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An analysis of mass spectrometric study of negative ions extracted from negative corona discharge in air

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Dedicated to Professor Tilmann D. Märk on the occasion of his 60th birthday and in recognition of his important contribution to study of electron impact processes relevant to discharge plasmas.

Abstract

In this paper we report the detection and mass analysis of negative ions formed in a negative corona discharge using both dry and ‘wet’ air at pressures between 5 and 27 kPa. The yield of individual ions is strongly affected by trace concentrations of ozone, nitrogen oxides and water vapour. In dry air the dominant ion is CO_3^-. In presence of water this is converted very efficiently to cluster ions containing one and more water molecules. If ozone and nitrogen oxides are added, or are produced in discharge in sufficient concentrations, NO_3^- ions and NO_3^- hydrated clusters are formed. Ozone concentrations greater than 25 ppm are sufficient to completely suppress the appearance of O_2^- ions and its clusters both in dry and wet air. Such observations allow a comprehensive review of the physical and chemical processes within the discharge.

Keywords: Corona; Ozone; Dry air

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1. Introduction

The identification of negatively charge ions in corona discharges is an efficient method for the study of elementary processes active in the discharge. The knowledge of the ion composition can contribute towards an understanding of the role of negative ions in devices using corona discharges, for example, electrostatic precipitators air cleaners, ionisers and the devices used for corona treatment of polymer surfaces.

As it has been discussed earlier, the mass spectrometric analysis of ions formed in a corona discharge is a complicated diagnostic technique [1–3]. This has nevertheless been used by many authors in both pure gases and gaseous mixtures, CO_2 and N_2O [4], CO_2 and O_2 [5], SF_6 and mixtures $SF_6 + H_2O$, SF_6 + Freon 113 [6], SF_6 [7,8], $SF_6 + H_2O$ [9], C_3F_6 [10].

Most of studies have been conducted in air over a wide pressure range (0.2–100 kPa) and with different relative humidities of air (from dry up to air close to air of 100% of relative humidity) [11–25]. The pioneering work of Shahin conducted over a wide-pressure range (up to 100 kPa) found NO_2^- and NO_3^- ions were dominant in negative corona discharge fed by dry air at low pressures [11]. These results were subsequently contradicted by Gardiner and Craggs [12] who at 1 kPa observed predominately CO_3^- ions, whose abundance was more than double that of O_3^-, O^- and CO_4^-. Only traces of O_2^- ions were detected. These results are in good agreement with our previous measurements conducted in air at a pressure 5 kPa at low discharge current [20].

The apparent differences between these experimental results might be due to different water concentrations in the ‘dry air’. The removal of the water may be accompanied by removal of at least part of the CO_2 component. The removal of CO_2 was shown by Shahin [11] to lead to a dramatic reduction in relative yield of CO_3^- ions. His observation was confirmed by Gravendeel and co-workers [21,22] who used synthetic air. The yield of CO_3^- ions was observed to be an order of magnitude below the yield O_3^- ions. Instead of these the NO_3^- ions were observed with intensity

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comparable to the ozone ions. At pressures close to 40 kPa the NO_3^- were dominant.

The water content substantially affects the yields of individual ions, although it must be noted that the effect of water on the product distribution of ions is less pronounced than in the case of positive corona discharge [11,26]. Almost all the parent ions found in dry air can form clusters with water [16,18,19,24], except the CO_4^- ions, which are destroyed even at the lowest water concentrations. With increasing discharge current (hence increasing electric field in the drift region of the discharge gap), the number of water ion clusters decreases [16].

In present paper the effect of ozone and nitrogen oxide impurities in both dry and humid air are explored for the first time in a controlled manner allowing us to interpret these earlier results and quantify the importance of controlling trace compounds in any negative ion air discharge.

2. Experimental apparatus

The apparatus used is that of the ELIOP group at NTH University of Trondheim, Norway and is shown schematically in Fig. 1. It consists of three main parts: (i) a discharge volume, (ii) an intermediate volume containing an electrode system to focus the extracted ions into (iii) the mass spectrometer. The discharge chamber contained point-to-plane electrodes for generating the corona discharge. The total volume of the stainless steel discharge chamber was 10 dm^3. A Pt wire ended by a tip with radius of 0.1 mm was fixed on axis separated from a gold plated brass plane electrode at a distance 10 mm. The electrodes were fed by a stabilised HV power supply. An extraction foil was placed in the central part of the plane electrode. Different type of extraction foils were tested [20]. Two of them were selected for presented experiments, both made of stainless steel foil, thickness of 10 μm within which was placed a nearly round orifice with diameter 10 and 30 μm, respectively. The extracted ions expand through the orifice into an intermediate region where the gas is pumped by diffusion pump away while the ions are focused onto a 2 mm in diameter skimmer opening leading to Balzers OMG 101 quadrupole spectrometer, which was pumped separately. The mass selected ions were finally detected by a photomultiplier. The relative yield Y_r of ions having a mass per charge smaller than 100 was calculated from the measured absolute yield of ions i-type in spectra Y_i by formula:

