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THE NEGATIVE CORONA DISCHARGE IN A MIXTURE OF AIR WITH HALOCARBONS IN THE CONCENTRATION RANGE OF 0—200 ppm[1)]

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The influence of the concentaration of halocarbon upon the discharge current of the negative corona discharge in air was studied. In a mixture of air with halocarbon a significant decrease of current compared with the discharge current in the negative corona discharge in air was measured. This is caused by a dissociative attachment of electrons on the halocarbon molecules. The values of the rate coefficients of the electron attachment for various halocarbons were estimated from the current decrease.

I. INTRODUCTION

The influence of halocarbon impurities upon the discharge current of the negative corona in air has been described earlier [1], [2]. The decrease of the discharge current due to the addition of halocarbon vapour to pure air has been observed to be evident even at very lowe densities of halocarbons in air. In the present paper, the rate coefficients for the dissociative attachment of electrons to halocarbons are assumed. The values of the rate coefficients for various halocarbon molecules are estimated from the mentioned current decrease.

II. THEORETICAL CONSIDERATIONS

Electrons created in the ionization region of a negative corona discharge in pure air are captured by oxygen molecules due to the dissociative attachment

$$e + O_2 \xrightarrow{k_1} O^- + O, \qquad (1)$$

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where k_1 is the rate coefficient. The attachment is effective only in the vicinity of the negative electrode. This reaction is followed by a sequence of reactions in which ions $CO_3^- (H_2O)_n$ are created. The ions $CO_3^- (H_2O)_n$ are the dominant types of ions in the drift region of the negative corona discharge in air atmospherical pressure [3]. The presence of halocarbon molecules in the discharge space gives electrons the chance to get attached also due to the competitive reaction

$$e + \text{R-X} \xrightarrow{k_x} \text{R} + \text{X}^-, \tag{2}$$

where R—X is the molecule of halocarbon containing the halogen atom (F, Cl, Br, I) and k_x is the rate coefficient for the dissociative attachment of halocarbons. This reaction is very effective for electrons with energies slightly above the thermal energy, therefore the reaction is effective also in the drift region of the discharge. Due to this reaction the electrons not attached to oxygen molecules can be attached to halocarbon molecules in the whole discharge space. As a result of this attachment the total number of free electrons is reduced and the discharge current is lower in comparison with the current in pure air at the same voltage on the electrodes.

For the negative corona discharge current I between coaxial electrodes (inner radius r_0 and outer radius R), the following formula was derived [4]

$$I = \frac{8\pi\varepsilon_0(U - U_0)\,Ub_i}{R^2 \ln R/r_0}\left(1 + \frac{\pi}{2R\sqrt{A|\ln\gamma|}}\right), \tag{3}$$

where U is the voltage on electrodes, U_0 is the corona onset voltage, b_i is the ion mobility and $\gamma = (b_e - b_i)/b_e$ (B_e — electron mobility). The term A contains the information about the electron attachment to electronegative molecules. The latter can be written as

$$A = \frac{\ln R/r_0}{2b_e U}\sum_i k_i[M_i], \tag{4}$$

where b_e is the mean mobility of electrons in the discharge space and k_i are the rate coefficients for the attachment reactions of electrons to the electronegative components i of air with the particle densities $[M_i]$. For the pure air we suppose only an attachment to oxygen molecules, therefore

$$A_0 = \frac{\ln R/r_0}{2b_e U}\,k_1[O_2], \tag{5}$$

while in the air containing halocarbon molecules the term A can be expressed as follows

$$A = \frac{\ln R/r_0}{2b_e U}\left(k_1[O_2] + k_x[\text{R-X}]\right). \tag{6}$$

The ratio of the discharge currents I/I_0 (I_0 is the current in pure air) can be expressed from (3), (5) and (6) by the following formula

$$\frac{I}{I_0} = \frac{1 + \dfrac{\pi}{2R\sqrt{A|\ln\gamma|}}}{1 + \dfrac{\pi}{2R\sqrt{A_0|\ln\gamma|}}}. \tag{7}$$

Since

$$\gamma = \frac{b_e - b_i}{b_e} \approx 1$$

the validity of the relation

$$\frac{\pi}{2R\sqrt{A|ln\,\gamma|}} \gg 1 \tag{8}$$

can be accepted. using this assumption from (7) there follows

$$\frac{I}{I_0} = \sqrt{\frac{k_1[O_2]}{k_1[O_2] + k_x[\text{R-X}]}}. \tag{9}$$

Thus the ratio k_x/k_1 can be estimated from the experimental I/I_0 values using the formula

$$\frac{k_x}{k_1} = \frac{[O_2]}{[\text{R-X}]}\left[\left(\frac{I_0}{I}\right)^2 - 1\right]. \tag{10}$$

III. EXPERIMENTAL RESULTS AND DISCUSSION

A system of coaxial cylindrical electrodes was used for the experiments. Details concerning the experimental apparatus were published earlier [1]. The experiments were carried out in flowing ambient air. The influence of halogenated alkanes (CCl_4, $C_2h_2Cl_4$, $CHCl_3$), alkanes (C_2Cl_4, C_2HCl_3) and arenes (C_6H_5Cl, C_6H_5Br, C_6H_5I) upon the discharge current of the negative corona in air was studied.

The onset voltage of the corona discharge U_0 depended neither upon the flow velocity of air, nor on the density of halocarbon vapours in air within the whole interval of the densities (0—200) ppm.

