STUDY OF POLYMERIZATION IN DESINTEGRATING PLASMA[1)]

A. TÁLSKÝ[2)], Brno

The electron spin resonance method was used for the study of the creation of toluene radicals in decaying nitrogen plasma. The measured dependence of toluene radicals concentration on the toluene vapour flow and the measured value of radicals concentration have shown that a multiple rending of bonds in the benzene kernel takes place.

ИССЛЕДОВАНИЕ ПОЛИМЕРИЗАЦИИ В ДЕЗИНТЕГРИРУЮЩЕЙ ПЛАЗМЕ

В работе описано использование метода электронного спинового резонанса для исследования образования радикалов толуола в дезинтегрирующей азотной плазме. Измеренная зависимость концентрации радикалов толуола от потока паров толуола и изумеренное значение концентрации радикалов показывают, что имеет место многократное расщепление связей в ядре бензола.

I. INTRODUCTION

In a recent paper [1] we have published our results concerning the polymerization of toluene in decaying nitrogen plasma. The effectivity of polymerization has been the same as that in the active discharge. It is well known that the first stage of polymerization is the creation of hydrocarbon radicals. This stage is often called the initiation. The formation of toluene radicals through the interaction of the nitrogen plasma afterglow with molecules of toluene can be described by the equation

$$N_2^* + C_7H_8 \rightarrow C_6H_5-CH_2 + H + N_2 + E_{1\,kin} \quad (1a)$$

$$\rightarrow CH_3-C_6H_4- + H + N_2 + E_{2\,kin} \quad (1b)$$

$$\rightarrow \overset{H\ H\ H\ H\ H\ CH_3}{\overset{|\ \ |\ \ |\ \ |\ \ |\ \ |}{=C-C=C-C=C-C=}} + N_2 + E_{3\,kin} \quad (1c)$$

$$\rightarrow \overset{H\ H\ H}{\overset{|\ \ |\ \ |}{=C-C=C-}} + \overset{H\ H\ CH_3}{\overset{|\ \ |\ \ |}{-C=C-C=}} + N_2 + E_{4\,kin} \quad (1d)$$

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[2)] Department of Physical Electronics, PF UJEP, Kotlářská 2, 611 37 BRNO, Czechoslovakia.

In the first case (1a) the bond in the group CH_3 (bond energy 3.6 eV) is disrupted. In the second case (1b) the bond between H and C in the benzene kernel (bond energy 4.42 eV) is disrupted. The bonds between the carbon in the benzene kernel are disrupted once in the case (1c) and twice in the case (1d) (bond energy 3.4 eV) [2].

In the nitrogen afterglow the maximum energy is transported by long-lived metastable molecules $N_2A^3\Sigma_u^+$ excited vibrationally at the state $v=3$ [3]. The energy of these molecules is $E_n \doteq 6.8$ eV. Then, calculating the kinetic energies, we obtain $E_{1\,kin}=3.2$ eV, $E_{2\,kin}=2.38$ eV, $E_{3\,kin}=3.4$ eV and $E_{4\,kin}=0$. The last case is a resonant case and its probability may be very high.

In the present paper we have studied only the process of creation of free radicals by means of the electron spin resonance (ESR) method.

II. EXPERIMENTAL ARRANGEMENT

We studied the formation of the radicals of toluene by the ESR method in the flow regime. The illustration of the apparatus is given in Fig. 1. Nitrogen (99.97 % N_2) was purified by the catalyst BASF R3–11 and the rest of the hydrocarbons was eliminated in the liquid nitrogen cold trap. The flow was measured by means of the flowmeter UPLS-3.

A needle valve was used for the regulation of the flow and the pressure in the silica discharge tube. The silica tube passes through a cylindrical resonant cavity, used for the excitation of the microwave discharge. The hf power at a frequency of 2350 MHz was supplied by a magnetron generator MG 200, working in

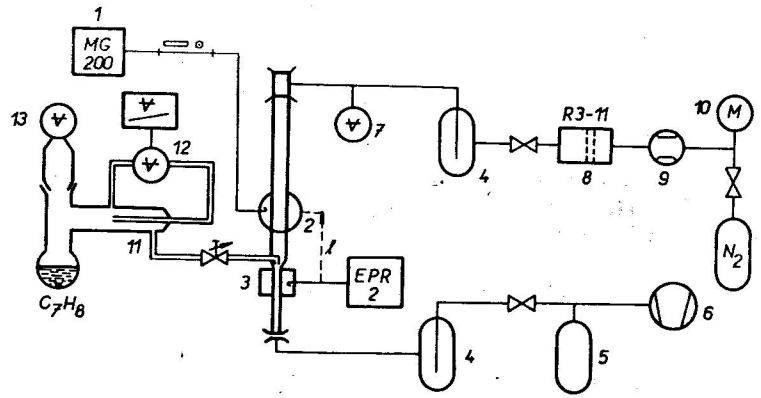

Fig. 1. Apparatus used for the study of radicals formation. 1 – magnetron generator, 2 – discharge cavity, 3 – ESR cavity, 4 – cold trap, 5 – vacuum reservoir, 6 – oil rotary pump, 7 – vacuometer Autovac, 8 – BASF Catalyst R3-11, 9 – flowmeter, 10 – manometer, 11 – Pitot tube, 12 – membrane vacuometer MMCT Varian, 13 – membrane vacuometer.

