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Laser-induced Chemical Reaction. II. Reaction Induced by a Giant Pulse Laser

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In a previous paper,[1] the reaction of hydrocarbons with carbon vapor produced by the irradiation of a normal laser on graphite carbon has been reported. From the distribution of the reaction products and from the results of a spectroscopic analysis, it was assumed that diatomic carbon (C_2) plays a dominant role. In this paper, the investigation of the reaction induced by a giant pulse ruby laser is described.

Experimental

The output power and the pulse width of the giant pulse laser used were 30 MW and 20 nsec respectively. The total output energy was 0.6 J, one-fifth of that of the normal laser in the previous report. The laser beam was focused by a lens 30 mm in focal length upon a carbon target placed in a 7 cc Pyrex cell filled with the vapor of hydrocarbons. After a 10—20 pulse irradiation, an analysis was peformed by gas chromatography using a silica gel and a squalane column. A quantitative analysis was also performed by mixing standards in the sample.

Results and Discussion

The reaction products in hydrogen are listed in Table 1, while the reaction products in ethylene and methane vapor at 10 Torr pressure are shown in Table 2. The gas pressure of 10 Torr was chosen so as to avoid any breakdown caused by the focused giant pulse laser. At a pressure higher than 100 Torr a breakdown was observed, as will be described later. Although the main products were C_2 compounds, as in the case of a normal laser reaction, the ratios of methane and ethane to acetylene were higher than those in normal laser reactions. This fact suggests that the distribution of carbon oligomers produced by the giant pulse laser is different from that produced by the normal laser; that is, the fraction of the monoatomic carbon (C_1) is larger in the former than in the latter. This may be due to the difference in the surface temperature of the carbon target. The estimated temperature[2,3] in the giant pulse laser is higher than in the normal laser.

TABLE 1. REACTION PRODUCTS IN HYDROGEN

Product	Yield ($\times 10^{-6}$ mol)	
	Normal laser (10 pulse irradiation in 700 Torr H_2)	Giant pulse laser (20 pulse irradiation in 720 Torr H_2)
Methane	0.3—0.4	0.1
Ethane	0	0.01
Ethylene	0	0
Acetylene	15.0—20.0	0.4

The breakdown[4,5] of the gas is known to be caused by the focused giant pulse laser. When the laser beam was focused on a carbon target, a breakdown of gases was observed in the focused-on region. In this case, the product ratios were a little different from those in the breakdown without a target. This may be due to the fact that most of the energy of the laser beam is spent producing the breakdown. The yields of products in the breakdown of various substrates are shown in Table 3.*[1] Spectroscopically, C_2 Swan bands were observed in the breakdown of these gases, as had previously been observed by Adelman.[6] These facts suggest that the products are mainly formed by the reaction of the substrate with the C_2 produced in the breakdown.

It is hard to produce the breakdown in gas at a low pressure.[5] No breakdown was, for instance, observed at 10 Torr ethylene or methane. However, in a mixture of 10 Torr ethylene and 750 Torr argon (ethylene mol fraction is 0.013), a breakdown was observed and argon lines were detected spectroscopically.

The product ratios, CH_4/C_2H_2 and C_2H_6/C_2H_2, and that of C_3 products to C_4 products are plotted as a function of the partial pressure of ethylene in the mixture with argon in Fig. 1. The figure shows

*1 The breakdown was not observed in the case of a normal laser.

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Table 2. Reaction products in ethylene and methane vapor at 10 Torr pressure

Substrate	Product	Yield ($\times 10^{-6}$ mol) Normal laser (10 pulse irradiation)	Giant pulse laser (12 pulse irradiation)
Ethylene	Methane	0.007	0.014
	Ethane	trace	0.009
	Acetylene	1.6	0.47
	C_3-Compounds	trace	0.018
	C_4-Compounds	0.48	0.19
Methane	Ethane	0.022	0.084
	Acetylene	1.52	0.32
	C_3-Compounds	0.02	0.024
	C_4-Compounds	0.5	0.19

