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Laser-induced Chemical Reactions. IV. Reactions of Carbon Vapor with Hydrogen at Various Pressures

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In previous papers,[1-3] the present authors have described the reaction of carbon vapor produced by the irradiation of a focused laser beam with hydrogen and low hydrocarbons. In this paper the effect of the hydrogen pressure in the reaction of the carbon vapor from graphite carbon is investigated; the reactions of hydrogen with the carbon vapor from silicon carbide and boron carbide are also investigated. The experimental procedures were almost the same as those described in the previous papers. The ruby laser used was a normal laser, the output energy and pulse duration of which were 3 J and 0.5 msec respectively. The laser beam was focused by a lens 35 mm in focal length upon the carbon target. The surface temperature[4] of the carbon target was estimated to be 3000—4000°K. After 2—5 pulse irradiations, the products were analysed by gas chromatography.

Results and Discussion

In the reaction of carbon vapor with hydrogen, the main products are acetylene and methane, as has previously been shown. In order to examine the reaction in detail, experiments were carried out at various hydrogen pressures; the representative product yields per pulse were 0.0063×10^{-7} mol for methane and 1.8×10^{-7} mol for acetylene at 20 Torr H_2, and 0.12×10^{-7} mol for methane and 4.7×10^{-7} mol for acetylene at 350 Torr H_2. The ratio of the acetylene to the methane varied with the

1) K. Taki, P. H. Kim and S. Namba, This Bulletin, **42**, 823 (1969).

2) K. Taki, P. H. Kim and S. Namba, *ibid.*, **42**, 2377 (1969).

3) K. Taki, P. H. Kim and S. Namba, *ibid.*, **43**, 1450 (1970).

4) S. Namba, P. H. Kim and A. Mitsuyama, *J. Appl. Phys.*, **37**, 3330 (1966).

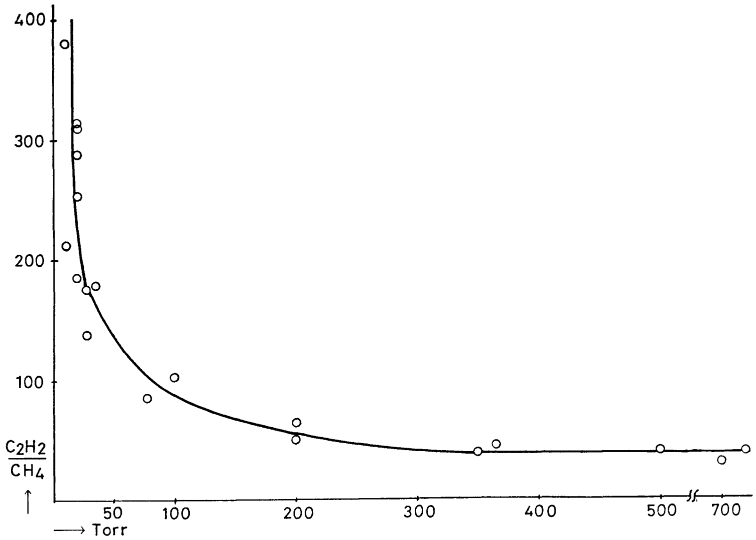

Fig. 1. Ratio of C_2H_2/CH_4 *vs*. hydrogen pressure.

hydrogen pressure, as is shown in Fig. 1. At a low hydrogen pressure, the methane yield is extremely small as compared with the acetylene yield, and the ratio of acetylene to methane increases. Such a variation was also observed in mixtures of helium or nitrogen: the C_2H_2/CH_4 ratio was about 150/1 at 30 Torr H_2 and 730 Torr He. From the above results, it may be considered that the ratio does not depend on the total pressure, but on the hydrogen concentration.

A pulse laser irradiated on a carbon target produces about a 10^{-6} mol carbon atom as a jet stream, which then reacts with the substrate*1 to form products. The volume of the carbon stream is estimated to be about 1 cm^3, as is shown in Fig. 2. A high hydrogen pressure (300—760 Torr)

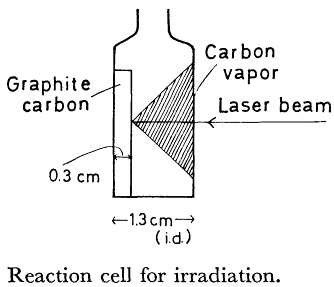

Fig. 2. Reaction cell for irradiation.

contains about 10^{-5} mol hydrogen molecules in each 1 cm^3 volume; therefore, the concentration of hydrogen in the reaction region is much higher than that of carbon vapor. On the other hand, at hydrogen pressures less than 100 Torr, the concentration of hydrogen is equivalent to or less than that of carbon vapor.

The reaction in a differently-designed cell*2 having a long passage (2.0 cm from the carbon target to the glass wall) gave a slightly smaller ratio of C_2H_2/CH_4 than in the former cell; the ratio of C_2H_2/CH_4 was about 200/1 at 20 Torr H_2. In this case, as the volume of carbon stream is larger than in the former cell, the concentration of carbon vapor is lower than in the former.

