CHEMICAL REACTIONS IN DESINTEGRATING PLASMA*

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The concentration and temperature of electrons, speed of molecules and neutral gas temperature are determined by means of microwave and probe methods in the flowing nitrogen plasma afterglow.

The knowledge of these parameters was employed for the study of toluene polymerization in the plasma afterglow.

ХИМИЧЕСКИЕ РЕАКЦИИ В ДЕЗИНТЕГРИРОВАННОЙ ПЛАЗМЕ

Из послесвечения потока азотной плазмы с помощью микроволнового метода и метода зондирования были определены концентрация и температура электронов, скорость молекул и температура нейтрального газа. Значения этих параметров использовались при изучении полимеризации толуена в свечении плазмы.

I. INTRODUCTION

In contrast to active plasma, particles with their internal energies have a decisive influence on chemical reactions in the plasma afterglow.

The kinetic energy of particles in the plasma afterglow is very low, it corresponds to the temperature of gas. This temperature is in most cases lower than 500 K, that is a few hundreds of eV.

The density of energy in the plasma afterglow is given by the concentration of various particles like: atoms, excited atoms, excited molecules, atomic ions, and molecular ions. The gas composed of these particles is usually called the active gas. The dissociation energy of molecules and the potential energy of atoms and molecules are responsible for the course of chemical reactions.

The chemical reactions in the plasma afterglow can be divided into three groups:

a) The active gas reacts with the molecule of some other gas and new compounds are produced — for example:

$$N + C_2H_4 \rightarrow CH_3 + HCN$$

or

$$N + HBr \rightarrow NH + Br.$$

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b) The active gas A reacts with the active gas B and produces a new compound — for example

$$N + O + M \rightarrow NO + M.$$

c) The active gas transfers its internal energy to other molecules to make their chemical reactions possible, though not being part of a new compound itself. The example of this reaction is

$$N + N + S_2Cl_2 \rightarrow N_2 + S_2Cl_2^* \longrightarrow S_2 + Cl_2 .$$

The influence of excited particles on chemical reactions is demonstrated for example by the dissociation of halides ThF, ThCl by active nitrogen [1]. This dissociation is caused by excited molecules $N_2(^5\Sigma_g^+)$, produced by the recombination of atomic nitrogen. The decompositions of ammonia and methane are other reactions caused by excited molecules [2, 3]

$$CH_4 + N_2(A^3\Sigma_u^+) \rightarrow CH_4^* + N_2(X^1\Sigma_g^+) \longrightarrow CH_3 + H$$

Into group c) there belong also reactions of an active gas with aromatic hydrocarbons, leading to their polymerization. The ionization of hydrocarbons by excited molecules of some basic gas (Ar, N_2) and also the dissociative energy in case of nitrogen play an important role in this reaction [4]. In the following we shall give

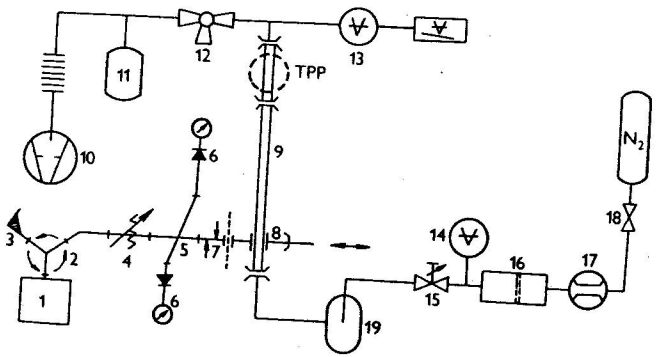

Fig. 1. Appartus used for study of nitrogen afterglow. 1 — magnetron generator, 2 — ferrite insulator, 3 — matching load, 4 — attenuator, 5 — directional coupler, 6 — reflectometer, 7 — matching screws, 8 — waveguide resonator, 9 — silica tube, 10 — oil rotary pump, 11 — vacuum reservoir, 12 — valve, 13 — membrane vacuometer, 14 — manometer, 15 — needle valve, 16 — BASF Catalyst R 3-11, 17 — flowmeter, 18 — valve, 19 — cold trap, TPP — measuring unit with thermocouple, Pitot tube and double probe.

