

DECOMPOSITION OF PROPANE IN A DEUTERIUM  
PLASMA JET

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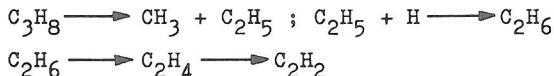
Compounds: propane, methane, ethane, ethylene, acetylene  
propylene

ABSTRACT

The reaction paths of propane decomposition in a hydrogen plasma jet have been studied by substituting deuterium for hydrogen. Propane decomposition was found irreversible; deuterium interacted with most reaction products, however with acetylene and ethane only slightly. To explain results a dual reaction scheme was postulated.

1. INTRODUCTION

Earlier studies on propane decomposition in a hydrogen plasma jet done in this laboratory /1/ showed as expected that methane, ethane, ethylene and propylene were the main products, however selectivities of formation of these compounds showed a pattern that couldnt be explained by reaction routes published for the chemistry of hydrocarbon reactions occurring in thermal plasmas /2/. In the work cited it has been found that there was considerably less methane in the products formed as the equivalent of the sum of ethane, ethylene and acetylene and therefore it had to be assumed that acetylene formation must have occured not only according to the generally accepted route



but other reaction paths, e.g. recombination of the methyl radicals to ethane might be responsible too. Additionally since hydrogen to hydrocarbon ratio was found to influence product composition /3/, interaction of plasma hydrogen with reaction products had to be suspected. These and similar observations prompted a more thorough study of the reaction paths occuring with hydrocarbons in

thermal plasmas. Different approaches have been tried, one among them was a series of runs carried out with different hydrocarbons in streaming deuterium plasmas, some results of which are the topic of this paper.

## 2. EXPERIMENTAL

Apparatus: the 2 kVA direct current plasma jet microreactor described previously /1,3/ had been used.

Analytical: Feed and product compositions were obtained by analysis with a Hewlett-Packard Reporting Gas Chromatograph Type 5830A on a 2 m long, 1/8 in. diameter stainless steel column filled with GSC-120 alumina /Woelm/ packing, using argon carrier gas at a rate of 30 ml/minute and a flame ionization detector. For deuterium distribution determination in the individual product compounds a portion of the product gas was led to a liquid nitrogen trap to concentrate the hydrocarbons; the hydrocarbon fraction was introduced into a GC-MS combination consisting of a Varian Type 1400 gas chromatograph with a similar alumina column as described above, and a Dupont 21-490B single focusing mass spectrometer operated at 70 eV. Corrected fragmentation spectra were evaluated with a PDP-8 computer.

Reagents: Commercial grade propane /93 wt% propane, 2,4 wt% ethane, 2,7 wt% iso-butane, 1,9 wt% n-butane/ was used. Commercial bottled deuterium with 99,4 atom% D-content was used without further purification.

## 3. RESULTS

Run conditions and results are summarized in Table 1.

Table 1. Pyrolysis of propane in deuterium plasma

Run number	Feed, Deuterium	moles/h Propane	Plasma temperature, K	Mixing temperature, K	Propane conversion %
25	33,8	3,92	2110	1500	16
13	33,8	1,96	2240	1840	33
7	33,8	1,17	2460	2220	38
15	33,8	1,96	2860	2590	67
16	33,8	1,96	2910	2650	70
10	33,8	1,17	3330	3240	96

Run number	S e l e c t i v i t y % to					
	methane	ethane	ethylene	propylene	acetylene	C <sub>4+</sub>
25	14,8	13,0	20,4	8,1	20,1	23,7
13	17,5	5,2	24,2	7,5	30,7	15,0
7	19,0	8,1	22,7	6,9	34,6	8,6
15	16,6	2,4	21,9	5,2	51,2	2,7
16	16,7	2,2	21,5	4,9	52,4	2,4
10	10,9	0,7	9,9	1,4	77,0	0,2

Results are expressed as selectivities calculated according to the following formula:

$$\text{Selectivity} = \frac{\text{moles of propane converted to compound "i"}}{\text{moles of propane converted}}$$

Plasma temperature was calculated from heat balance around the plasma generator, starting temperature for the reaction mixture was calculated assuming adiabatic mixing of the plasma and cold propane gas. Thermodynamic data of Duff and Bauer /4/ have been used for these calculations.

