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Laser-induced Chemical Reactions. VI. On the Formation Processes of Acetylene

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The reactions of the carbon vapor produced by various methods[1-9] with hydrocarbons have been extensively studied. In previous papers,[10,11] the present authors have described the reactions of carbon vapor produced by the irradiation of a focused laser beam with hydrogen and low-molecular-weight hydrocarbons.

It has been assumed that, in the reaction of the carbon vapor produced by the laser irradiation with hydrocarbons, C_2 species play the main role in the product-forming step. Acetylene is the main product. The formation of acetylene has been considered to consist of hydrogen abstraction by C_2 species. However, there have been some doubts as to the product-forming processes, because acetylene may also be formed by the thermal decomposition of the reactant on the heated target surface or by the decomposition caused by the collision of the vaporized species with the reactant (collisional decomposition). The evidence for this is that when the laser beam was irradiated on a nickel metal target in ethane,[12,13] some decomposed fragmented hydrocarbons (mainly acetylene) were produced. In this case, the fraction of the thermal decomposition is considered to be small as compared with the collisional decomposition, because when the power density of the irradiated beam was lowered so as not to vaporize the target material, the acetylene yield decreased remarkably.

In this paper, by using a ^{14}C-enriched carbon target and a hydrocarbon reactant, or by using a graphite target and ^{14}C-labeled ethane as the reactant, the details of the formation processes of acetylene were investigated.

Experimental

Preparation of the ^{14}C-enriched Carbon Target. The ^{14}C-enriched carbon target was prepared by the thermal decomposition of ^{14}C-labeled acetylene at 1000°C in a quartz tube, as is shown in Fig. 1. The carbon film deposited on the quartz plate was used as the target. In a preliminary experiment, the target did not give gas chromatographically any other gaseous products except carbon monoxide[14] upon laser irradiation in a vacuum.

Preparation of the ^{14}C-labeled Ethane. The ^{14}C-labeled ethane was prepared by the reduction of ^{14}C-labeled acetylene by using PtO_2 and H_2 in a closed system, and it was purified gas chromatographically using a silica gel column.

Laser Irradiation. The laser-irradiation apparatus and experimental procedures were described previously.[10,11] The carbon target in a 7-ml cell filled with ethane or ethylene was irradiated by a focused laser beam. The output energy

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10) K. Taki, P. H. Kim, and S. Namba, This Bulletin, **42**, 823 (1969).
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12) K. Taki, P. H. Kim, and S. Namba, *ibid.*, **45**, 2052 (1972).
13) K. Taki, P. H. Kim, and S. Namba, to be published.

14) Carbon monoxide was produced by the heating of carbon in quartz tube at about 1000 °C.[15]

15) P. Gouverneur, M. A. Schreuders, and P. N. Degens, *Anal. Chim. Acta*, **5**, 293 (1951).

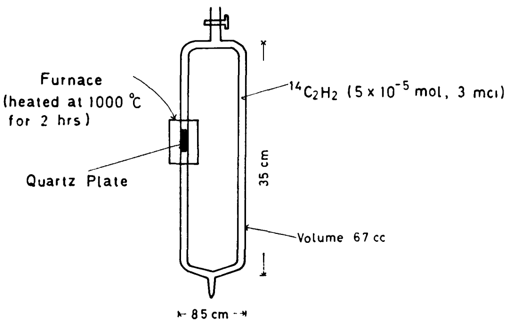

Fig. 1. Preparation of ^{14}C-enriched carbon target.

and pulse duration of the ruby laser were about 3 J and 0.5 ms respectively.

Analysis and Measurement of Radioactivity. The analysis of the products and the measurement of the radioactivity were performed on a radio-gaschromatograph. In the reaction of the ^{14}C-labeled ethane with carbon vapor from the graphite target, the specific activity was calculated from both the radioactivity and the product yield. In the reaction of ethane or ethylene with radioactive carbon vapor from the ^{14}C-enriched carbon target, the radioactivity was enough to be detected by one-pulse laser irradiation, but the product yield was too small to be determined[16] by radio-gaschromatography. In this case, the total activity was measured by adding a carrier.

Results and Discussion

When the laser beam was irradiated on nonradioactive graphite in ^{14}C-labeled ethane, the main product was acetylene, as has been described previously; the radioactivity was also found in acetylene, as is shown in Table 1. The radioactivity of acetylene indicates that the formation process of acetylene is due not only to the abstraction by C_2, but also to the decomposition of ethane.

On the other hand, when the laser beam was irradiated on the ^{14}C-enriched carbon film in ethane, radioactivity was found in the acetylene produced, but not in the ethylene produced. The above results indicate that ethylene is produced by the decomposition of ethane.

When the laser beam was irradiated on the ^{14}C-enriched carbon film in ethylene, the radioactivity of the acetylene produced was about twice that of the C_4-compounds produced, but the yield of acetylene was about six times that of the C_4-compounds, as is shown in Table 2. The data show that the formation of acetylene is due to the decomposition of ethylene, also.

