acta phys. slov. 29 (1979), No. 2

DEPENDENCE OF NEGATIVE CORONA CURRENT IN AIR UPON OZONE DENSITY*

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Dependences of the negative corona current upon the ozone density were measured in air at laboratory temperatures and pressures 46.55—86.45 kPa. Using a simple theory the rate coefficient k_3 of the three-body attachment of electrons to ozone molecules was calculated. The obtained values 3.95—4.70×10^{-40} m^6s^{-1} are higher than those for the three-body attachment to molecular oxygen.

ЗАВИСИМОСТЬ ТОКА ОТРИЦАТЕЛЬНОГО КОРОННОГО РАЗРЯДА В ВОЗДУХЕ ОТ ПЛОТНОСТИ ОЗОНА

В работе приведены результаты измерений зависимости тока отрицательного коронного разряда в воздухе от концентрации озона при комнатной температуре в диапазоне давлений 46,55—86,45 кПа. Для вычисления константы скорости k_3 захвата электронов молекулами озона использовалась простая теория. Полученные значения коэффициента в пределах $3{,}95$—$4{,}70 \times 10^{-40}$ м$^{-6}$с$^{-1}$ выше значений для трёхчастичного захвата молекулярным кислородом.

I. INTRODUCTION

In earlier papers [1], [2] the decrease of the negative corona current in air dependent upon time had been qualitatively explained. Better experimental techniques allowed us to measure the mentioned dependences of the corona current upon the ozone density at constant voltage on the electrodes. Experimental curves were used to the calculation of the rate coefficient k_3. The three-body attachment process to ozone was presumed.

II. EXPERIMENTAL APPARATUS

The block diagram of the experimental arrangement is in Fig. 1. Two synchronous time dependences of the corona current and ozone density were taken. Ozone

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* Contribution presented at the Second Symposium on Elementary Processes and Chemical Reactions in the Low Temperature Plasma, Vrátna dolina near Žilina, 1978.

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density was measured from the absorption of UV light in the middle of the Hartley zone at 250 nm. The beam of light was parallel to the inner electrode and crossed the outer zone of the discharge. The light intensity was registered with a photomultiplier and the time dependence of the transmittance plotted on an X—Y plotter. Because the light of the discharge is strong enough and disturbed the measurement of the transmittance, we had to eliminate it. The discharges were created within short intervals with a duration of three seconds. During an interruption the measurement of the transmittance was done. The dependence of the discharge current on the ozone density was constructed from the two measured time dependences.

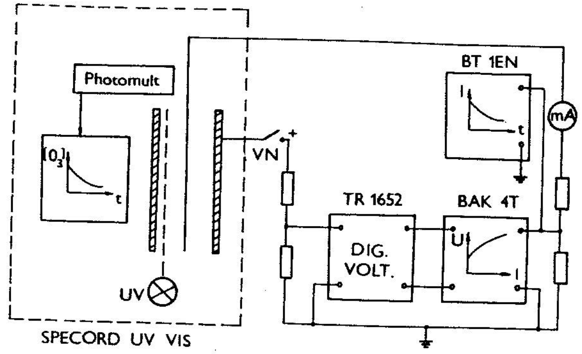

Fig. 1. Block diagram of the experimental apparatus.

The discharge tube consisted of coaxial cylindrical electrodes, an inner one with the radius 0.05 mm and an outer one with the radius 7.5 mm and the length 40 mm. The electrodes were inserted into a glass tube with quartz windows. A parallel tube with the same dimensions was connected with the above by a glass cock. Both tubes were filled with air and then separated by the cock. The parallel tube served as the comparative normal. The experiments were carried out at laboratory temperatures 46.55—86.45 kPa. The air was not treated in any special way.

III. EXPERIMENTAL RESULTS

In Fig. 2 are three of the measured dependences. In all experiments the initial discharge current was 80 μA per cm of the length of the outer electrode. All currents were normalized to this value. The duration of intervals for the creation of the corona discharge and intervals for the measurmeent of the ozone density had no influence on the reproducibility of the curves. The experimental curves were used to calculate the rate coefficient k_3 as follows.