a continuous regime. The microwave power was adjusted by a change of the anode voltage. The desintegrating nitrogen plasma was pumped through a thin-wall teflon tube inserted into the ESR cavity. The inner diameter of the teflon tube was 0.7 cm. The first derivative of the ESR absorption curve was registered by the EPR-2 measuring apparatus. The pressure in the discharge tube was measured by the Pirrani Autovac 3294 B vacuometer and the Diavac membrane manometer. The vapour of toluene was fed directly into the teflon tube close to the ESR cavity. The quantity of the toluene vapour was determined by means of the Pitot tube.

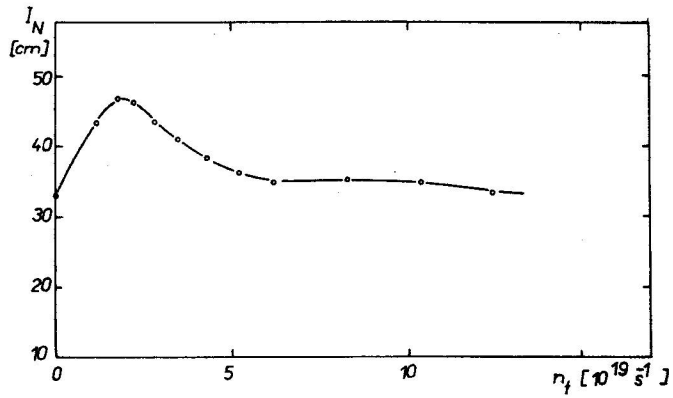

Fig. 2. Intensity of nitrogen atoms spectral line in dependence on toluene flow. Pressure 665 Pa, nitrogen flow $n_N=6.3\times10^{19}$ molecules s^{-1}. Microwave power $P_i=130$ W.

III. THE RESULTS OF MEASUREMENT

The distance of the peaks of the registered first derivative of the absorption curve is marked as intensity I [cm], and if the width of the resonant curve is constant, I is proportional to the number of the uncompensated electron spins.

In the case of a variable width, the value proportional to spin concentration is obtained by multiplying the intensity and width of the resonant curve.

The standard DPPH width a number of uncompensated spins $n_s=0.896\times10^{15}$ was used for the determination of the absolute concentration of atomic nitrogen and free toluene radicals.

The resonant curves of nitrogen atoms, toluene radicals and standard DPPH were measured under the same experimental conditions and the comparison of surfaces below the absorption curves gives the number of the nitrogen atoms and radicals in the ESR cavity.

In pure nitrogen the well-known three-line spectrum arising from the $^4S_{3/2}$ ground state of the N^{14} was registered [4]. If toluene vapour was present, a large

resonant curve of toluene radicals covered the nitrogen spectrum. To examine the mechanism of formation of the toluene radicals in the nitrogen plasma afterglow, the intensity of the nitrogen atoms spectrum and the toluene radicals spectrum was measured at the same time in dependence on the toluene vapour flow.

The results of measurement are shown in Fig. 2 and Fig. 3. The intensity of the nitrogen spectrum grows and reaches the maximum for flows of toluene $n_t = 2 \times 10^{19}$ molecules s^{-1}. For high flows the intensity falls to the primary value.

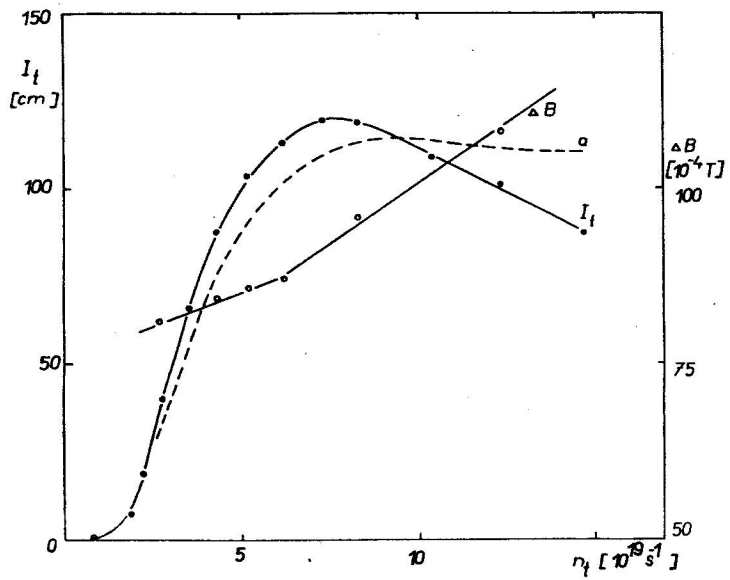

Fig. 3. Dependence of toluene radicals spectrum on toluene flow. I_t – intensity of spectral line, ΔB – width of spectral line, $a = \Delta B I_t$. const.

