OXIDATION OF 3,4-BENZOPYRENE IN THE CORONA DISCHARGE*

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The possibility of oxidation of 3,4-benzopyrene in the negative corona discharge has been experimentally studied. Remarkable differences between the oxidation in neutral ozonized air and the oxidation in ionized air have been observed. It can be concluded that in both cases only ozone molecules are effective in the oxidation process. The velocity of oxidation with negative ozone ions is fifty times higher than that of the neutral ozone molecules.

ОКИСЛЕНИЕ 3,4-БЕНЗОПИРЕНА В КОРОННОМ РАЗРЯДЕ

Проведено экспериментальное исследование возможности окисления 3,4-бензопирена в отрицательном коронном разряде. Обнаружены заметные различия между окислением в нейтральном озонизированном воздухе и окислением в ионизированном воздухе. Можно сделать вывод, что в обоих случаях только молекулы озона оказывают влияние на процесс окисления. Скорость окисления в присутствии отрицательных ионов воздуха в пять раз больше скорости окисления в случае нейтралщных молекул озона.

I. INTRODUCTION

The cleaning effect of the negative corona discharge on pollutants in automobile exhaust fumes has been referred to earlier [1]. The infrared analysis showed the growth of C=O bonds in reaction products, which corresponds to the oxidation of polycyclic hydrocarbons occurring in smog. The purpose of experiments reported below is to estimate the contribution of the mentioned oxidation to the cleaning processes of the automobile smog. 3,4-benzopyrene has been chosen from other aromatic substances because its carcinogenicity and harmful effect of the human body are well known [2].

Oxidation of 3,4-benzopyrene in molecular oxygen at laboratory temperatures is negligible [3]. On the other hand the oxidation of benzopyrene in methylene

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chloride with one molecular equivalent of ozone, or the oxidation in nitrogen with 0.2 % of ozone has been reported [3]. A mixture of quinones can be extracted (Fig. 1). Since the production of ozone in the negative corona discharge is a well-known process, oxidation of 3,4-benzopyrene is possible.

Two groups of experiments have been realized. In the first group the oxidation of benzopyrene in ozonized air has been investigated while in the second experiment the effect of negative ions O_2^- and O_3^- has been observed.

II. EXPERIMENTAL APPARATUS

Pure 3,4-benzopyrene was dissolved in isopropanol. The concentration of the solution was 1 mg/100 ml. Circular paper filters with a diameter of 23 mm made of

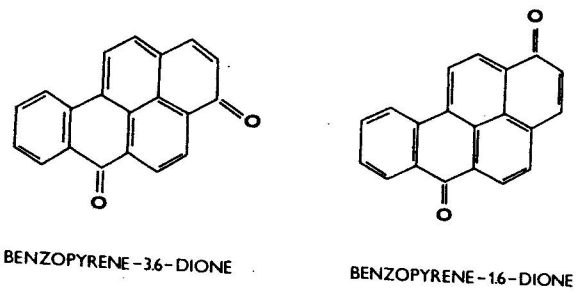

Fig. 1.

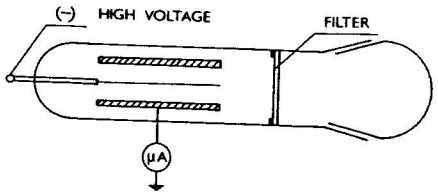

Fig. 2. Discharge tube

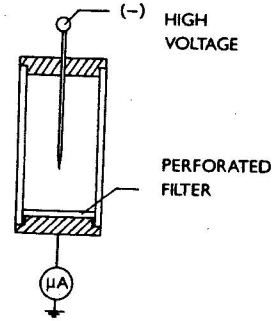

Fig. 3. Discharge tube

chromatographic paper Whatman 31 ET were prepared in the mentioned solution and then dried. Dry impregnated filters were inserted into discharge tubes with ozonized or with ionized air. The exposure time was between 0.5—60 minutes. Exposed filters were eluated in isopropanol p.a. Extracts were evaporated in special vessels [1]. After complete evaporation of isopropanol the inside of the

vessel was rinsed three times with small amount of isopropanol, in order to collect the extracted 3,4-benzopyrene and the reaction products in the tip of the vessel. Then 2.5 ml isopropanol were added and spectra in the visible region were recorded by the spectrometer Specord UV VIS. The absorption coefficient of 3,4-benzopyrene in an isopropanol solution at a 370 nm wave length was employed for the calculation of benzopyrene concentrations in extracts.

Two kinds of discharge tubes with differently placed impregnated filters were employed in the experiments. In the first set of experiments cylindrical electrodes were used with diameters of 0.1 and 15 mm, respectively. Filters were placed outside the discharge space (see Fig. 2). In the second case a needle-to-plane geometry of electrodes was used with a 15 mm distance between the electrodes. Fourty tiny holes were perforated at regular intervals on the whole area of the filters. Perforated and impregnated filters were placed on the plane electrode (see Fig. 3). All experiments were performed at laboratory temperature and at atmospherical pressure.

III. EXPERIMENTAL RESULTS

In the first group of experiments the typical ozonization of benzopyrene was observed. The exposure time varied between 15—60 minutes. The discharge current was constant. The time dependence of the ozone concentration in the discharge tube was measured spectrophotometrically [4]. The equilibrium value of the ozone concentration was 0.24 %. The residue [m] of the unreacted 3,4-benzopyrene on the filters was determined in extracts from the exposed filters for all the exposure times (Fig. 4). The same dependence for the second type of the discharge tube is on the Fig. 5.

