

## Decomposition of Saturated Gaseous Hydrocarbons in Induction-Coupled Argon Plasma Jet

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The decomposition of methane, ethane, and isobutane has been studied in an induction-coupled argon plasma jet at atmospheric pressure. Methane was decomposed to give mainly acetylene, soot, and hydrogen, and to give the traces of ethylene and ethane. From the dependence of both the conversion of methane and the product distribution on methane feed rate, the input and argon flow rate, it was concluded that methane was not completely mixed with the plasma jet but the decomposition of methane took place mainly in the outer flame of the plasma jet and its surroundings. In the decomposition of ethane, ethylene, and methane were formed in 20—27% and 3—5% selectivity based on carbon, respectively, in addition to acetylene, soot, and hydrogen. In the decomposition of isobutane, propylene was produced in 10—14% selectivity based on carbon, besides the above mentioned products. From these results together with those on propane and *n*-butane, it was suggested that radicals formed by a fission of C-H or C-C bond played the main role in the decomposition of saturated gaseous hydrocarbons in the induction-coupled argon plasma jet.

The thermodynamic calculation of the carbon-hydrogen system at pressures ranging from 0.1 to 10.0 atm suggests that among the products at equilibrium above 2500°K acetylene is the only gaseous hydrocarbon that is stable at room temperature.<sup>1,2)</sup> It is also reported that in the reaction of graphite with hydrogen, the formation of acetylene is favored over that of methane and ethylene above 2500°K.<sup>3)</sup> On the other hand, in the decomposition of propane<sup>4)</sup> and *n*-butane<sup>5)</sup> which are charged into the plasmas jet countercurrently, methane and ethylene have been obtained in 5—8% and 16—20% selectivity based on carbon, respectively. Furthermore, we assumed in the previous paper<sup>5)</sup> that the decomposition of *n*-butane occurred mainly in the outer flame of the plasma jet and its surroundings, and methane and ethylene were formed in the comparatively lower temperature region.

The present paper describes the decomposition of methane, ethane and isobutane, and discusses the region in which the decomposition of hydrocarbons occurs and the decomposition process of saturated gaseous hydrocarbons in the induction-coupled argon plasma jet.

### Experimental

**Material.** Argon was supplied from Osaka Sanso Co. Methane, ethane, and isobutane were obtained from Seitetsu Kagaku Co. (above 99.0% purity) and were used without further purification.

**Apparatus and Procedures.** Details of the apparatus have been already given in the previous papers.<sup>4,5)</sup> Hydrocarbons were countercurrently fed into the induction-coupled argon

plasma jet through the spiral coil. The analysis of products was carried out by gas chromatography. Molecular sieve 13X column was used for the separation of hydrogen and methane, and 3% squalane supported on alumina column was used for the analysis of the other gaseous products. The conversion, the selectivity and the yield were calculated on carbon base. The selectivity and the yield of soot were estimated from the carbon balances.

### Results and Discussion

**Decomposition of Methane.** The effect of operating conditions was discussed in terms of the conversion of methane and selectivities of carbon-containing products. Figure 1 shows the effect of methane feed rate on the conversion and the selectivities of carbon-containing products at  $9.35 \pm 0.01$  kW input and  $1.56 \pm 0.02$  l/min argon flow rate. Besides the products shown in Fig. 1,

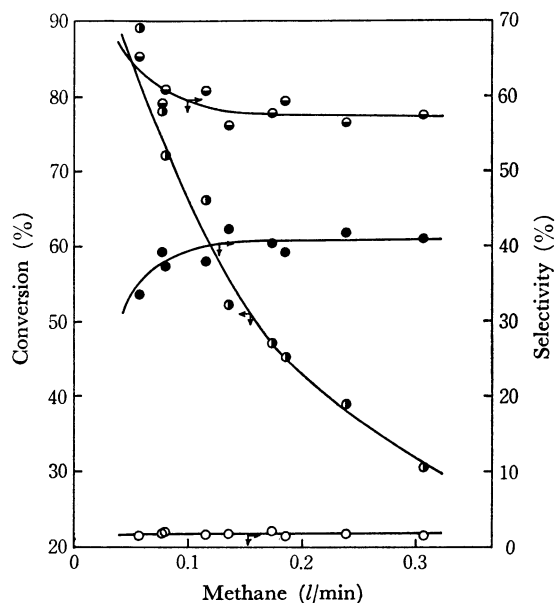


Fig. 1. Effect of methane feed rate on conversion and selectivities of products.