IV. THE CALCULATION OF k_3 AND DISCUSSION

The discharge current at a constant voltage on the electrodes is proportional to the mobility of ions in the outer zone of the corona discharge as it follows from the Townsend formula for the current-voltage characteristic and other formulas [3]. It had been shown [2] that a small part of the electrons issuing from the ionizing zone impinge on the outer electrode. Taking this into account, the effective mobility b of the charged particles in the, outer zone could be employed in formulas for current voltage characteristics

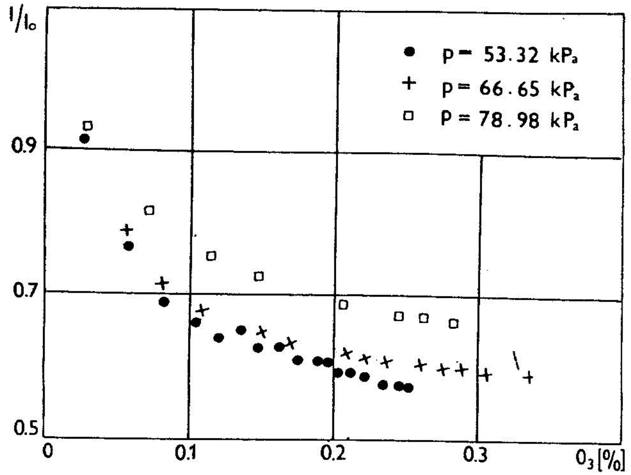

Fig. 2. Dependences of the negative corona discharge current on the ozone density at various pressures.

$$b = \frac{1}{R}\int_0^R \frac{b_e n_e + b_i n_i}{n_e + n_i}\,dr\,, \qquad (1)$$

where R is the radius of the outer electrode; b_e, b_i are the mobilities of electrons and ions; n_e, n_i are the corresponding densities.

Two kinds of ions can be considered O_2^- and O_3^-. They are formed via three-body attachment processses because the pressure is high.

$$e + O_2 + O_2 \xrightarrow{k_2} O_2^- + O_2 \qquad (2)$$

$$e + O_2 + O_3 \xrightarrow{k_2} O_2 + O_3^-\,. \qquad (3)$$

We neglected the charge transfer processes between the two ions because the differences in the mobilities of ions are not higher than 20 %. Other kinds of ions can be neglected in the first estimation [4]. Then we can write for ions densities

$$\frac{dn_e}{dt} = -\frac{dn_i}{dt} \tag{4}$$

$$\frac{dn_e}{dr} = -\frac{b_i}{b_e}\frac{dn_i}{dr}. \tag{5}$$

We have used the transformation

$$\frac{dn}{dt} = v\frac{dn}{dr} = bE\frac{dn}{dr}; \tag{6}$$

v is the drift velocity of the charged particle and E is the intensity of the electric field. If we presupose only (2) and (3), then we can write for the electron density the following equation

$$\frac{dn_e}{dr} = -\frac{r \ln\frac{R}{r_0}}{b_e U}(k_2[O_2][O_2] + k_3[O_2][O_3])\, n_e\,, \tag{7}$$

where $[O_2]$, $[O_3]$ are densities of neutral molecules, r_0 the radius of the inner electrode and U the voltage on the electrodes. After integration (7) we obtain

$$n_e = n_e(r_{ion}) \exp[A(r_{ion}^2 - r^2)]\,, \tag{8}$$

where $n_e(r_{ion})$ is the density of electrons on the boundary of the ionizing zone with the radius r_{ion} and

$$A = \frac{k_2[O_2][O_2] - k_3[O_2][O_3]}{2b_e U} \ln\frac{R}{r_0}.$$

Using expressinon (8) in equation (5) we have

$$n_i = \frac{b_e}{b_i} n_e(r_{ion})(1 - \exp[A(r_{ion}^2 - r^2)])\,. \tag{9}$$

Under the usunal experimental conditions we can neglect the attachment in the ionizing zone and write

$$n_i = \frac{b_e}{b_i} n_e(r_{ion})(1 - \exp[-Er^2]) \tag{10}$$

$$n_e = n_e(r_{ion})\, exp\,[-Ar^2]\,. \tag{11}$$

Substituting (10) and (11) into relation (1), the effective mobility is given by formula

$$b = \frac{b_i}{R_e}\int_0^R \frac{1}{1 - \gamma \exp[-Ar^2]}\, dr\,, \tag{12}$$

where

$$\gamma = \frac{b_e - b_i}{b_e}.$$

Since $\gamma \doteq 1$ and $\exp[-Ar^2] \ll 1$, relation (12) can be written

$$b = \frac{b_i}{R}\int_0^R [1 + \gamma \exp[-Ar^2] + \gamma^2 \exp[-2Ar^2] + \ldots]\, dr \tag{13}$$