The intensity of the toluene radicals spectrum reaches the maximum at about the same flow of toluene and that of nitrogen. Measurements were carried out in the nitrogen flow $n_N = 6.3 \times 10^{19}$ molecules per second at the pressure inside the discharge tube of 665 Pa and the microwave power excited discharge $P_i = 130$ W.

In Fig. 3 also the dependence of the width of the resonant curve of toluene radicals on the toluene flow is shown. Curve a) is obtained by the multiplication of the intensity I and the width ΔB and is proportional to the concentration of toluene radicals in the ESR cavity.

Table 1

Microwave power	p_i	130 W
Distance ESR and discharge cavity		0.30 m
Pressure in discharge tube	p	665 Pa
Flow of N_2 molecules	n_N	6.3×10^{19} s^{-1}
Concentration of N_2 molecules		1.7×10^{23} m^{-3}
Concentration of N atoms		1.9×10^{21} m^{-3}
Flow of toluene molecules	n_t	2.5×10^{19} s^{-1}
Concentration of spin in toluene radicals		1.5×10^{24} m^{-3}

The obtained results confirm that the creation of radicals is caused by metastable molecules and not by the direct interaction of toluene molecules with atomic nitrogen.

The absolute value of the concentration of nitrogen atoms and toluene radicals is given in Table 1.

The number of uncompensated spins in toluene radicals is greater than the number of the original toluene molecules. That fact gives evidence of the multiple rending of the bonds in the benzene kernel according to equation (1d).

Fig. 4 shows the dependence of the intensity of the toluene radicals spectrum at the distance of the ESR cavity from the discharge cavity. From Fig. 5 it is evident that the creation of toluene radicals is proportional to the microwave power supplied to the discharge.

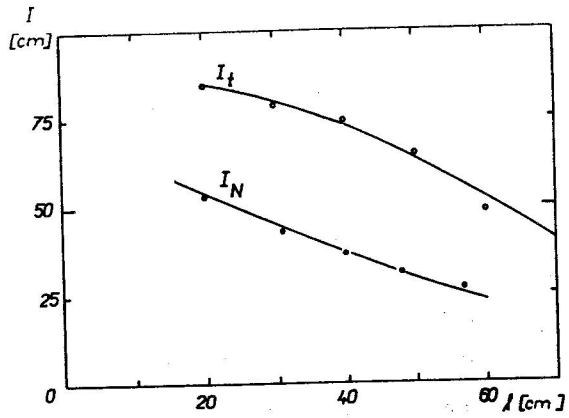

Fig. 4. Dependence of spectrum intensity on distance l of ESR cavity from discharge cavity. I_t – toluen radicals, I_N – nitrogen atoms.

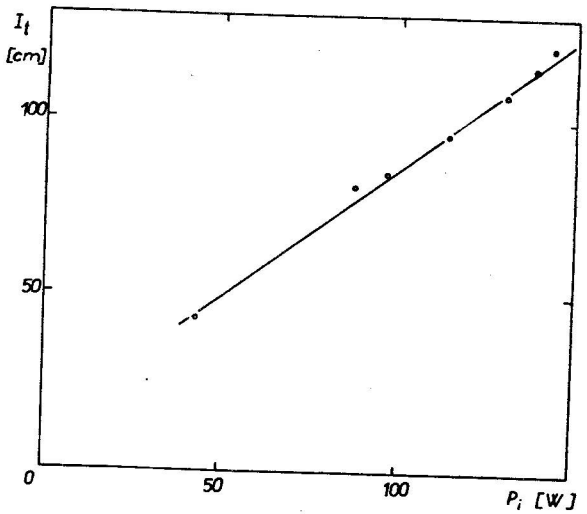

Fig. 5. Dependence of toluene radicals spectrum intensity on microwave power exciting the discharge.

IV. CONCLUSIONS

In the present paper the possibility of application of the ESR method to the study of the toluene radicals creation in the desintegrating nitrogen plasma was demonstrated. The above method was used for determining the dynamics of this plasma — chemical reaction. Measurement results have proved the formation of toluene radicals arising through the interaction of toluene molecules with metastable nitrogen molecules.

The measured value of toluene radicals concentration shows that the inelastic collisions between toluene molecules and nitrogen metastable molecules may lead to the multiple rending of the bonds in the benzene kernel.

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