Input:  $9.35 \pm 0.01$  kW, Argon flow rate:  $1.56 \pm 0.02$  l/min  
 —●— conversion, —◐— C<sub>2</sub>H<sub>2</sub>, —○— C<sub>2</sub>H<sub>4</sub>, —●— soot

1) R. F. Baddour and J. L. Blanchet, *Ind. Eng. Chem. Process Des. Develop.*, **1**, 169 (1964).

2) R. E. Duff and S. H. Bauer, *J. Chem. Phys.*, **36**, 1754 (1962).

3) J. T. Clark, "The Application of Plasma for Chemical Processing," ed. by R. F. Baddour and R. S. Timmins, The M. I. T. Press, Cambridge, Massachusetts and London, England (1967), p. 140.

4) Y. Nishimura, K. Takeshita, Y. Adachi, F. Nakashio, and W. Sakai, *Sekiyu Gakkai Shi*, **12**, 698 (1969).

5) Y. Nishimura, M. Nishimura, K. Takeshita, and W. Sakai, *Kogyo Kagaku Zasshi*, **73**, 1974 (1970).

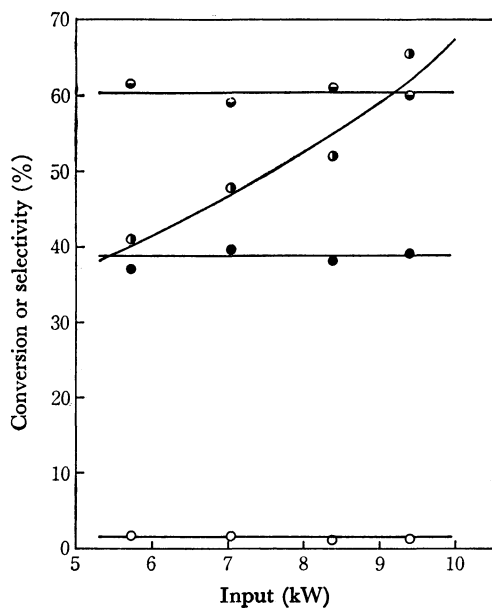


Fig. 2. Effect of input on conversion of methane and selectivities of products.

Feed rate of  $\text{CH}_4$ :  $0.100 \pm 0.005$  l/min,

Argon flow rate:  $1.56 \pm 0.02$  l/min

—●— conversion, —◐—  $\text{C}_2\text{H}_2$ , —○—  $\text{C}_2\text{H}_4$ , —●— soot

a large amount of hydrogen and a trace of ethane were obtained. Acetylene and soot are formed in 56–65% and 34–42% selectivity, respectively, but the selectivity of ethylene reduced to less than 2%, in contrast to the case of the decomposition of *n*-butane in which ethylene was formed in 18–20% selectivity.<sup>5)</sup> It is seen from Fig. 1 that the conversion decreases with increasing methane feed rate, while the product distribution reaches almost constant at higher feed rates of methane. A similar dependence of the conversion and the product distribution on hydrocarbon feed rate was also observed

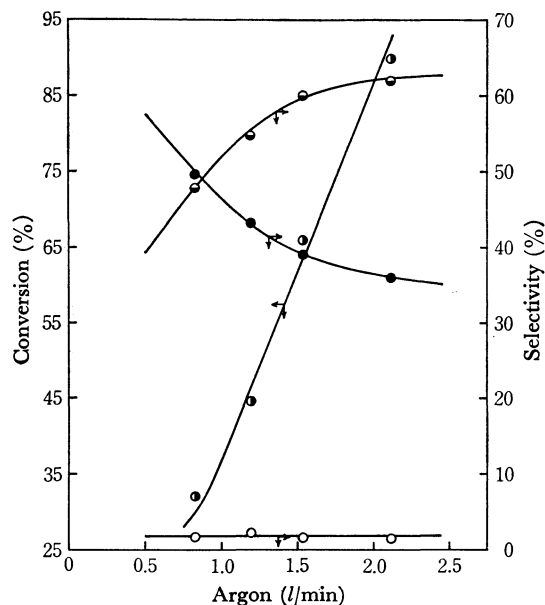


Fig. 3. Effect of argon flow rate on conversion of methane and selectivities of products.