Or

$$B = \frac{B_i}{R}\left[R + \int_0^R \sum_{n-1}^{\infty} \gamma^n \exp[-nAr^2]\, dr\right]. \tag{14}$$

Substituting $x = \sqrt{nA}\, r$ into (14), we have

$$b = \frac{b_i}{R}\left[R + \sum_{n=1}^{\infty} \frac{\gamma^n}{\sqrt{nA}} \int_0^{\sqrt{nA}R} e^{-x^2}\, dx\right]. \tag{15}$$

As the value $\sqrt{nA}\, R$ is high enough we put $\int_0^{\sqrt{nA}R} e^{-x^2}\, dx = \sqrt{\pi}/2$. Then expression (15) is transformed into

$$b = b_i\left[1 + \frac{\sqrt{\pi}}{2R\sqrt{A}} \sum_{n-1}^{\infty} \frac{\gamma^n}{\sqrt{n}}\right]. \tag{16}$$

The following condition can be applied to the estimation of the latter progression

$$\sum_{n-1}^{\infty} \frac{\gamma^n}{\sqrt{n}} > \int_1^{\infty} \frac{\gamma^x}{\sqrt{x}}\, dx > \sum_{n=2}^{\infty} \frac{\gamma^n}{\sqrt{n}}, \tag{17}$$

and so

$$\sum_{n=1}^{\infty} \frac{\gamma^n}{\sqrt{n}} = \gamma + \sum_{n=2}^{\infty} \frac{\gamma^n}{\sqrt{n}} < \gamma + \int_1^{\infty} \frac{\gamma^x}{\sqrt{x}}\, dx \lesssim \gamma + \sqrt{\frac{\pi}{-\ln\gamma}}. \tag{18}$$

As $\gamma \doteq 1$, we neglect γ in the latter formula. Using this estimation in the form (16), we have obtained the final form for the effective mobility of charged particles in the outer zone of the discharge

$$b = b_i\left[1 + \frac{\pi}{2R\sqrt{-A \ln\gamma}}\right]. \tag{19}$$

Formula (19) can be employed to the calculation of the rate coefficient k_3 if everything else is known. Under our conditions we have used the following constants: $k_2 = 1.9 \times 10^{-42}$ $m^6 s^{-1}$, $b_e = 0.8\, m^2 v^{-1} s^{-1}$, $b_i = 2.3 \times 10^{-4}\, m^2 v^{-1} s^{-1}$. Us ing these constants, the rate coefficient k_3 *has the form*

$$k_3 = \frac{4x10^{-41}}{[\%\ O_3]}\left\{\frac{8.07x\ 10^{-3}\ U}{\left[m\left(1 - \frac{0.09}{\delta}\sqrt{\frac{U}{\delta}}\right) - 1\right]^2 \delta^3} - 1\right\}, \tag{20}$$

Table 1

p [kPa]	86.45	79.80	73.15	66.50	59.85	53.20	46.55
k_3 [m^6s^{-1}] × 10^{40}	4.60	4.70	4.35	3.96	4.00	4.10	3.95

δ is the relative density of air and [% O_3] is the percentage concentration of ozone in the discharge tube.

The rate m is defined as $I/I_0 = b/b_0 = m$ and is measured experimentally. The rate koefficient k^3 was calculated by formula (20) for all the measured pressures. The calculation was made at different points of the individual curves $I/I_0 = f$ ([% O_3]). The average values for the measured pressures are in Table 1.

The calculated values are hundred times higher than the equivalent value for the attachment to molecular oxygen. The existence of process (3) was presupposed by V. Samojlovich and his coworkers [5]. They had concluded that the attachment coefficient for ozone in mixtures with nitrogen or argon is 10—1000 times higher than the same coefficient for oxygen. Their experiments had been carried out at pressures lower than 5 kPa. The existence of the presupposed three-body attachment to ozone can be indirectly predictable from mass spectrometric studies of R. K. Curran [6]. The appearence of the weak peak in the mass spectrum at the maximum working pressure 0.1 Pa corresponds to ions O_3^-. As the pressure was very low, the yield of O_3^- ions is low. The quadratic dependence of the yield on pressure for the three-body process is known. At low pressures the predominant process of interaction of electrons with ozone molecules is the dissociative attachment [7]

$$e + O_3 \rightarrow O^- + O_2 .$$

The experiments prepared for the study of the dependence of the negative corona current in $O_2 + N_2$ mixtures on the ozone density may throw more light on the presupposed process.

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Received October 4th, 1978