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The Reaction of Water Vapor and Carbon Vapor Produced by Laser Irradiation

Pil Hyon KIM, Ko TAKI,* and Susumu NAMBA

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351

**Faculty of Industrial Hygiene, Kitasato University, Sagamihara-shi, Kanagawa 228*

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Synopsis. The carbon vapor produced by laser irradiation was found to react with the water vapor. The main products were carbon monoxide, hydrogen, and acetylene, the last of which is not found in the water-gas. Acetylene is considered to be formed by the reaction of the C_2 species of the carbon vapor.

The present authors have previously studied the reactions of gaseous substances with the vapor of the solid target produced by laser heating.[1,2] In these cases, only a small region of the target is heated rapidly by the irradiation of the pulsed laser beam, and the gaseous substances can react with the vaporized species produced at high temperatures. Moreover, because of the localized heating and the short-pulse heating, the gaseous products are prevented from thermal decomposition.

In the reaction of hydrogen or hydrocarbons with the carbon species vaporized from the graphite carbon target,[1] acetylene was obtained as the main product; it had been assumed that the C_2 species played the main role in the product-forming step. From the above results, the carbon vapor produced by laser heating can be expected to react with the water vapor, which is most simple and easily obtainable hydrogen compound, to produce hydrocarbons as gaseous fuel.

It is well known in the fuel and coal-product industries that the reaction of heated carbon and water vapor gives a water-gas[3] which contains hydrogen and carbon monoxide as the main components, plus a small quantity of methane and carbon dioxide, but no acetylene. However, the reaction of the water vapor with the carbon vapor produced by the laser heating has never been reported.

This paper will describe the reaction of the water vapor with the carbon vapor produced from the graphite carbon target by the irradiation of the pulsed laser beam.

Experimental

The graphite carbon target and a small amount of water ($\sim 10^{-2}$ g) were placed in a 7-cm^3 Pyrex cell, as is shown in Fig. 1. The cell had been preheated to increase the vapor pressure of water ($\sim$100 Torr). Then, the target was irradiated by means of a ruby laser beam focused by a lens 35 mm in focal length. The ruby laser used was a normal laser, the output energy and pulse duration of which were about 3 J and 1 ms respectively. The temperature of the irradiated region ($\sim 10^{-3}$ cm^2) is estimated to be above 3000 K, and the carbon vapor produced is considered to be the C_1, C_2, C_3 . . . species.[4] After 5—7 pulse irradiations, the reaction products were analysed by gas chromatography using silica gel and squalane columns and by mass spectroscopy.

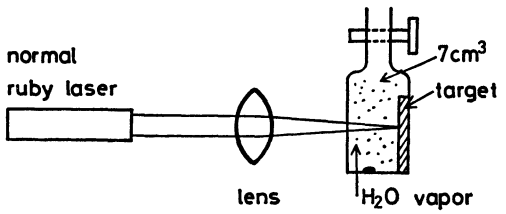

Fig. 1. Experimental block diagram.

Results and Discussion

The product yields in the reaction of water vapor with the carbon vapor produced by six pulse-laser irradiations are shown in Table 1. The yields are proportional to the number of laser irradiations. For a comparison of the product yields, the product ratios of the water-gas[3] produced by conventional heating are also shown in Table 1. In laser irradiation, the main products are carbon monoxide, hydrogen, and acetylene, the last of which is not contained in the water-gas.

TABLE 1. PRODUCT YIELD IN THE REACTION OF WATER VAPOR WITH CARBON VAPOR AFTER 6 PULSE LASER IRRADIATIONS AND RELATIVE YIELD IN WATER-GAS

Product	Yield (10^{-6} mol) in laser irrad.	Relative yield (%) in water-gas
CO	6	30—42
H_2	5	44—52
C_2H_2	2	
CO_2	$\sim 10^{-2}$	2— 8
CH_4	$\sim 10^{-2}$	0.5—1.0
C_2H_4	$\sim 10^{-2}$	
N_2		2— 6

In the case of water-gas, it has been considered that monatomic carbon reacts with water vapor to give carbon monoxide and hydrogen as the main products. In laser irradiation of the carbon target, the reaction of the C_1 species of the carbon vapor with water vapor may also give carbon monoxide and hydrogen. As has been described in a previous paper,[1] acetylene may be formed by the reaction of the C_2 species of the carbon vapor in this system. Therefore, as in the reaction of C_2 species with hydrogen or hydrocarbons, the elementary formation processes of acetylene may be considered to be as follows:

1) $C_2 + H_2O \longrightarrow \cdot C_2H + \cdot OH$

2) $\cdot C_2H + H_2O \longrightarrow C_2H_2 + \cdot OH$

By the addition of about 100 Torr NO to the reaction system, the yield of acetylene was decreased to about one-tenth, but that of carbon monoxide increased about 1.5 times. In this case, NO may scavenge the acetylene precursor, C_2, to give carbon monoxide, because it has also been reported that the C_2H radical is not affected by this scavenger.[5] Moreover, by the addition of about 100 Torr oxygen, the yield of acetylene decreased to a trace.

The reaction of the C_2 species with the hydrogen produced may also give acetylene. However, the contribution to the yield is considered to be smaller than that of the reaction with water vapor, because the partial pressure of the hydrogen produced is several Torr for about a hundred Torr of water vapor.

The two reasons for the formation of acetylene in the laser irradiation are considered to be as follows: one is that the carbon vapor produced by laser irradiation contains a considerable amount of the C_2 species, and the other is that the acetylene produced is prevented from thermal decomposition because the laser heating features rapid heating and rapid quenching.

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