NEW INSIGHTS INTO THE KINETICS OF PLASMA PYROLYTIC METHANE CONVERSION FROM SINGLE PULSE SHOCK TUBE INVESTIGATIONS

H.-D. Klotz, H. Drost and H.-J. Spangenberg
Akademie der Wissenschaften der DDR, Zentralinstitut für physikalische Chemie, DDR 1199-Berlin, Rudower Chaussee 5

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ABSTRACT

The plasma pyrolytic methane conversion was studied behind reflected shock waves at dwell times 0,2 - 5 ms and at temperatures 1500 - 3200 K. Pyrolysis products C_2H_6, C_2H_4, and C_2H_2 show maxima, which positions depend on its saturation degree temperature and dwell time. Product formation is discussed by means of a successive hydrogen detachment from C/H spezies and the recombination of the remainding radicals.

1. INTRODUCTION

Studies of pyrolytic methane decomposition behind reflected shock waves / 1 / are mainly concerned in determining the reaction rate and the initiation reactions. These informations however are mostly unsufficient for explaining the kinetics of product synthesis, particularly the acetylene formation. There is especially a lack of data on the dependence of composition and concentration of the products from temperature and residence time of methane in the high temperature region. Accordingly to this lack of data our investigations are concerned with such dependence, performed in a

single pulse shock tube.

2. EXPERIMENTAL

The single pulse shock tube is based on the design of GLICK et.al./ 2 /. However, to give more precise control, the timing of the rupture of the diaphragms is achieved electrically. The shock tube is constructed from stainless steel tubing of 8 cm int. diam.; driver and driven section are 1,7 m and 5 m in length, resp. The dump tank consists of mild steel and has a volume of 350 l. The reactants are confined to a small section of the tube separated from the driven section by two sliding vane valves.

The aim of our investigations concerns the dependence of the pyrolysis products of methane on the reaction dwell times. For this purpose such operating conditions had to be found that dwell times could be varied in a wide range.The dwell time is the time between the arrival of the heating shock to the reaction system and the arrival of the cooling rarefaction wave; it could be varied by changing the speed of the rarefaction wave. For this purpose diverse driver gases with different speeds of sound were used. A variation of dwell times at constant reaction temperature could be achieved by a siutable choice of the pressures in the driven and driver section.

Dwell times are obtained from the oscilloscope traces of the signals from piezo-electric pressure transducers mounted in the end wall of the test section and in the tube wall 10, 20, and 30 cm from the end wall. In the present experiments the driven pressures were altered in the range 6,6 - 33 kPa. The driver section was filled with Ar, He, H_2,N_2, and suitable mixtures of these gases up to 10^6 Pa.

Incident shock velocities are measured by means of the same transducers. Reflected shock temperatures were calculated from incident velocity measurements assuming one dimensional behaviour / 3 /.

Analysis of methane and of the pyrolysis products (ethane,

ethylene, acetylene, hydrogen were carried out by gas chromatography. Methane was diluted by the carrier gas Ar to 1, 5, and 9%. Dwell times were varied in the range 0,2 - 5ms, reflected shock temperatures reached 1540, 1850, and 2400 K. The quenching rate varied between $3 - 8 \cdot 10^5$ Ks^{-1}.

3. RESULTS

The results of the measurements are presented in figures 1 and 2. From the curves of these figures the following conclusions can be drawn:

- all measured pyrolysis products show a remarkable dependence on reaction dwell time,
- the methane decomposition increases with rising dwell times and rising temperatures,
- all the products show in its concentrations a tendency to pass through a maximum; the position of these maxima depends on the saturation degree of the hydrocarbons and on the pyrolysis temperature. The greater saturation degree and the higher reaction temperature the smaller the dwell times, at which concentration maxima appear. Accordingly, at a constant temperature the highest yields of products occur in the order ethane, ethylene, and acetylene via increasing dwell times.
- the acetylene concentration maximum increases with increasing temperature
- the similar behaviour of the acetylene and the hydrogen curves up to the acetylene maximum may be explained by hydrogen formation during acetylene synthesis. The further rising of the hydrogen curve is due to the acetylene decomposition.

Additional investigations have shown a decrease of the acetylene concentration at temperatures above 2500 K. At temperatures higher than 3200 K and dwell times $\geq 5 \cdot 10^{-3}$s hydrogen and soot appeared as main products of the methane pyrolysis. In the case of acetylene pyrolysis at the same temperatures the main products are hydrogen and soot too,

whereas at temperatures below 2500 K the pyrolysis products consist of higher molecular weight hydrocarbons, mainly C_4H_2 and C_4H_4.

4. DISCUSSION

The curves of fig. 1 and 2 show no indication that the pyrolysis products convert into each other according to the KASSEL-model / 4 /.

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \; . \qquad (1)$$

From fig. 1 is further seen that the reaction products C_2H_6, C_2H_4, and C_2H_2 temporally appear one after another. Moreover, if the methane would be converted to acetylene via scheme (1), C_2H_6 concentration should have been in the same order of magnitude as the C_2H_2 yield, particularly at low temperatures and small dwell times. This can be concluded from calculations of the C_2H_6 yield according to the reaction rate of ethane / 5 /. It is clearly seen from fig. 1, 2 that these demand coudn't be varified; the measured amounts of C_2H_6 were always 1,5 order of magnitude lower than the C_2H_2 concentration. This fact additionally indicates that the scheme (1) is not valid under the investigated conditions.