There are remarkable differences between both groups of experiments. The short exposure time (30 seconds) is sufficient to the decrease of the unreacted amount of 3,4-benzopyrene on to half of the initial value in ionized air. The experimental method was not able to distinguish between the individual components of the extracted mixtures from the filters. On the other hand, the identity of the visible spectra in both experiments proved the identity of the reaction products. That means that in both cases only the ozonolysis is the effective reaction and the electric field only accelerates the transport of the negative charged ozone ions to the filter.

It follows from the experiments that the observed ozonolysis of 3,4-benzopyrene in the negative corona discharge participates only to a small extent in the cleaning processes of the exhaust automobile fumes [1] and cannot explain the described effects [1]. The mean time 30 seconds necessary for the 50 % cleaning effect measured in our experiments is too long in comparison with the transport time of smog particles in earlier experiments [1]. In the work referred to a 70 % cleaning

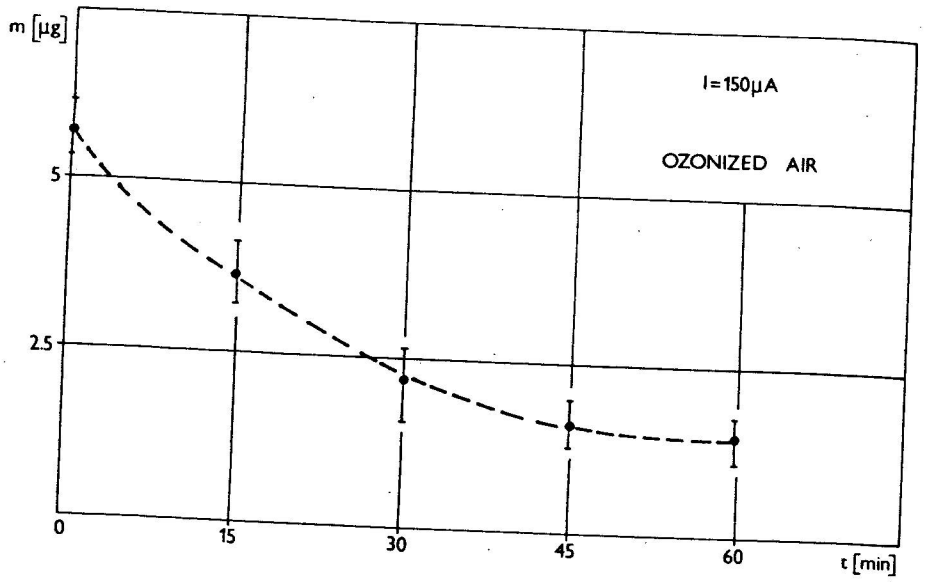

Fig. 4. Dependence of the unreacted amount of 3,4-benzopyrene on the exposure time in ozonized air

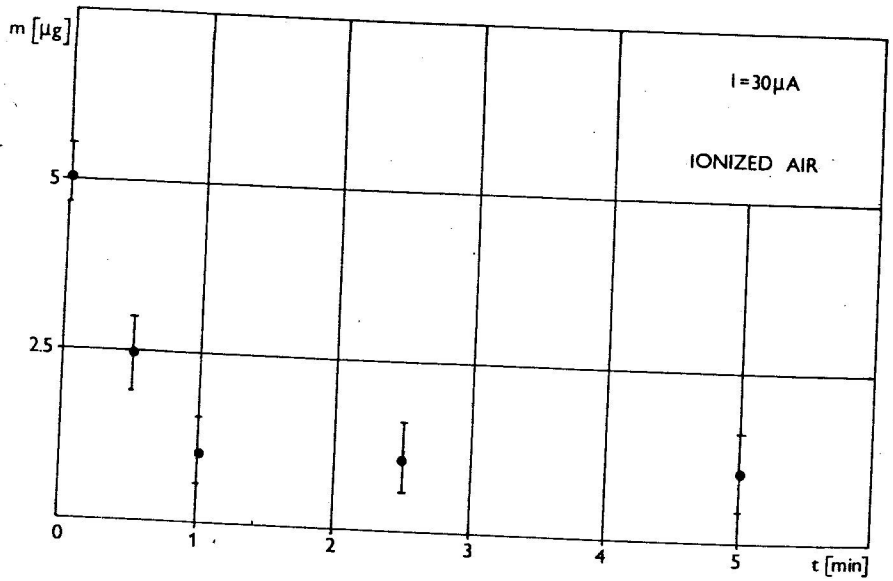

Fig. 5. Dependence of the unreacted amount 3,4-benzopyrene on the exposure time in ionized air

effect was observed, while the transport time of particles in the outer zone of the corona discharge was shorter than 0.1 sec. It seems more probable that the cleaning effect is the electrostatic precipitation of negative ions towards the hydrocarbon molecules.

A second conclusion based on our experimental results can be made. E. J. Moriconi suggested three possible ways of this ozonization of 3,4-benzopyrene [3]. The fifty times higher reaction velocity observed in our experiment for the reaction of O_3^- ions in comparison with the reaction velocity of the neutral ozone suggests that the electrophiling attack of the ozone molecules is more probable than the nucleophiling attack.

REFERENCES

[1] Veisová, M., Skalný, J.: Acta F. R. N. — Formatio et Protectio Naturae, *3* (1977), 183.
[2] Clear, E.: *Polycyclic Hydrocarbons.* Academie Press. London, Springer Verlag, Berlin—Göttingen—Heidelberg 1964.
[3] Moriconi, E. J., Rakoczy, B., O'Connor, W. F.: J. Amer. Chem. Soc., *83* (1961), 4618.
[4] Černák, M., Skalný, J., Veis, Š., Dindošová, D.: Acta phys. slov. ibid.

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