When radioactive ethane is used as the reactant, by assuming the C_2 species to be the reaction species, the main formation processes of acetylene may be estimated as follows:

$$C_2H_6^* + C_2 \xrightarrow{K_1} C_2H_2 + \text{other hydrocarbons} \quad \text{abstraction.} \tag{1}$$

$$C_2H_6^* + C_2 \xrightarrow{K_2} C_2H_2^* + \text{other hydrocarbons} \quad \text{decomposition.} \tag{2}$$

$$C_2H_6 + C_2 \xrightarrow{K_3} C_2H_2 + \text{other hydrocarbons} \quad \text{abstraction.} \tag{3}$$

$$C_2H_6 + C_2 \xrightarrow{K_4} C_2H_2 + \text{other hydrocarbons} \quad \text{decomposition.} \tag{4}$$

$C_2H_6^*$ and $C_2H_2^*$ indicate radioactive ethane and acetylene. Reactions (2) and (4) show the collisional decomposition of ethane. The ratio of the amount of the active material to that of the nonactive one is derived from the specific activity, and the value of $C_2H_6^*/C_2H_6=\alpha$ and $C_2H_2^*/C_2H_2=\beta$ are extremely small. The ratio of the product yield can be derived as follows:

$$\frac{C_2H_2}{C_2H_2^*} = \frac{K_1[C_2][C_2H_6^*]+K_3[C_2][C_2H_6]+K_4[C_2][C_2H_6]}{K_2[C_2][C_2H_6^*]} = \frac{1}{\beta} \tag{5}$$

Since the two rates of abstraction reactions, (1) and (3), and also the two rates of decomposition reactions, (2), and (4), are equal,

$$K_1 = K_3 \text{ and } K_2 = K_4 \tag{6}$$

Then,

Table 1. Specific activity in the reaction of carbon vapor with ^{14}C-labeled ethane

Specific activity (μCi/mol)		Specific activity ratio of ethane to acetylene (α/β)	K_1/K_2 ($\alpha/\beta-1$)
Ethane (Substrate)	Acetylene (Product)		
1.95 0.94	0.92 0.60	1.6—2.1	0.6—1.1

Ethane pressure: 400—700 Torr.

Table 2. Activity in the reaction of ^{14}C-enriched carbon vapor with ethylene

Total activity of products (cps)			Activity ratio of C_4-compounds to acetylene (γ)	Yield ratio of acetylene to C_4-compounds (δ)	K_9/K_{10} ($1/(\gamma\delta-2)$)
C_4-compounds		Acetylene			
Diacetylene	Vinylacetylene				
4500 3130	680 420	8550 7730	0.46—0.61	—6	0.6—1.3

Ethylene pressure: 600—700 Torr.

16) The product yield was determined by the flame ionization detector.

$$\frac{K_1}{K_2}=\left(\frac{\alpha}{\beta}-1\right)\frac{1}{\alpha+1}$$
$$\approx\frac{\alpha}{\beta}-1 \qquad (7)$$

The ratio of the rate constant of the abstraction to that of the decomposition was calculated from the experimental data; the value thus obtained was from 0.6 to 1.1 under those experimental conditions.

Similar results are also obtained in the reaction of the carbon vapor from the ^{14}C-enriched carbon target with ethylene. In this case, the following schemes are assumed:

$$C_2H_4 + C_2^* \xrightarrow{K_8} C_4^*\text{-compounds} \qquad (8)$$

addition.[17]

$$C_2H_4 + C_2^* \xrightarrow{K_9} C_2H_2^* + C_2H_2 \qquad (9)$$

abstraction.

$$C_2H_4 + C_2^* \xrightarrow{K_{10}} C_2H_2 + \text{other hydrocarbons} \qquad (10)$$

decomposition.

17) If the nonradioactive C_4-compounds are produced partly by the thermal decomposition of two molecules of ethylene, the value K_9/K_{10} becomes smaller than $1/(\gamma\delta-2)$ by the similar calculation. The result may not be conflicted with the conclusion of this paper.

Reactions (8), (9), and (10) are also applicable to nonactive C_2 species. The ratio of the total activity of C_4-compounds to that of acetylene shows the ratio of the rate constant of K_8 to K_9 ($K_8/K_9=\gamma$). The ratio of the acetylene yield to the C_4-compound yield can be derived as follows:

$$\frac{\text{Acetylene}}{C_4\text{-compounds}}=\frac{2K_9+K_{10}}{K_8}=\delta \qquad (11)$$

Therefore,

$$\frac{K_9}{K_{10}}=\frac{1}{\gamma\delta-2} \qquad (12)$$

The ratio of the rate constant of the abstraction to that of the decomposition was calculated to be from 0.6 to 1.3 under those experimental conditions. This is in agreement with the result obtained in the reaction of carbon vapor with ^{14}C-labeled ethane.

From the above results, it may be concluded that the formation processes of acetylene are due to the collisional decomposition of the reactant with the vapor produced by the laser irradiation, as well as to the abstraction by C_2 species.

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