In a single pulse shock tube the yields of products are mainly determined by the quenching process in which all radicals formed during the pyrolysis, recombine. Therefore, low intensities of C_2H_6 and C_2H_4 can be reducted to low intensities of CH_3 and CH_2. On the other hand, a high C_2H_2 yield can be regarded as the result of a high CH concentration. According to the model of high temperature pyrolysis of organic molecules / 6 / for the case of the pyrolytic methane decomposition we suppose a successive detachment of hydrogen atoms

$$CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C_{solid} \qquad (2a)$$

$$\text{or} \quad CH_4 \rightarrow CH_2 \rightarrow CH \rightarrow C_{solid} \qquad (2b)$$

The abundance of the radicals in 2a and 2b are shifted from the left to the right by increasing temperature and dwell time. This shifting may be amplified by subsequent reactions of H atoms / 1 /

$$CH_4 + H \longrightarrow CH_3 + H_2 \qquad (3a)$$

$$CH_3 + H \longrightarrow CH_2 + H_2. \qquad (3b)$$

As well in the hot phase as during the quench process the formation of the products C_2H_2, C_2H_6, and C_2H_4 results from the interaction of these radicals according tø the following scheme

$$\begin{array}{ccccccccc} CH_4 & \longrightarrow & CH_3 & \longrightarrow & CH_2 & \longrightarrow & CH & \longrightarrow & C_s, H \\ & & +(M) & & +(M) & & +(M) & & \end{array} \qquad (3)$$

$$\begin{array}{ccccccccc} CH_4 & \longrightarrow & CH_3 & \longrightarrow & CH_2 & \longrightarrow & CH & \longrightarrow & C_s, H \\ & & \downarrow & & \downarrow & & \downarrow & & \\ & & C_2H_6 & & C_2H_4 & & C_2H_2 & & \end{array}$$

at which acetylene additionally may be formed via a C_2H radical. M indicates to a third impact partner increasing the reaction probability. This is concluded from the influence of the Ar-content on the reaction rate in our investigations.

With regard to the plasma jet synthesis of C_2H_2 from CH_4 our investigations indicate that the maximum of C_2H_2 yield is not only determinated by temperature but also by the residence time of CH_4 in the jet. For an optimal C_2H_2 yield the residence time of CH_4 had be the shorter the higher the plasma temperature is choϕsen.

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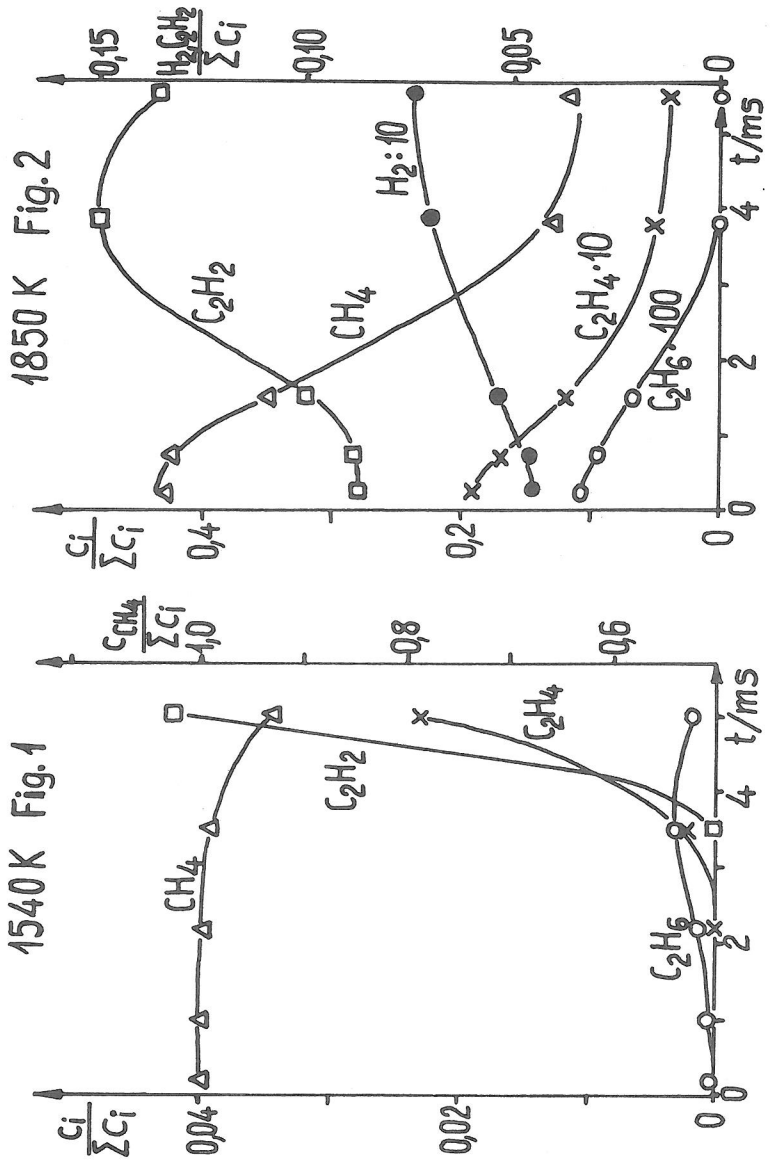
1540 K Fig. 1
$\frac{c_i}{\sum c_i}$
0,04
0,02
0
$\frac{c_{CH_4}}{\sum c_i}$
1,0
0,8
0,6
CH_4
C_2H_2
C_2H_4
C_2H_6
0
2
4 t/ms
1850 K Fig. 2
$\frac{c_i}{\sum c_i}$
0,4
0,2
0
$\frac{H_2, C_2H_2}{\sum c_i}$
0,15
0,10
0,05
0
C_2H_2
CH_4
$H_2 : 10$
$C_2H_4 \cdot 10$
$C_2H_6 \cdot 100$
0
2
4 t/ms