Input:  $9.35 \pm 0.01$  kW, Feed rate of  $\text{CH}_4$ :  $0.100 \pm 0.005$  l/min

—●— conversion, —◐—  $\text{C}_2\text{H}_2$ , —○—  $\text{C}_2\text{H}_4$ , —●— soot

for the decomposition of propane<sup>4)</sup> and *n*-butane.<sup>5)</sup> Figure 2 shows the effect of the input at  $0.100 \pm 0.005$  l/min methane feed rate and  $1.56 \pm 0.02$  l/min argon flow rate. The conversion of methane decreases almost linearly with the lowering of the input, but the product distribution is independent of the input. On the other hand, it has been reported that in the decomposition of propane<sup>4)</sup> and of *n*-butane,<sup>5)</sup> the lowering of the input was inclined to decrease the selectivities of acetylene and soot, but to increase those of methane and ethylene. This reflects that more energies are required for the complete decomposition of propane and *n*-butane to atomic carbon and atomic hydrogen compared with that of methane to atomic carbon and atomic hydrogen.

Figure 3 shows the effect of argon flow rate at  $0.100 \pm 0.005$  l/min methane feed rate and  $9.35 \pm 0.01$  kW input. As for *n*-butane,<sup>5)</sup> the conversion decreases markedly with reducing argon flow rate. At the same time, the lowering of argon flow rate decreases the selectivity of acetylene and increases that of soot. At argon flow rate below 0.82 l/min, the formation of soot tends to be favored over that of acetylene, and from the thermodynamic consideration<sup>1,2)</sup> it suggests that the decomposition temperature rises with reducing argon flow rate. On the other hand, as shown in Fig. 4, ArI line (4158

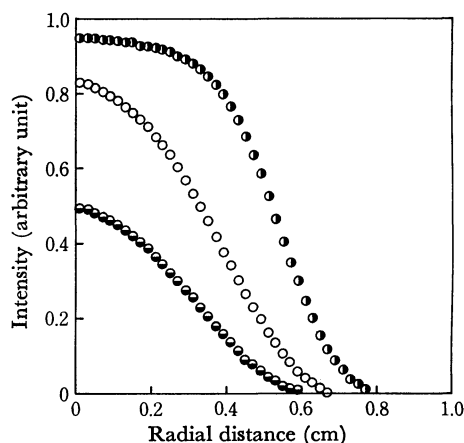


Fig. 4. Radial intensity profiles of ArI (4158 Å) at a distance of 1 cm from methane inlet at various argon flow rate.

—●— 1.19 l/min, —○— 1.56 l/min, —◐— 2.12 l/min

Å) is observed at a distance of 1 cm from the methane inlet and its intensity decreases with the lowering of argon flow rate. These results suggest that at the higher argon flow rate, the comparatively high temperature region extends over the neighborhood of the methane inlet and methane can be decomposed in this region. But the decomposition temperature is presumed to be lower in this region than in the upstream of the plasma jet since it has been reported that the temperature of the induction-coupled argon plasma jet dropped toward the downstream of the plasma jet.<sup>6)</sup> Therefore, the decomposition at the lower argon flow rate occurs apparently at the higher temperature. These results further suggest that methane is not completely mixed with the plasma jet. That is, from the results stated above together with those on the decomposition of propane<sup>4)</sup>

6) T. B. Reed, *J. Appl. Phys.*, **32**, 821 (1961).

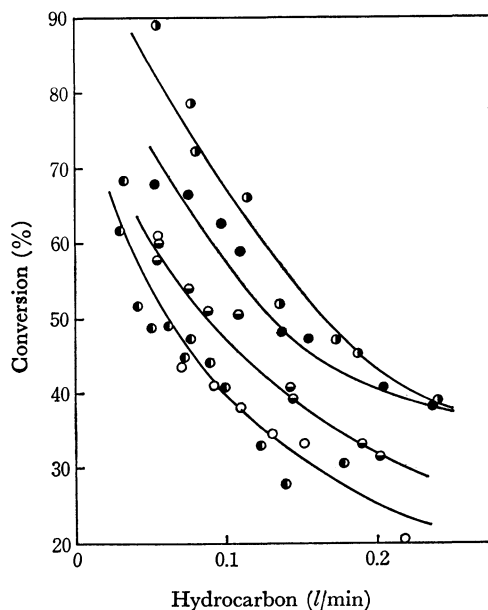


Fig. 5. Variation of conversion with feed rate of hydrocarbons.