Results were compared with those obtained using hydrogen as plasma gas /1/ in order to see if any difference due to deuterium existed. Data plotted along those obtained with hydrogen plasma gas gave the same curves therefore absence of isotope effect could be ascertained. Figures 1 and 2 show methane and acetylene formation selectivities plotted in function of propane conversion for runs with hydrogen and deuterium.

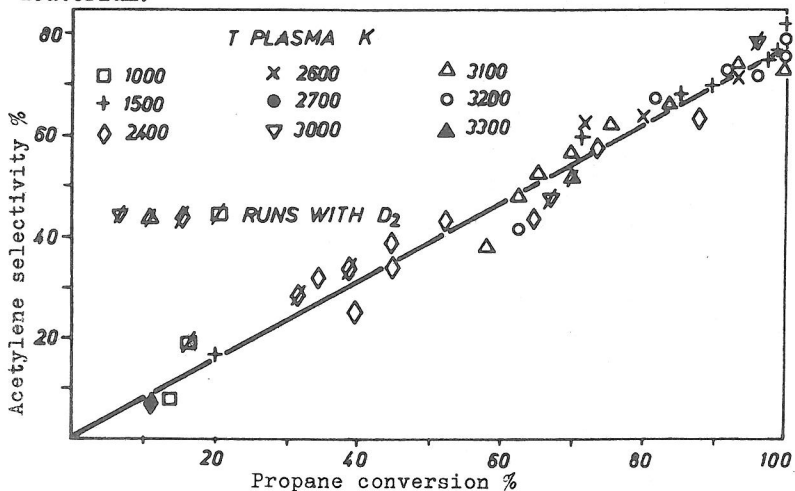


Fig.1. Acetylene formation selectivity

Deuterium distribution data for the C<sub>1</sub>-C<sub>3</sub> hydrocarbons in the reaction products at low and medium conversion are summarized in Table 2.

#### 4. DISCUSSION

Data of Table 2. show that methane had a very high deuterium content, approaching equilibrium composition. Ethane consisted mainly of the d<sub>0</sub>-species, with 10-20 % monodeuter-

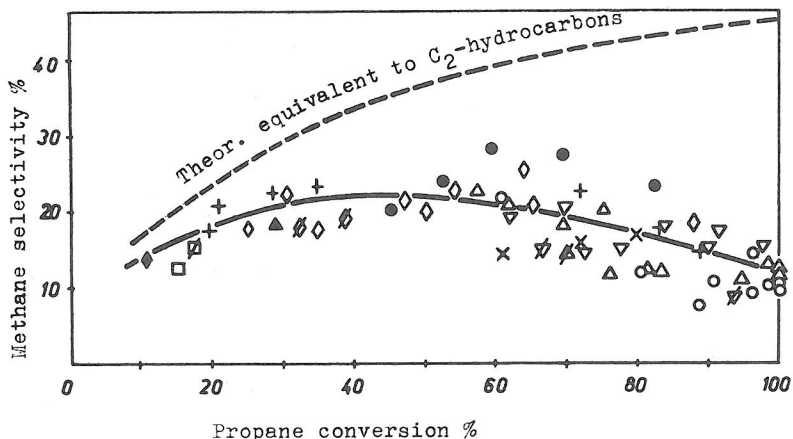


Fig.2. Methane formation selectivity  
/For symbols see Fig.1./

Table 2. Deuterium distribution in the products  
from propane pyrolysis in a deuterium  
plasma jet in percentages

