BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 823—825 (1969)

Laser-induced Chemical Reaction. I. Reaction of Carbon Vapor Produced by a Pulse Ruby Laser

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(Received July 2, 1968)

An intense laser beam is known to produce a high-temperature region when it hits the surface of a suitable target, resulting in the evaporation of the target material. This note will describe an investigation of the reaction of such a vapor with hydrocarbon.

The target material employed in this work was Shimadzu spectroscopic electrode graphite preheated under a vacuum. The laser used was a pulse ruby laser, the output energy and pulse duration of which were about 3 joules and 0.5 msec respectively.

The laser beam was focused by a lens of 30 mm focal length upon the graphite carbon in a 7-cc Pyrex cell filled with ethylene vapor. After a 10—20 pulse irradiation, the analysis was performed by gas chromatography; the principal products were acetylene, diacetylene, and vinylacetylene. The ratio of C_3 to C_4 products*1 was about 0.03—0.05. The data are listed in Table 1.

TABLE 1. YIELD OF PRODUCTS FROM THE REACTION OF ETHYLENE WITH CARBON VAPOR PRODUCED BY THE LASER BEAM

Product	Yield ($\times 10^{-6}$ mol)
Methane	0.15—0.22
Ethane	0.06—0.08
Ethylene	—
Acetylene	24.0—26.0
Vinylacetylene	0.5
Diacetylene	3.5—4.0
C_3 compounds	0.12—0.15
C_4 compounds	4.0—4.5
C_3/C_4	0.03—0.05

Ethylene: 700 Torr
Carbon consumed: $3.0—4.0 \times 10^{-5}$ mol
Laser: 10 pulses

*1 All the reaction products were catalytically reduced by PtO_2 and hydrogen, and the propane and butane produced from C_3 and C_4 products were analysed by gas chromatography using a silica gel column; the area ratio was calibrated to the molar ratio.

There have been intensive investigations of the reaction of free carbon atoms produced by nuclear recoil reaction[1,2] and by the photolysis of carbon suboxide[3] and a carbon arc.[4] However, the reaction products and their distributions differ greatly from case to case. In the recoil reaction, it has been shown that the most common primary processes are the additions of the C atom (monoatomic carbon) to C–H and C=C bonds; the resulting adducts then undergo secondary processes. On the other hand, the carbon vapor produced in the carbon arc reacts with butenes to give spiropentane derivatives and bisethanoallene derivatives, which have been suggested to be produced from the reactions of monoatomic carbon (C_1) and triatomic carbon (C_3)[5] respectively, but no formation of acetylene has yet been found. This difference has been considered[6] to be due to the facts that the reaction conditions are not the same, and that, in a recoil reaction, free carbon atoms are apparently reaction species, while in the case of carbon vapor produced in the carbon arc the carbon atoms are complexed on the surface material.

From the fact that the products consist of C_2 and C_4 compounds in the laser-induced reaction, it seems likely that the reaction may involve the interaction of a diatomic carbon intermediate (C_2) with ethylene. There have been a few reports on the reaction of C_2, in which the diatomic carbon intermediate is the precursor of the production of acetylene[7] and other products.[8] It was considered to be highly desirable to confirm the presence of C_2 and, if possible, to observe its chemical properties. Spectroscopically, the presence of C_2 in the carbon vapor produced by laser irradiation was confirmed by the observation of the C_2 Swan bands in the vacuum system, in a hydrogen atmosphere, and in ethylene vapor. The C_2 Swan bands were also observed by Howe[9] and by Mentall and Nicholls[10] in air.

Laser-induced reactions in hydrogen, lower alkanes, butadiene, and butene-1 were also investigated.

In the reaction with hydrogen, the principal product was acetylene (about 80%, based on the carbon consumed), while no ethylene was detected, as is shown in Table 2. On the other hand, a carbon atom was produced by a recoil reaction with hydrogen[11] to produce CH, CH_2, and CH_3 radicals, these radicals undergo further reaction to produce acetylene, ethylene, and other products.

Table 2. Yield of products from the reaction of hydrogen with carbon vapor produced by the laser beam

Product	Yield ($\times 10^{-6}$ mol)
Methane	0.3—0.4
Acetylene	15.0—20.0
Ethylene	0
C_3 compounds	0.1
C_4 compounds	1.0
C_3/C_4	0.1

Hydrogen: 700 Torr
Carbon consumed: $3.0—4.0 \times 10^{-5}$ mol
Laser: 10 pulses

In the reaction with a hydrogen and ethylene mixture (8 : 1), no pentene-1 was detected. As has been suggested by Wolfgang and his coworkers,[12] the addition of methyne (CH) to an ethylene molecule gives pentene-1. Therefore, the possibility that methyne was a precursor of acetylene may be excluded.