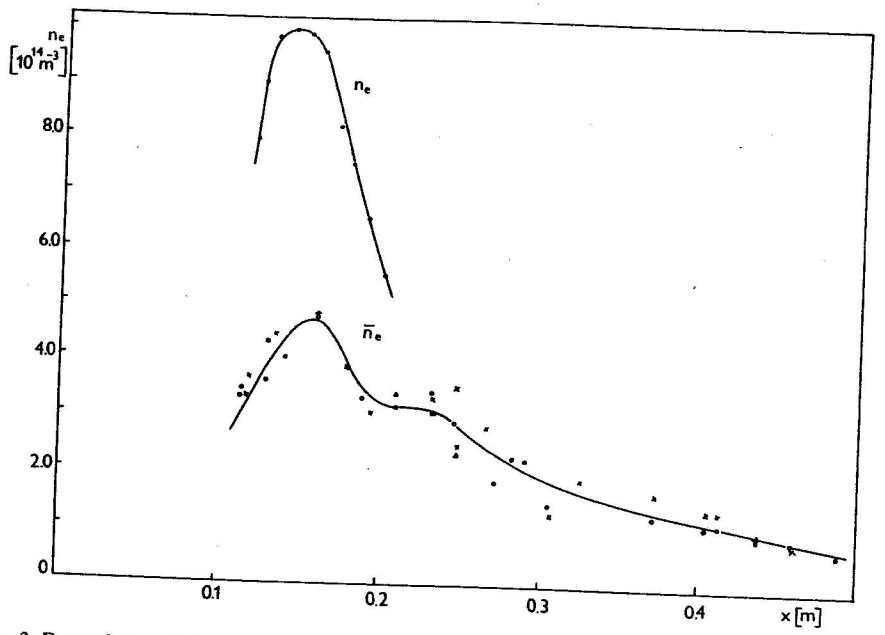

Fig. 2. Dependence of electron concentration on the distance from the centre of waveguide resonator, n_e — maximal value, measured by double probe in axis of tube, $\bar{n}_e$ — average value, measured by microwave method.

results of experimental studies of parameters of nitrogen afterglow plasma in the flowing regime and results of experimental studies of toluene polymerization.

II. PROPERTIES OF THE NITROGEN PLASMA AFTERGLOW IN THE FLOWING SYSTEM

The optical, microwaves and probe methods were used for the study of parameters of the nitrogen plasma afterglow. The plasma was created by the microwave discharge, burning in a silica tube. The tube passes through a waveguide resonant cavity. The illustration of the apparatus is given in Fig. 1. The hf power at a frequency of 2450 MHz was supplied by a magnetron generator GUM 2S. The power was measured by means of a calibrated reflectometer. The discharge silica tube had a diameter of 1.5 cm. A rotary pump RV 20 was used for the pumping of the discharge tube. The nitrogen was additionally purified in a De-oxo unit with the BASF Catalyst and then passed through a trap containing liquid nitrogen. The pressure inside the tube in all experiments was 1330 Pa. The flow of nitrogen was 1.04 Pa m^{3}s^{-1}.

The microwave power 85 W was absorbed in the discharge.

a) Electron concentration

The dependence of the electron concentration on the distance from the centre of the discharge was measured by the microwave resonator method. The measuring was carried out with a cylindrical cavity working on the frequency band S. The measuring of the electron concentration was also made by means of a double probe. The results are given in Fig. 2. The electron concentration had a maximum at the distance of 15 cm from the discharge, caused by the secondary ionization in the plasma afterglow, due to inelastic collisions of metastable molecules of nitrogen.

b) Temperature of electrons

A symetrical double probe was used for the determination of the electron temperature. The probe was of molybdenum wires of 0.3 mm diameter, the length of the probe was 5 mm. The course of the electron temperature is shown in Fig. 3. The electron temperature maximum occurs at the beginning of the secondary ionization.

