ANALYSIS OF CHEMICAL PRODUCTS FORMED IN A R.F. DISCHARGE BURNING IN ETHANOL VAPOURS

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ABSTRACT

The investigation of plasma reactions was performed using a rf discharge of 27,6 MHz and outlet power of 300 W, coupled inductively and capacitatively. Ethanol vapours were introduced in the discharge system under the optimal choosen experimental conditions. For the analysis of a rf discharge plasma a quadrupole mass spectrometer was used. The following molecular species have been detected: CH_4, C_2H_2, C_2H_4, H_2, HCHO, CO and H_2O.

1. INTRODUCTION

There is a number of papers concerning the investigations of the decomposition reactions of C-H systems in radiofrequency discharges /1,2 at al./, which can be brought in connection with the great interest in synthetic hydrocarbons.
The appropriate energetic conditions and low pressure in rf discharge make possible the formation of different radicals. Therefore, the possibilities for occuring of chemical reactions in these conditions are numerous and more favourable than in other discharges.
One of the important aspects of these investigations is the explanation of chemical reaction mechanism which take part in the discharge, in order to find the optimal conditions for practical application. This can be realized either by the direct searching out of the plasma composition /3,4 at al./ or by analysing the obtained products /5,6 at al./.
In the systems containing oxygen besides carbon and hydrogen in rf discharge a greater variety of radicals, than in C-H system, could be expected. In this work we intended to analyse the products created in such a type of low pressure discharge in ethanol vapours.

2. EXPERIMENTAL

A schematic diagram of the apparatus used for the examination of ethanol vapours decomposition in rf discharge in shown in Fig. 1. It is consisted of the cylindrical plasma reactor made of Pyrex, being 50 cm long and with the radius of 3 cm. Water cooling of the plasma reactor was possible.
A desired power from 27,6 MHz rf generator was coupled inductively on the discharge tube using 16-turn copper coils.

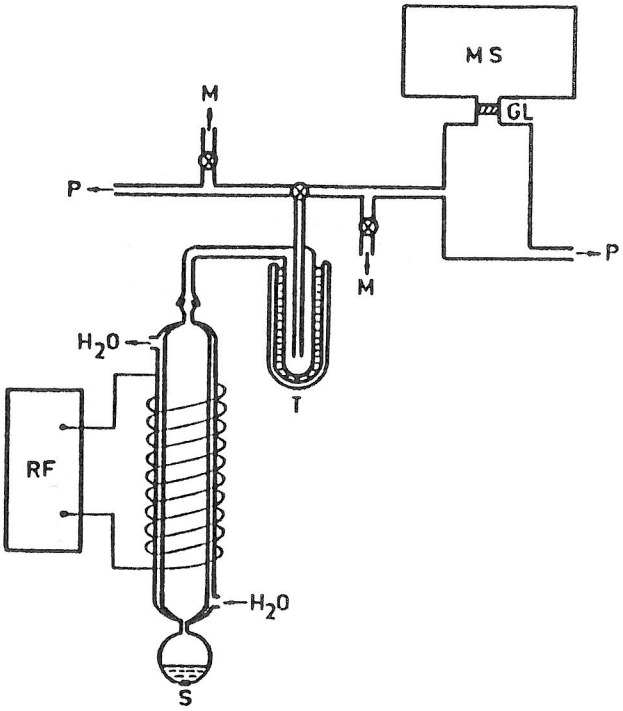

Fig. 1. SCHEMATIC DIAGRAM OF THE EXPERIMENTAL EQUIPMENT: D-DISCHARGE TUBE; P-PUMPS; RF – RADIOFREQUENCY GENERATOR; S-BULB WITH ETHANOL; T-COLD TRAP; M-MANOMETERS; MS – MASS SPECTROMETER; GL-GOLDEN LEAK

Secondly, the plasma was produced by capacitative coupling using two outside 2 cm cylindrical brass electrodes at mutual distance of 17,5 cm. The power output to the plasma could be controlled by varying the anode current /the applied current was in the range from 50 to 300 mA/.
The discharge time was 3,5 min.
Ethanol was contained in bulb S. The ethanol vapour pressure was 2,7 mbar. The condensable products were identified by their mass spectra obtained by the quadrupole mass spectrometer.

On the basis of the deteremined sensitivities of the instrument the partial pressures of the components were calculated.

3. RESULTS

Previous investigations have shown the influence of the reactor geometry on the product yields. We shall present only our results relating to the already described geometry of the plasma reactor.

Applying the inductrively and capacitatively coupled discharges, we analysed the products of different chemical reactions. The following molecular species have been detected: CH_4, C_2H_4, C_2H_2, H_2, HCHO, CO and H_2O. The influence of the anode current on the final products in capacitatively coupling discharge was considered. It was found that the current intensity influences the quantitative ratio of the obtained products. At the lower anode current the total pressure of products was decreased while the C_2H_2 and HCHO among the final products have not been found.
Comparing the data relating to the inductively and capacitatively coupled plasma at the same current, a significant decrease of partial pressure of C_2H_2 in the inductively coupled plasma was noticed.

Partial pressures of the molecular species containing C and H, measured for both types of discharges, are presented in Table 1.

Table 1. Measured partial pressures of components formed in rf discharge for different types of coupling

Type of coupling	I_a/mA/	Partial pressure /mbar/			
		CH_4	C_2H_4	C_2H_2	H_2
capacitative	95	1,07	4,37	0,47	3,16
	55	1,17	1,61	-	2,53
inductive	95	0,93	4,49	0,21	3,63

The molecular species containing besides C and H and O too, CO, H_2O and HCHO were identified /Table 2./

Table 2. Peak hights /arbitrary units/ of molecular species containing oxygen, formed in rf discharge for different types of coupling

Type of coupling	I_a/mA/	Peak hights /arbitrary units/ CO	HCHO	H_2O
capacitative	95	10,3	7,0	-
	55	8,5	-	5,5
inductive	95	9,5	4,5	8,5

The influence of the inductive and capacitative coupling as well as of anode current on the formed products is remarkable. In connection with our experimental results one can conclude that the reactor cooling has the same effect, during the discharge, as the decrease of anode current.

It can be pointed out that under the applied experimental conditions no ethanol was detected among condensable products, thus indicating the complete decomposition of ethanol molecules in plasma.

On the basis of our results a certain approach to the chemical reactions in the applied discharge can be given.

The presence of CH_4, CO and HCHO molecules among the discharge products indicates that in the decomposition mechanism of ethanol, the predominant role can be ascribed to the C-C break. HCHO, CO and H_2O were formed during simultanous dehydrogenation and dehydration reactions of the $^{\bullet}CH_2OH$ radical. CH_4, C_2H_4 and C_2H_2 are products of the recombination and dehydrogenation of hydrocarbon radicals.

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