In the reaction with methane, ethane, and cyclopropane, the principal product was acetylene, and only a trace amount of ethylene was formed, as shown in Table 3. A carbon atom has been known to react with methane to produce ethylene and acetylene in an almost equivalent yield by insertion:[13,14]

$$C + CH_4 \rightarrow (CH_3\text{-}\dot{C}\text{-}H) \rightarrow C_2H_4 \text{ and } C_2H_2$$

The reaction of a carbon atom with cyclopropane should give an equivalent amount of acetylene and ethylene[13,15] *via* the carbene formed by the insertion reaction:

In the reaction with 1,3-butadiene and butene-1, neither spiropentane nor bisethanoallene derivatives are detected gas chromatographycally. Thus, monoatomic carbon is not considered to be an

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TABLE 3. YIELD OF PRODUCTS FROM THE REACTION OF METHANE, ETHANE, AND CYCLOPROPANE WITH CARBON VAPOR PRODUCED BY THE LASER BEAM

Substrate	Methane	Ethane	C-Propane
Pressure (Torr)	700	670	680
Product ($\times 10^{-6}$ mol)			
Methane	—	2.9—4.2	2.6—2.8
Ethane	1.1	—	0.1
Ethylene	0	4.2—6.6	2.0—2.3
Acetylene	12.7—17.1	16.1—23.5	22.6—23.2
Propane	—	1.4	—
Propylene	0.31—0.41	—	14.5—16.6
C_3 products	0.5—0.7	1.4—2.7	—
C_4 products	1.8—3.9	3.6—4.0	8.8—10.0
C_3/C_4	0.1—0.4	0.4—0.7	—

Carbon consumed: $3.0—4.0\times10^{-5}$ mol
Laser: 10 pulses

important reactive intermediate in this reaction, since the product patterns are quite different from those in the reaction of the carbon atom.

The yield of C_3 compounds is higher in the reaction with ethane than with ethylene, and the C_3/C_4 ratios in the reaction with ethane and ethylene are 0.7 and 0.04 respectively. If the C_1 atom is the reaction species, C_3 compounds would be formed more easily in ethylene than in ethane.[1,13] In the recoil reaction, the ratio of C_3 compounds to C_4 compounds in ethylene vapor is 2.6.[1,2] These observations suggest that C_2 reacts with ethylene and ethane as follows:

$$C_2H_4 + C_2 \rightarrow (C_2H_4C_2)^* \begin{cases} \nearrow C_3 \text{ compounds} \\ \searrow C_4 \text{ compounds} \end{cases}$$

$$C_2H_6 + C_2 \rightarrow (C_2H_6C_2)^* \begin{cases} \nearrow C_3 \text{ compounds} \\ \searrow C_4 \text{ compounds} \end{cases}$$

In the laser-induced reaction with the mixture of H_2 and D_2 (the D_2/H_2 ratio is 1.1), the isotopic composition*2 of acetylene (C_2H_2 : C_2HD : C_2D_2) was detected to be 1 : 2.1 : 1.3 by mass spectrometrical analysis. From the highest yield of C_2HD, the mechanism of the molecular process, $C_2+H_2\rightarrow C_2H_2$ may be excluded; acetylene may be formed mainly as follows:

$$C_2 + H_2 \rightarrow C_2H + H \qquad \Delta H = -29 \text{ kcal}^{*3}$$

$$C_2H + H_2 \rightarrow C_2H_2 + H \qquad \Delta H = -10 \text{ kcal}$$

Since, in this experiment, the temperature at the surface of graphite carbon irradiated by ruby laser is estimated at 3000—4000°K[18] and since a high concentration of carbon vapor containing C_1, C_2, C_3, *etc.*[10] is produced, reaction product from C_1, C_2, and C_3 should be detected in the reaction. The methane (a small yield) actually formed in the hydrogen atmosphere might be the reaction product of C_1.

In conclusion, diatomic carbon (C_2) is considered to play the dominant role in the laser-induced reaction with olefin (ethylene) and hydrogen to produce acetylene and diacetylene.

The authors wish to acknowledge the valuable assistance of Miss K. Motegi in carrying out this work as well as to express their appreciation to Mr. S. Satooka for his mass spectrometric analysis.

*2 The isotopic composition was determined mass spectrometrically, using the published cracking pattern of C_2HD, C_2D_2, and C_2H_2.[16] The latter two of these compared well with our measured patterns of pure C_2H_2 and C_2D_2.

*3 The C_2H bond energy is from Ref. 17.

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