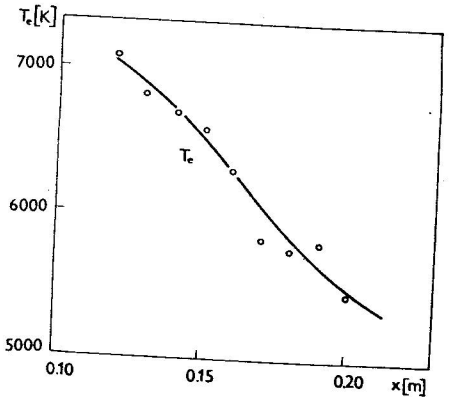

Fig. 3. Temperature of electrons in dependence on distance.

c) Measuring the spead of the flowing gas

According to the variation of the neutral gas temperature and dissociation of molecules, the speed of the gas particles along the axis is variable. If the speed and the temperature of the gas are known, the degree of dissociation may be determined. The speed was calculated from the dynamic pressure $\Delta p = \frac{1}{2}\varrho v^2$, measured by means of the Pitot tube [5, 6]. The pressure was measured by a differential capacitance Varian — MMCT vacuometer. The course of the

dynamic pressure and the speed of molecules along the axis of the discharge tube are shown in Fig. 4.

The knowledge of the neutral gas temperature is necessary for the dermination of the dissociation degree. Two thermocouples Pt-PtRh were used for its determination. The second thermocouple was isolated by a thin film of simax glass. A similar arrangement had been used by Vinogradov [7]. He supposed the temperature measured by this thermocouple to be the kinetic gas temperature.

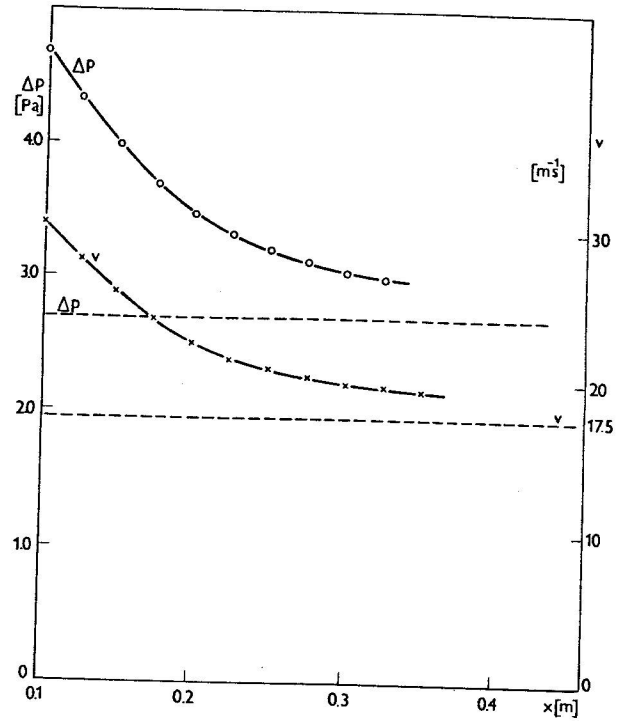

Fig. 4. Dependence of dynamic pressure and speed of gas flow on distance, measured from the centre of discharge. p_o and v_o — values without discharge.

Measured gas temperature in dependence on distance is given in Fig. 5.

From the comparison of the measured speed of gas with the measured temperature at constant flow, it is clear that the temperature measured by means of the thermocouple covered by glass is also higher than the kinetic temperature of gas thanks to the recombination and deexcitation on the surface of the thermocouple, which cannot be neglected. Therefore, the measured temperatures cannot be used for the calculation of the dissociation degree.

From measurements of the parameters of flowing plasma it follows that for the chamical reactions in our apparatus the best conditions are at a distance of 15 cm from the centre of the discharge. The distance corresponds to the relaxation time of the plasma afterglow $t = 5 \times 10^{-3}$ s in all cases where the nitrogen flow was $F_N = 1.64$ Pa m^{3}s^{-1}.

III. POLYMERIZATION

The apparatus used for the investigation of toluene polymerization is shown in Fig. 6.

The plasma was flowing into a glass sphere of a diameter of 15 cm. The toluene vapour was fed into the plasma at a distance of 1 cm from the nozzel of a silica tube. The polymer layer formed on thin glass plates of a surface of 4 cm^2, placed at a distance of 5 cm from the nozzel of the silica tube. The quantity of the formed polymer was determined in dependence on the exposure time. The flow of the toluene vapour was $F_t = 0.38$ Pa m^{3}s^{-1}. The quantity of the polymer was determined by the weight of the glass plate.

