BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 711—712 (1975)

Photolysis of Ethylene at 1470 Å

Hiroshi HARA, Kenji KODAMA, and Ikuzo TANAKA

Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

(Received on July 1, 1974)

Synopsis. Relative quantum yields of the primary processes in the photolysis of ethylene at 1470 Å were determined. No energized vinyl radical was found. Photolysis in the presence of nitric oxide suggests that about 20% of 1-butene is produced through the direct addition reaction of excited ethylene to ground state ethylene, $C_2H_4^* + C_2H_4 \rightarrow 1\text{-}C_4H_8$.

The primary process of the photolysis of ethylene has been reported to be as follows.[1-4]

$$C_2H_4 + h\nu \longrightarrow C_2H_2 + H_2 \qquad \phi_1 \qquad (1)$$

$$\longrightarrow C_2H_2 + 2H \qquad \phi_2 \qquad (2)$$

$$\longrightarrow C_2H_3 + H \qquad \phi_3 \qquad (3)$$

The energized vinyl radical formation was found at 1634 Å.[5]

$$C_2H_4 + h\nu \longrightarrow H + C_2H_3^{**} \xrightarrow{k_d} C_2H_2 + H + H$$

$$\qquad\qquad\qquad\qquad\qquad\quad \searrow^{k_s[M]}$$

$$\longrightarrow H + C_2H_3^* \longrightarrow C_2H_3 + H$$

In this investigation, ethylene was photolyzed at 1470 Å in order to examine the existence of the energized vinyl radical and to determine the relative quantum yields of the primary processes.

Experimental

Experimental procedures were almost the same as described previously.[4] The light source of 1470 Å was an electrodeless discharge xenon lamp. The reaction cell was equipped with a LiF window.

Results and Discussion

The products of photolysis at 1470 Å were hydrogen, acetylene, ethane, *n*-butane, and 1-butene, and were the same as those at 1634 Å. No C_4 compounds other than *n*-butane and 1-butene were observed.

If the energized vinyl radical is formed at this wavelength, the ratio of 1-butene to *n*-butane should follow a straight line with a definite slope against ethylene pressure.[5] The ratios plotted as a function of ethylene pressure in Fig. 1 show no pressure dependence. Thus, existence of the energized vinyl radical in the photolysis at 1470 Å can be excluded. This is reasonable for the following reason. If the energized vinyl radical were formed at 1470 Å, the maximum available energy of the vinyl radical would be 89 kcal mol^{-1}, and that at 1634 Å 70 kcal mol^{-1}. At 1470 Å, therefore, the energized vinyl radical would decompose into acetylene and a hydrogen atom before being stabilized by collision.

Relative quantum yields of the primary processes were obtained assuming the same secondary processes as in the photolysis at 1634 Å[4]. The values are given in Table 1 together with other reported ones. Both values are seen to agree. The quantum yields at 1470 Å are shown in Table 2 together with those at 1634 and 1849 Å.[4] The relative quantum yields are wavelength dependent, *viz.*, ϕ_2 decreases and ϕ_3 increases with increasing wavelength, but not ϕ_1.

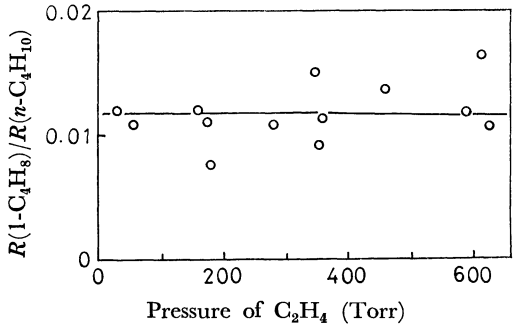

Fig. 1. $R(1\text{-}C_4H_8)/R(n\text{-}C_4H_{10})$ *vs.* pressure of ethylene (Torr).

Table 1. Relative quantum yields at 1470 Å

ϕ_1	ϕ_2	ϕ_3	Ref.
45%	54%	1%	This work
40	59	1	(3)
46	54	—	(6)

Table 2. Quantum yields at 1470, 1634, and 1849 Å

Wavelength	ϕ_1	ϕ_2	ϕ_3
1470 Å	45%	54%	1%
1634	47	48	5
1849	53	33	14

Relative yields of 1-butene and *n*-butane to acetylene were measured at various nitric oxide pressure with a fixed ethylene pressure (350 Torr) as shown in Table 2. On addition of nitric oxide, the yield of 1-butene decreased rapidly by about a factor of 5 and then became constant. On the other hand, the formation of *n*-butane was completely suppressed even at 0.46% nitric oxide. 1-Butene and *n*-butane removed by nitric oxide are formed through the recombination reactions of vinyl and ethyl radicals, and two ethyl radicals, respectively, since nitric oxide scavenges both ethyl[7] and vinyl radicals.[8] However, about 20% of 1-butene can be formed through a nonradical reaction, which is probably the direct addition of excited ethylene to a ground state one:

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

The relative quantum yield ϕ_4 of this process, can be roughly estimated as follows.

Table 3. Relative yields of 1-C_4H_8 and n-C_4H_{10} to C_2H_2 in the presence of NO (C_2H_2=350 Torr)

(NO/C_2H_4)%	0	0.46	1.1	1.3	2.7	5.0	9.3
1-C_4H_8	0.0061	0.0011	0.0013	0.0010	0.0016	0.0013	0.0014
n-C_4H_{10}	0.52	0	0	0	0	0	0

$$\phi_4 = \phi(1\text{-}C_4H_8)/5 = \frac{k_7}{k_5+k_6+k_7} \cdot \frac{\phi_3}{5} = 0.08\%$$

where the k's are the rate constants of the reactions.

$$C_2H_3 + C_2H_5 \longrightarrow 2C_2H_4 \quad (5)$$
$$\longrightarrow C_2H_2 + C_2H_6 \quad (6)$$
$$\longrightarrow 1\text{-}C_4H_8 \quad (7)$$

The quantum yield is very small compared with the others. At present, our results do not permit us to speculate on the nature of C_2H_4*.

References

1) Y. Inel, A. Siddiqi, and G. G. Meisels, *J. Phys. Chem.*, **75**, 1317 (1971).
2) P. Borrell, A. Cervenka, and J. W. Turner, *J. Chem. Soc. B*, **1971**, 2293.
3) P. Potzinger, L. C. Glasgow, and G. Von Bunau, *Z. Naturforsch.*, **27a**, 628 (1972).
4) H. Hara and I. Tanaka, This Bulletin, **46**, 3012 (1973).
5) H. Hara and I. Tanaka, *ibid.*, **47**, 1543 (1974).
6) M. C. Sauer, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).
7) H. Seng and F. W. Lampe, *J. Phys. Chem.*, **76**, 3303 (1972).
8) M. G. Bellas, J. K. S. Wan, W. F. Allen, O. P. Strausz, and H. E. Gunning, *ibid.*, **68**, 2170 (1964).