Input:  $9.35 \pm 0.01$  kW, Argon flow rate:  $1.56 \pm 0.02$  l/min

—●—  $\text{CH}_4$ , —●—  $\text{C}_2\text{H}_6$ , —●—  $\text{C}_3\text{H}_8$ ,  
—●—  $n\text{-C}_4\text{H}_{10}$ , —○—  $i\text{-C}_4\text{H}_{10}$

and of *n*-butane,<sup>5)</sup> we may conclude that saturated gaseous hydrocarbons are not completely mixed with the plasma jet but the decomposition of these hydrocarbons takes place predominantly in the outer flame of the plasma jet and its surroundings under the condition that hydrocarbons are charged into the plasma jet countercurrently.

**Decomposition of Ethane and Isobutane.** As stated above, the decomposition of methane gave mainly acetylene, soot, and hydrogen with a small amount of ethylene. Consequently, we studied the decomposition of ethane and isobutane in order to know the effect of the structure of hydrocarbons on the conversion, the product distributions and formation processes of methane and ethylene in the decomposition of propane and

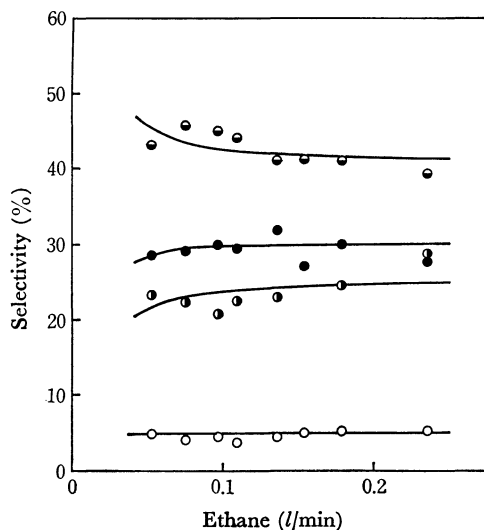


Fig. 6. Effect of ethane feed rate on selectivities of products.

Input:  $9.35 \pm 0.01$  kW, Argon flow rate:  $1.56 \pm 0.02$  l/min

—○—  $\text{CH}_4$ , —●—  $\text{C}_2\text{H}_2$ , —●—  $\text{C}_2\text{H}_4$ , —●— soot

TABLE 1. SELECTIVITIES OF CARBON-CONTAINING PRODUCTS IN ISOBUTANE DECOMPOSITION

$i\text{-C}_4\text{H}_{10}$ (l/min)	Selectivity of product (%)					
	$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_6$	$\text{C}_2\text{H}_2$	Soot
0.056	9.7	1.3	10.1	10.7	42.0	26.2
0.073	9.8	2.1	9.5	9.7	45.7	23.2
0.092	9.1	1.3	9.6	10.8	43.4	25.8
0.108	10.1	2.3	10.3	12.6	41.2	23.5
0.131	11.7	1.9	11.3	13.6	37.8	23.7
0.154	11.7	1.5	11.6	13.3	37.1	24.8
0.221	11.3	1.7	11.3	11.6	40.5	23.6

*n*-butane. Ethane and isobutane were decomposed under the same condition as methane were. Figure 5 shows the variation of conversion of ethane and isobutane with the feed rate of hydrocarbons. Conversions of methane, propane and *n*-butane are included in Fig. 5 for comparison. It is seen from Fig. 5 that the saturated gaseous hydrocarbons become difficult to be decomposed as carbon chains increase and both butane isomers are decomposed in the similar way.

