and 1849 Å using δ values instead of γ values. They are summarized in Table II, and are in good agreement within experimental error.

Table 2. Relative quantum yield at 1634 Å and 1849 Å

		Relative quantum yield from			
		(15) and (17)	(16) and (17)	(15) and (18)	(16) and (18)
1634 Å	Φ_1	47(±6)%	51(±6)%	47(±5)%	51(±4)%
	Φ_2	48(±6)	45(±4)	48(±5)	45(±4)
	Φ_3	5(±4)	4(±4)	5(±1)	4(±2)
1849 Å	Φ_1	53(±3)%	—	53(±6)%	—
	Φ_2	33(±5)	—	33(±4)	—
	Φ_3	14(±2)	—	14(±4)	—

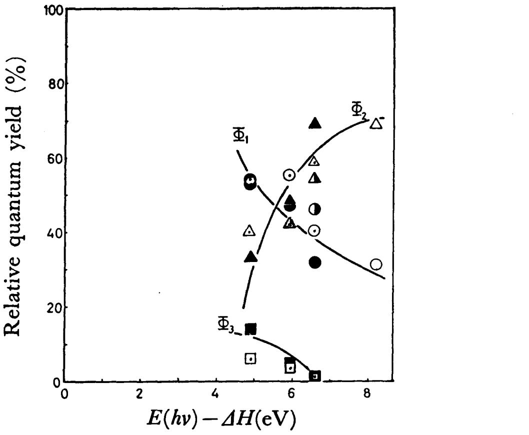

Fig. 7. Relative quantum yield *vs.* $E(h\nu)-\Delta H$.
circle, Φ_1; triangle, Φ_2; square, Φ_3.
(●, ▲, ■) this work, and Ref. 15, (◑, ◭) Ref. 2, (○, △) Ref. 3, (⊙, ◬, ⊡) Ref. 7.

Formation of vinyl radical in the primary process, proposed in the flash photolysis study of ethylene[5] and 1470—1931 Å photolysis of ethylene,[7] explains the presence of 1-butene as a product which should be formed by the recombination reaction of vinyl and ethyl radicals.

Another fact supporting the formation of vinyl radical is the good agreement between the ratio of Φ_3 to Φ_2 from γ and that from δ. At 1634 Å, the ratio of Φ_3 to Φ_2 is 0.091 from γ and 0.10 from δ. At 1849 Å it is 0.41 from γ and 0.41 from δ. Agreement of the ratios indicates the formation of vinyl radical in the primary process.

The precursors proposed by Potzinger *et al.*, leading to the three different primary processes, are of great interest. In this study, however, the quantum yields determined are relative and cannot support or deny their proposed mechanism. Our data can be compared with their data extrapolated to zero pressure in their mechanism.

The relative quantum yields obtained in this investigation are shown in Fig. 7 as a function of the excess energy together with the reported results[2,3,7,15,16]. The excess energy is defined by

$$E(\text{excess energy}) = E(h\nu)-\Delta H \qquad (18)$$

where $E(h\nu)$ is the photon energy of the excitation light, and ΔH is heat of reaction:

$$C_2H_4 = C_2H_2 + H_2 \quad \Delta H = 41.7\ \text{kcal/mol} = 1.8\ \text{eV} \qquad (19)$$

Figure 7 would permit the interpretation that the internal energy of an excited ethylene molecule increases as the irradiation photon energy increases, so that molecular mechanism of the primary process could take place less easily than atomic mechanism at shorter wavelengths.

It is concluded that ethylene shows a similar wavelength dependence of the primary processes to that of ethane, where the experimental data of some simple molecules, such as ethylene, ethane ammonia and water, have been qualitatively interpreted by a simple theoretical treatment of the RRKM theory.[17]

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[15] Y. Ogata, unpublished data.

[16] In an unpublished experiment at 1470 Å, we found the relative quantum yield of the primary process (3) to be 1~2%.

[17] K. Obi, Y. Ogata, and I. Tanaka, This Bulletin, **44**, 3190 (1971).