The above experimental facts indicate that acetylene and methane may not be produced from a common precursor. The acetylene and methane precursors may be C_2 and C_1 respectively, as has previously been shown.[1,2] Acetylene and methane are produced throughout several reaction steps. The details of the formation processes of acetylene and methane are not yet clear, and the rate constant of each step is also unknown, but the reaction may be as follows. In a low concentration of hydrogen, both the C_1 and C_2 species may react with hydrogen competitively. In this case, acetylene may be formed more easily than methane, because two hydrogen molecules are necessary for the formation of methane, while one molecule is enough for the formation of acetylene. It may also be considered that acetylene is formed by the reaction of the methane precursor with C_1, consequently increasing the C_2H_2/CH_4 ratio.

Similar experimental results were obtained in the C_3-compound formations. The ratio of C_4/C_3*3

*1 This reaction has been called an energetic carbon plasma-type reaction by Wiley and Veeravagu.[5]

5) R. H. Wiley and P. Veeravagu, *J. Phys. Chem.*, **72**, 2417 (1968).

*2 At pressures of less than 100 Torr of hydrogen, the reaction cell was contaminated by the deposited carbon vapor, but the long cell was less contaminated.

*3 The yields of C_3 and C_4 compounds were determined by the measurement of the yields of the propane and butane which are formed by the catalytic hydrogenation of products. The main C_4 compounds are diacetylene, and the main C_3 compounds are propylene and allene.

Table 1. Product yield of C_2, C_3 and C_4 compounds at various pressure of hydrogen in graphite carbon

Pressure of H_2 (Torr)	Number of irradiation	Product yield ($\times 10^{-7}$ mol)			Ratio	
		C_2-comp.	C_3-comp.	C_4-comp.	C_4/C_2	C_4/C_3
350	2	13	0.17	0.74	0.057	4.4
350	2	15	0.17	0.63	0.042	3.7
350	1	6.0	0.077	0.25	0.042	3.2
20	4	11	0.045	0.87	0.079	19
21	2	6.0	0.023	0.40	0.067	17

increases at a low hydrogen pressure, but the ratio of C_4/C_2 is almost constant, as is shown in Table 1. C_3 compounds need much more hydrogen than C_4 compounds need hydrogen.

Another experimental finding also supports the above discussion. When the power density of the irradiated beam was lowered by defocusing, the decrease in methane as compared with that in acetylene was not remarkable at hydrogen pressures of 20 Torr and 350 Torr, as is shown in Table 2. This result may be explained by the fact that the concentration of the carbon vapor produced by such weakened beam is lower than that of hydrogen.

Table 2. Product yield of methane and acetylene produced by the weakenned laser beam in graphite carbon

Power density	Pressure of H_2 (Torr)	Number of irradiation	Product yield ($\times 10^{-7}$ mol)		Ratio C_2H_2/CH_4
			CH_4	C_2H_2	
1/4 of the focused beam	350	2	0.078	3.0	38.0
	20	5	0.019	2.6	137
1/10 of the focused beam	350	4	0.16	6.5	40.6
	20	10	0.063	3.8	60.3

Moreover, from the fact that the product yields[2)] were not affected by such radical scavengers as NO and O_2, it may be considered that the reaction is brought about in a jet stream of carbon vapor, and that, because of the high concentration of carbon vapor, all the scavengers react mainly with carbon vapor and do not react with the acetylene and methane precursors.

The carbon vapor from silicon carbide and boron carbide*4 also gave acetylene and methane in the reaction with hydrogen. However, the product yields were about one-tenth as much as in the reaction of carbon vapor from graphite carbon. This may be explained by the fact that the concentration of the carbon vapor produced from silicon carbide and boron carbide is less than that from graphite carbon. The data are listed in Table 3. Spectroscopically, the Swan bands were also observed in the carbon vapor from silicon carbide, as had been observed in that from graphite carbon. In the reaction of the carbon vapor from silicon and boron carbide with hydrogen, no pressure dependence such as that described above was observed. These experimental results also support the explanation of the pressure dependence in acetylene and methane formation. The reaction occurs in a jet carbon stream.

Table 3. Product yield of methane and acetylene in silicon carbide(SiC) and boron carbide ($B_{12}C_3$)

Target	Pressure of H_2 (Torr)	Number of irradiation	Product yield ($\times 10^{-7}$ mol)		Ratio C_2H_2/CH_4
			CH_4	C_2H_2	
SiC	700	3	0.078	5.1	65.4
	350	3	0.044	4.6	105
	100	5	0.016	1.8	113
	20	10	0.013	trace	
$B_{12}C_3$	760	6	0.047	0.53	11.3
	20	6	0.028	0.26	9.3
	20	6	0.026	0.35	13.5

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*4 The silicon carbide (SiC) was purchased from the Siliconit Konetsu Kogyo Co., while the boron carbide ($B_{12}C_3$) was kindly provided by Dr. Atoda of this Institute.