The measured dependences $\Delta I = I_0 - I = f(c)$, where c is the density of halocarbons in air, are shown in Figs. 1, 2, 3. The comparative current in air was kept constant in all experiments $I_0 = 120\ \mu A$. it may be seen from these figures that the discharge current is substantially reduced due to the addition of halocarbons to the air. The ΔI value depends strongly upon the number of the substituted chlorine atoms on the same hydrocarbon radical (Fig. 1), which means that the main part of the halocarbon molecules is destroyed due to the sequential reactions

$$e + C_xH_yCl_z \rightarrow Cl^- + C_xH_yCl_{z-1} \xrightarrow{e} Cl^- + C_xH_yCl_{z-2}. \qquad (11)$$

Only a slight effect of radicals can be deduced from the experiments (Fig. 2.).

More important is the effect of the substitued atoms on the same radical, as can be seen from Fig. 3. An analogous effect was observed by Alge et al. [5], who found that the rate coefficient for the dissociative attachment of electrons with CH_3I is substantially higher than that with CH_3Br.

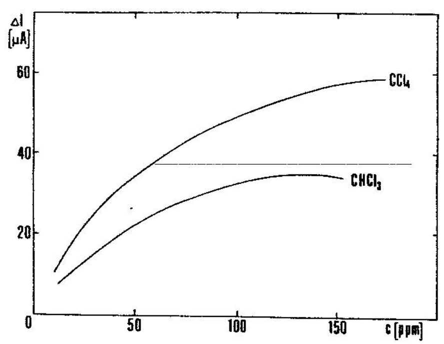

Fig. 1. Dependence of the discharge current of the halocarbon density for CCl_4 and $CHCl_3$.

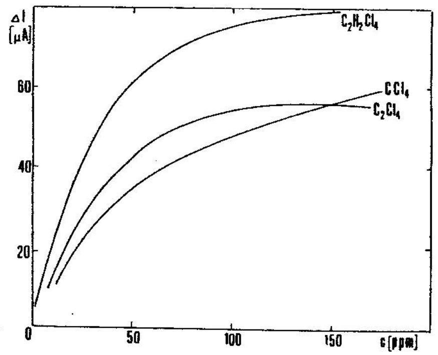

Fig. 2. Dependence of the discharge current of the halocarbon density for $C_2H_2Cl_4$, C_2Cl_4 and CCl_4.

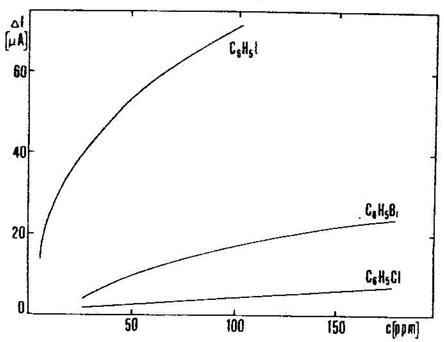

Fig. 3. Dependence of the discharge current of the halocarbon density for C_6H_5I, C_6H_5Br and C_6H_5Cl.

Table 1

Rate coefficients for the dissociative attachment of electrons to various halocarbon molecules k_x $[cm^3 . s^{-1}]$

	C_6H_5Cl	C_6H_5Br	C_6H_5I	CCl_4	$CHCl_3$	C_2HCl_3	C_2Cl_4	$C_2H_2Cl_4$
our	3 10^{-10}	7.8 10^{-10}	9.5 10^{-9}	2.8 10^{-9}	3.6 10^{-9}	2.2 10^{-9}	3.6 10^{-9}	6.7 10^{-9}
others	9 10^{-10}	7.1 10^{-10}	?	2.4 10^{-7}	3.4 10^{-9}	1.7 10^{-9}	?	?

All constants were taken from [7]

Experimental data $\Delta I = f(c)$ were used for the calculation of the rate coefficients k_x for various compounds. These rates were calculated by using the simple formula (10), in which k_1 was equal to $1 \times 10^{-12}\ cm^3 s^{-1}$ as the mean value of the known values of other authors. The values of k_x were calculated as the mean value from calculations for 10 different densities. The standard deviation was less than 30 percent of the mean value. The summarized values of k_x obtained from the calculations are given in Table 1 together with some previous values of k_x determined by other authors. Except for CCl_4, a reasonable agreement of our data with those of other authors can be seen. It must be noted that our data are the mean values of k_x valid for the interval of electron energies of 1—10 eV, while the data of other authors are determined for nearly thermalized electrons. As it follows from theoretical calculations [6], the attachment coefficient for CCl_4 decreases very strongly if the ratio E/N increases. This fact can explain the discrepancy between our value of the rate coefficient for CCl_4 and the values of other authors.

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НЕГАТИВНЫЙ КОРОННЫЙ РАЗРЯД В СМЕСИ ВОЗДУХА С ГАЛОИДЗАМЕШЕННЫМ УГЛЕВОДОРОДОМ В КОНЦЕНТРАЦИИ ОТ 0 ДО 200 ppм

В работе изучено влияние концентрации галоидзамещенного углеводорода на ток разряда в негативном коронном разряде в воздухе. В смеси воздуха с галоидзамещенным углеводородом была измерена заметное понижение тока по сравнению с разрядным током в негативном коронном разряде. Это обуславливается диссоциативным прицоединением электронов к молекулам галоидзамещенного углеводорода. На основе уменьшения интенсивности тока были оценены значения коэффициентов скорости присоединения электронов для разных галоидзамещенных углеводородов.