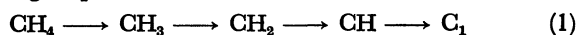
Figure 6 and Table 1 show selectivities of products at various feed rates of ethane and isobutane, respectively. In ethane, appreciable amounts of methane and ethylene are obtained in addition to acetylene, soot, and hydrogen. Especially, ethylene is obtained in 20—27% selectivity. In isobutane, the selectivity of ethylene reduces to 10—12%, but propylene is obtained in 10—14% selectivity and methane is formed in higher selectivity than in the decomposition of ethane, propane,<sup>4)</sup>

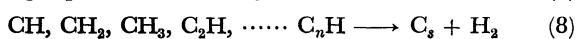
TABLE 2. YIELDS OF DECOMPOSITION PRODUCTS IN VARIOUS HYDROCARBONS

Hydrocarbon:  $0.100 \pm 0.005$  l/min, Ar:  $1.56 \pm 0.02$  l/min, Input:  $9.35 \pm 0.01$  kW

Hydrocarbon	Yield (%)						
	$\text{CH}_4$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_2\text{H}_2$	Soot
$\text{CH}_4$	—	1.0	trace	—	—	40.0	25.5
$\text{C}_2\text{H}_6$	2.7	12.8	—	—	—	27.1	20.2
$\text{C}_3\text{H}_8$	3.1	8.3	trace	2.9	—	19.8	14.4
$n\text{-C}_4\text{H}_{10}$	2.6	8.5	trace	1.1	trace	17.6	10.5
$i\text{-C}_4\text{H}_{10}$	4.1	4.0	0.9	5.1	—	16.1	9.3

and *n*-butane.<sup>5)</sup> Table 2 illustrates the products and their yields for the decompositions of methane, ethane, propane, *n*-butane, and isobutane at the hydrocarbon feed rate of  $0.100 \pm 0.005$  l/min. As is seen from Table 2, the decomposition products and their distributions closely relate with the structure of hydrocarbons. In the decomposition of methane, major products are acetylene, soot, and hydrogen. Acetylene and soot occupy above 98% of carbon-containing products. Thus, methane introduced into the decomposition region is decomposed almost to carbon and hydrogen, and then, acetylene, soot, and hydrogen are formed. That is, the decomposition of methane is assumed to proceed *via* following steps;

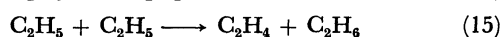
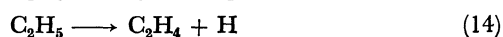
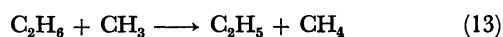
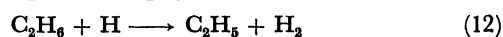
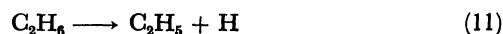




where  $C_s$ : soot

It is difficult to explain the formation process of ethylene, but it may be concluded that ethylene is formed from carbon and hydrogen under the condition used in this experiment. Saturated hydrocarbons with two or more carbon atoms are decomposed to give appreciably byproducts such as methane, ethylene, or propylene, in addition to acetylene, soot, and hydrogen. If these hydrocarbons are decomposed mostly to carbon and hydrogen, and then, a large portion of methane, ethylene, or propylene is formed, a similar product distribution must be obtained in the decomposition of both *n*-butane and isobutane. The high selectivity of propylene in isobutane decomposition gives the strong support for the intervention of isopropyl radical in the decomposition step.<sup>8)</sup> Therefore, it may be concluded that radicals formed by a fission of C-H or C-C bond intervene in the decomposition of saturated

gaseous hydrocarbons in the induction-coupled argon plasma jet. That is, these radicals are decomposed to give appreciably methane, ethylene, or propylene, *etc.* at the comparatively lower temperature region in the reaction zone. At the higher temperature region in the reaction zone, these radicals are further decomposed to carbon and hydrogen, and then, acetylene, soot, and hydrogen are produced. For example,



in the decomposition of ethane, methyl and ethyl radicals are formed by the reactions (10), (11), (12), and (13).<sup>9-11)</sup> In the lower temperature region, methane and ethylene are formed from these radicals by the reactions (13), (14), (15), and (16). In the higher temperature region, methyl and ethyl radicals are further decomposed to carbon and hydrogen or partly to methyne and methylene radicals, and then, acetylene, soot, and hydrogen are formed through the same process as that for methane decomposition.

7) A. R. Fairbairn, *Proc. Roy. Soc., Ser. A*, **312**, 229 (1969).

8) R. S. Konar, J. H. Purnell, and C. P. Quinn, *J. Chem. Soc., A*, **1967**, 1543.

9) C. P. Quinn, *Proc. Roy. Soc. Ser. A*, **275**, 190 (1963).

10) M. C. Lin and M. H. Back, *Can. J. Chem.*, **44**, 505 (1966).

11) M. C. Lin and M. H. Back, *ibid.*, **44**, 2357 (1966).