Propane conversion %		33	67	70
Methane	d0	4	23	25
	d1	29	35	34
	d2	27	23	21
	d3	24	12	12
	d4	16	7	8
Ethane	d0	75	72	70
	d1	10	15	17
	d2	8	7	7
	d3	4	4	4
	d4+	3	2	2
Ethylene	d0	34	32	24
	d1	26	28	31
	d2	21	24	26
	d3	14	12	15
	d4	5	4	4
Acetylene	d0	96	93	90
	d1+	4	7	10
Propane	d0	99+	99+	99+

ated and 5-10 % bideuterated ethane. Ethane molecules with more than two deuterium atoms were practically absent. Ethy-

lene showed a high deuterium content; the relative amounts of d0, d1, d2, d3 and d4 species were 25-35, 25-30, 20-25, 10-15 and cca. 5 %, respectively. Acetylene consisted over 90 % of the d0-species with small amounts of d1. The d2 content was below the detection limit. Unconverted propane contained practically no deuterium at all. The propylene consisted of about 60 % d0, 30 % d1 and small amounts of d2 and d3 species.

The fact that deuterium was found in most of the reaction products clearly shows that plasma deuterium /or hydrogen/ not only acts as a heat source for the reaction, but strongly interacts with the reaction intermediates.

The decomposition of the starting propane is a unidirectional reaction, since no deuterium could be detected in the unconverted propane.

The acetylene formed contains only a slight amount of deuterium, therefore most of the hydrogen atoms in the molecule must have come from the original propane. This suggests that the ethyl radicals formed on primary cleavage of the propane molecule directly yield acetylene without being transformed either to ethane or ethylene. Ethylene as an intermediate step seems highly unlikely since the ethylene formed contains deuterium in nearly equilibrium concentration, so if ethylene were the precursor of acetylene, the latter should contain a much higher percentage of deuterium.

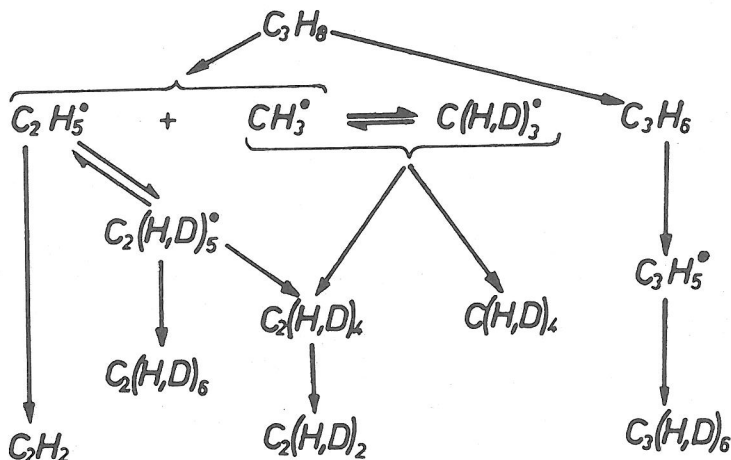
The amount of acetylene formed at high conversion exceeds the equivalent of the starting propane, therefore an other way for acetylene formation must exist too: this may occur from the methyl radicals formed during the primary cleavage, which being highly reactive undergo fast deuterium exchange reactions giving rise to all possible deuterated species. Methyl radicals either stabilize to different deuteromethanes or form deuterio-ethylenes simultaneously losing hydrogen. Ethane as an intermediate step might be excluded, since the ethane fraction contains far less deuterium as either the methane or the ethylene. Acetylene formation occurs through dehydrogenation of the ethylene and the ratio of these two acetylene forming reactions is a function of severity. At low severities methane and ethylene are formed in this way, at high severities the ethylene so formed undergoes dehydrogenation to acetylene.

The ethane fraction consists mostly from hydrogen containing ethane molecules, that may come mostly from undecomposed ethane impurities of the feed. Deuterium containing ethane molecules may result from ethyl radical and deuterium recombination reactions.

The reaction product contains propylene too, two third of which being on the average deuterium containing species points to the possible existence of propenyl radicals that

stabilize with deuterium to deutero-propylene. Hydrogen containing propylene results from simple thermal dehydrogenation of the starting propane.

From the above observations the following picture for propane decomposition in a hydrogen /deuterium/ plasma jet may be deduced:



#### ACKNOWLEDGEMENT

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