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The Decomposition of Organic Substances by Laser Heating

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Synopsis. Gaseous organic substances were decomposed by the laser heating of various solid targets (boiling points are different) which were placed in them. This method gives the products which have never been obtained by means of the conventional heat decomposition.

The laser irradiation of a solid target causes the vaporization of the target material. Laser irradiations of graphite carbon and copper cyanide have been reported previously by the present authors.[1-3] In these cases, the vaporized or fragmented species produced by the laser irradiation (carbon atoms or CN radicals) have reacted with gaseous substances to give various products containing the target material.

In the reaction of carbon vapor with hydrocarbons, an isotopic experiment[4] using carbon-14 labeled ethane as the substrate or carbon-14 enriched graphite as the target showed that the carbon vapor not only reacts with the substrate, but also decomposes the substrate by means of the collision. This decomposition may be considered to be heat decomposition.

The pulse-laser irradiation of the target produces a vapor of the target material, the temperature of which is about the boiling point of the target. It is expected that the collision of this vapor with a gaseous substance or the heated target surface induces the heat decomposition of the substance. In this case, it is considered that the decomposition temperatures of the substances have distributed from the boiling point of the target material to the lower temperature.

In pulse-laser irradiation, the vapor is produced so quickly (less than 10^{-3} s), and the temperature of vapor or the heated target surface decreases so rapidly, that decomposition at the boiling point of the target is possible. In the conventional heating method, however, the heating rate is not so fast as the pulse-laser heating, so the heat decomposition at a temperature above the decomposition temperature of the organic compound is not exactly possible because the organic compound is decomposed during the heating process before reaching the desired temperature.

In laser heating, as, in view of the above considerations, the decomposition temperature of the substance may be decided by the boiling point of the target material, the gaseous substances can be decomposed at various temperatures by using various targets. For instance, in case of the nickel target the maximum decomposition temperature is about 2850 °C (the boiling point of nickel).

In this investigation, the decomposition of gaseous organic substances has been studied by means of the pulse-laser irradiation of various targets of nickel, zinc and red phosphorus.

Table 1. Relative product yield in the decomposition of methane, ethane, toluene and ethanol for 7 pulse laser irradiations on nickel, zinc or phosphorus target

Substance	Product	Relative yield		
		Ni target	Zn target	P target
Methane	C_2H_6	0.26	1.3	($\sim 10^{-7}$ mol)
	C_2H_4	0.03	0.12	
	C_2H_2	1.00 ($\sim 10^{-6}$ mol)	1.00 ($\sim 10^{-7}$ mol)	(0)
Ethane	CH_4	0.86	0.57	2.2
	C_2H_4	2.08	2.4	42.4
	C_2H_2	1.00	1.00	1.00
	C_4H_{10}	0.23	0.58	10.4
Toluene	CH_4	0.40	0.12	
	C_2H_6	0.13	0.16	
	C_2H_4	0.04	0.07	
	C_2H_2	1.00	1.00	
Ethanol	CH_4	4.13		
	C_2H_6	0.23		
	C_2H_4	4.7		
	C_2H_2	1.00		

Experimental

The decomposition techniques were almost the same as those reported previously.[1-4] Nickel (bp 2850 °C) and zinc (bp 908 °C) plates, and a red phosphorus (bp 280 °C) tablet were used as the targets. Each target, placed in a 7-cm^3 cell filled with the substance gas, was irradiated by means of a focused laser beam. The laser used was a normal ruby laser, the output energy and pulse duration of which were 3J and 0.5 ms respectively. The gas pressure of the gaseous substance was 600—700 Torr, while that of the liquid substance was the saturated vapor pressure at 60—70 °C.

The volatile products were collected and analyzed by gas chromatography using silica gel and squalane columns. The most reliable value of the detection was about 10^{-8} mol.

Results and Discussion

The relative product yields in the decomposition of methane, ethane, toluene, and ethanol are shown in Table 1.

In methane decomposition, the acetylene yield goes down with the decrease in the boiling point of the target material; finally, at the decomposition temperature under the phosphorus boiling point no acetylene is obtained at all but the ethane yield increases. It is roughly estimated that the high-temperature decomposition gives C, CH, and CH_2, mainly resulting in acetylene, while low-temperature decomposition gives

CH_3 mainly resulting in ethane. The main processes of the decomposition may be estimated to be as follows:

$$(1)\quad CH_4 \xrightarrow{\text{Ni target}} \text{fragmented C, CH and } CH_2 \longrightarrow C_2H_2$$

$$(2)\quad CH_4 \xrightarrow{\text{Zn target}} \text{fragmented C, CH, } CH_2 \text{ and } CH_3 \longrightarrow C_2H_2 \text{ and } C_2H_6$$

$$(3)\quad CH_4 \xrightarrow{\text{P target}} \text{fragmented } CH_3 \longrightarrow C_2H_6$$

The fact that the acetylene yield is decreased by lowering the decomposition temperature was also observed by the following experiment. When the power density of the irradiated laser beam was decreased to about 1/10 by the use of a filter, no vapor was produced from the nickel target and the substance was decomposed at the heated target surface whose temperature was below the boiling point of nickel. In this case, the acetylene yield decreased to 1/40, but the ethylene yield was not so affected.

The conventional heat decomposition[5] of methane at 800—1120 °C gives two elements (C and H). The main reaction process is the elimination of hydrogen from methane. On the other hand, the arc discharge gives traces of acetylene and ethane. The products are the same as those in the case of laser heating.

In ethane decomposition, acetylene was produced mainly at high temperatures and butane was produced mainly at low temperatures, as is shown in Table 1. The shock-wave heating of ethane[6] at 1250—1660 K gives methane, ethylene, and acetylene as in laser heating. The acetylene yield increases with the temperature, as in laser heating. However, no butane is detected. This is probably because the butane produced is broken down rapidly by staying at the high temperature. The proposed mechanism may be similar to that in laser heating, but the butane produced in laser heating may be not broken down by the rapid quenching.

In toluene decomposition, the gaseous hydrocarbons were obtained as is shown in Table 1; traces of bibenzyl and biphenyl were also detected. In this case, the substituted methyl group may be cleaved easily, and these fragments undergo further product formation. However, the decomposition at the phosphorus boiling point did not give acetylene or other gaseous hydrocarbons.

The decomposition of methanol gave hydrogen, carbon monoxide, and a small amount of hydrocarbon, but no acetylene was obtained at various temperatures. Methyl iodide and dimethylamine gave acetylene, but methylamine did not give acetylene. In the conventional decomposition of methanol[5] above 500 °C, the processes are considered to be the elimination of hydrogen, giving formaldehyde, and the subsequent decomposition to carbon monoxide and hydrogen. In methanol and methylamine, it may be difficult to form the carbon species which are the precursors of acetylene because carbon monoxide and the CN radical are easily produced; consequently, acetylene is not obtained.

In the decomposition of ethanol, methane, acetylene, and, ethylene were obtained as is shown in Table 1. In the conventional heating,[5] the main products are ethylene and methane, but acetylene is not obtained. In arc discharge,[5] however, the acetylene yield is comparable with that of ethylene.

It may be noted that the laser heating induces the decomposition of organic substances at high temperatures and gives products which are not obtained in the conventional heating, such as acetylene in methane decomposition and butane in ethane decomposition. These results may be caused by the rapid heating and rapid quenching which are the characteristics of the pulse-laser heating.

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