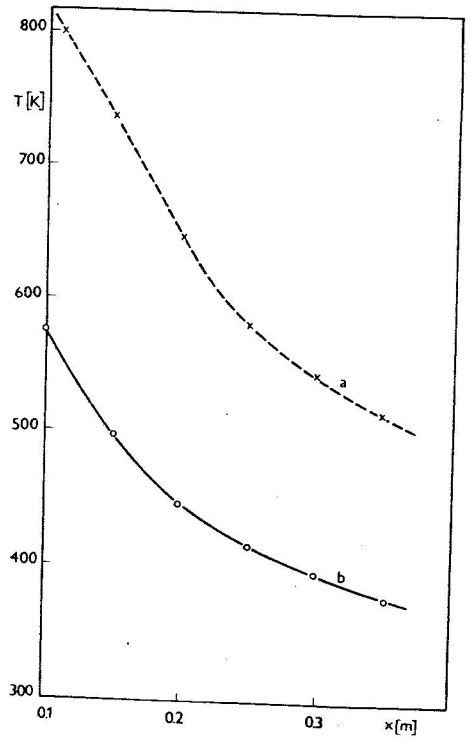

Fig. 5. Course of thermocouples temperature along axis of discharge tube. A) Thermocouple Pt-PtRh, b) Thermocouple Pt-PtRh covered by thin film of glass.

The flow of the toluene vapour was calculated from the measured vapour pressure and the speed of toluene molecules, measured by means of a Pitot tube. The results are shown in Fig. 7. All the measuring was made at a nitrogen flow $F_N = 1.64$ Pa m^{3}s^{-1}.

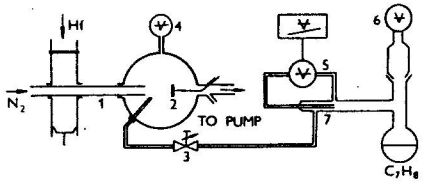

Fig. 6. Apparatus used for study of polymerization. 1 — silica tube, 2 — holder of glass plate, 3 — needle valve, 4 — resistance vacuometer, 5 — differential membrane vacuometer, 6 — membrane vacuometer, 7 — Pitot tube.

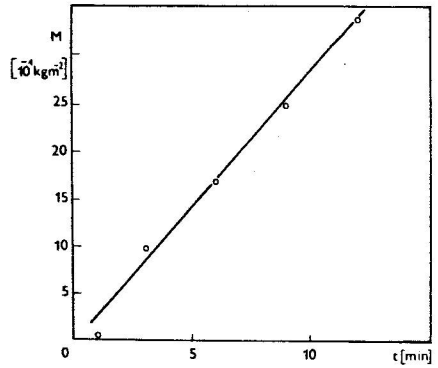

Fig. 7. Time dependence of created polymer quantity.

IV. CONCLUSIONS

The results of measurements show that the active discharge with electrons and ions of high energies is not necessary for the polymerization of aromatic hydrocarbons.

The polymerization is caused, by excited nitrogen molecules or atomized nitrogen.

The polymeric films deposited in the afterglow are smooth, homogeneous and the rate of deposition is comparable with that in commonly used active discharges.

REFERENCES

[1] Phillips, L. F.: Can. J. Chem., *41* (1963), 732, 2060.
[2] Mc Taggart, F. K.: *Plasma Chemistry in Electrical Discharges.* Amsterdam 1967.
[3] Amorous, J., Rapakoulins, D.: *3rd Symp. Int. Chem. Plasma.* Limoges 1977, T1 G 15.
[4] Sabadil, H., Deutsch, H., Görs, E. W.: Report 1975, Sect. Phys. Univ. Greifswald, p. 83.
[5] Hošek, J.: *Aerodynamics of High Speeds.* NV Praha 1949.
[6] Hare, A. L.: *3rd Symp. Int. Chem. Plasma.* Limoges 1977, 52, G 31.
[7] Vinogradov, G. K. et all.: *Plasmochemical Reactions and Processes.* Edited by L. C. Polak, Moskva 1977.

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