Table 3. Products yields in the breakdown of various substrates

Product	Yield ($\times 10^{-6}$ mol) in 10 pulse irradiation, Substrate: Methane	Ethane	Ethylene	Cyclopropane
Methane		0.5—0.7	0.05—0.08	0.4—0.5
Ethane	0.1—0.2		0.2—0.3	0.02
Ethylene	0	0.3—0.5		0
Acetylene	0.5—0.7	1.1—1.4	1.7—2.7	0.8—1.2
C_3-Products	0.1	0.3	0.03	
C_4-Products	0.1	0.2	0.4—0.5	0
Propane				0.1
Propylene				1.5—2.0

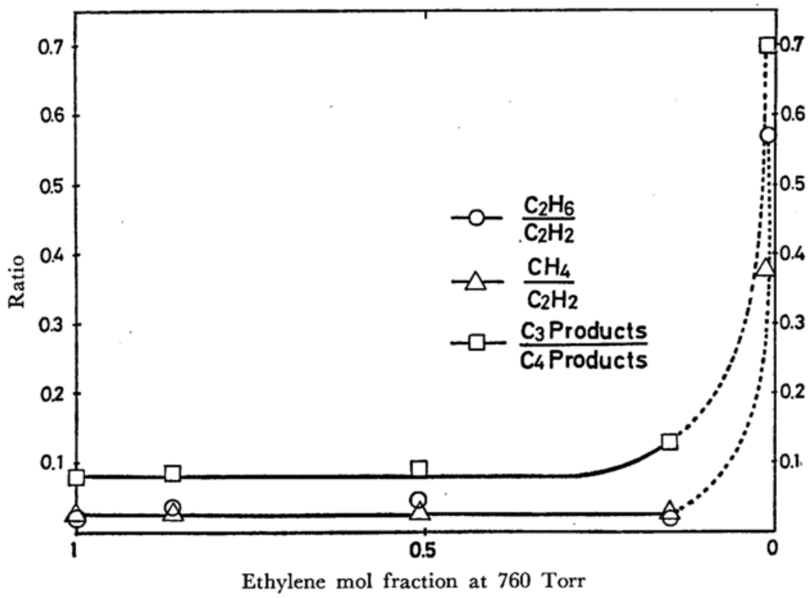

Fig. 1. Relation between product ratios and gas pressure in the mixture of ethylene and argon.

TABLE 4. RELATIVE YIELD IN THE γ-RADIOLYSIS AND IN THE LASER IRRADIATION IN THE MIXTURE OF ETHYLENE AND ARGON

Product	Relative *G* value in γ-radiolysis			Relative yield in laser irradiation
	Ethylene mol fraction in Ar			
	1.0*	0.7*	0.013	0.013
Methane			0.13	0.38
Ethane	0.26	0.18	0.16	0.57
Acetylene	1.00	1.00	1.00	1.00
n-Butane	0.33	0.26	0.18	0.35
C_3-Products			0.17	0.27

* From Ref. 7.

that the product ratios remain constant in the region of higher mol fractions (0.15) of ethylene, but at lower concentrations (0.013) these ratios rise sharply. At a higher partial pressure of ethylene, a breakdown reaction may occur on the ethylene molecule because its ionization potential (10.5 eV) is lower than that of argon (15.7 eV). On the other hand, at a lower concentration, breakdown may occur mainly on the argon rather than on the ethylene molecule, and the reaction products may be almost entirely formed by the decomposition of the excited ethylene produced by energy transfer to ethylene from the excited argon formed by the breakdown. The radiolysis of an inert gas and hydrocarbon mixture has been known to involve energy transfer reaction. However, the product ratios in the radiolysis of a 10-Torr-ethylene and 750-Torr-argon mixture are different from those in laser irradiation, as Table 4 shows. Radiolysis was performed at room temperature, and the total dose was about 10^{19} eV. This difference might be due to the difference between the reactions in the excited states of ethylene.

The methane and argon system showed almost identical results; ethane was the only condensable product at the pressure of 10 Torr methane and 750 Torr argon. In the presence of nitric oxide (4 Torr), the breakdown of the mixture of methane (12 Torr) and argon (744 Torr) did not give ethane. This suggests that the reaction involves free radical processes, as in the case of radiolysis. The radiolysis of methane[8-10] and a methane-argon mixture[11] has been known to involve free radical processes and to produce hydrogen and ethane, but not acetylene.

In the giant pulse laser-induced reaction, diatomic carbon (C_2) is considered to play a dominant role, but at a low concentration of the substrate in the argon mixture the reaction process may be due to the energy transfer from argon.

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