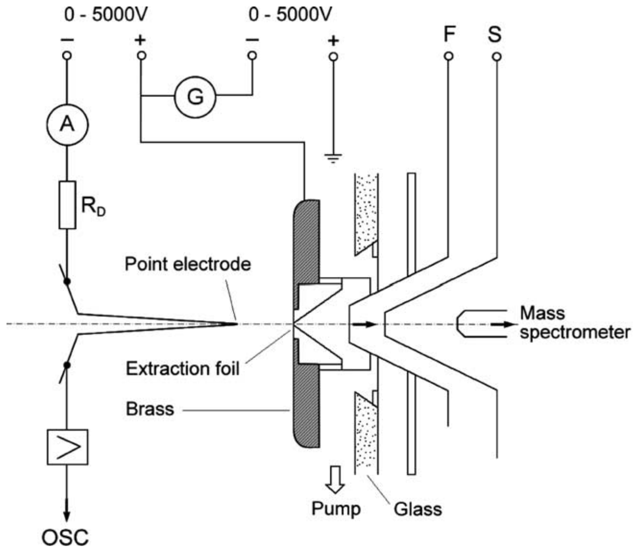

Fig. 1. Schema of experimental apparatus.

$$Y_r\ (\%) = \frac{Y_i}{\sum Y_i} \times 100$$

Both ‘wet’(ambient) and dry air was used in our experiments. Dry air was prepared from ambient air by removal of water by two step procedure. The humid ambient air was passed through a trap cooled by CO_2 ice and finally through a trap filled with dry P_2O_5. A flow rate 50 cm^3/s was maintained by an electronically regulated valve. In order to study the effect of ozone concentrations on the relative ion yields ozone was prepared using a coaxial cylindrical corona discharge ozoniser. The ozoniser was fed by a separate high voltage power supply. It was not possible to measure ozone concentrations directly in the inlet of air into the discharge gap. Therefore the ozone concentration was measured as a function of discharge current in ozoniser in separate experiment by using UV light absorption spectrometry. The current was calibrated as a function of ozone concentration at a constant flow rate 50 cm^3/s. The calibrated ozoniser was finely used as a source of ozonised ambient air.

The maximum air pressure in the discharge gap was 27 kPa and was limited by efficiency of the diffusion pump used for pumping of the intermediate space (see Fig. 1). To exclude ion–molecule reactions in the intermediate space, the pressure in this was kept always below the value of 0.2 Pa. At such critical value the mean free length of neutral gas molecules was comparable with the distance between extraction foil and the entrance to the mass spectrometer (drift length of ions in the intermediate space). At lower pressures in the discharge gap, the pressure in the intermediate space was considerably below the mentioned critical value. Hence in our experiments the effect of ion–molecule reactions in the intermediate space is only marginal.

3. Experimental results and discussion

Our experimental results may be conveniently divided into two groups: (i) results obtained in dry and (ii) in ‘wet’ air. In wet air the effect of ozone on abundance of ions was observed in flowing regime and also under static conditions (in which the gas flow through the discharge gap was stopped). In dry air only the static regime was investigated since passing ozonised air through the two drying traps reduced the concentration of ozone to an unknown value. The effect of

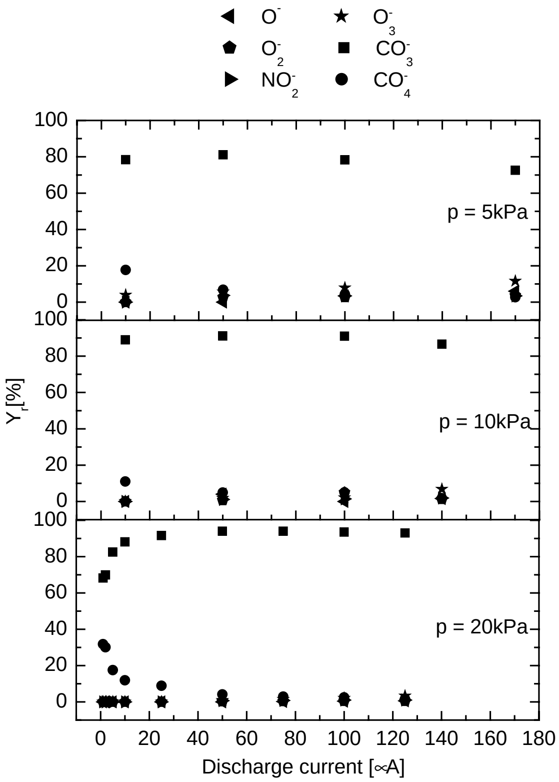

Fig. 2. The dependence of relative yield of individual negative ions in dry air at three different pressures on the discharge current.

the gas pressure in discharge gap and the discharge current was also investigated.

3.1. *Results in dry air*

The relative yields of observed ions for three different pressures in flowing dry air are shown as a function of discharge current in Fig. 2. It is evident, that the $CO_3{}^-$ ion is the most abundant negative ion at pressures from 5 up to 20 kPa. Shahin [11] and Gardiner and Craggs [12] also reported the dominance of $CO_3{}^-$ ions over similar range of gas pressures. In contrast Gravendeel and co-workers [21,22] found the $O_3{}^-$ ion to be dominant in spectrum. The reason for such disagreement is most likely the low concentration of CO_2 in synthetic air that Gravendeel et al. used in their experiment. This was close to 0.1 ppm what is substantially below the standard concentration of CO_2 in ambient air (≈300 ppm). The high sensitivity of abundance of $CO_3{}^-$ ions in spectra taken in ambient air against the changes in CO_2 concentration was reported also earlier by Shahin [11].

Gas pressure and the discharge current considerably affect the ion yield. With increasing gas pressure the relative yield of $CO_3{}^-$ ions increases while other ions are removed from the spectra. At a pressure of 27 kPa only $CO_3{}^-$ and $CO_4{}^-$ ions were observed. This is, however, in contrast to the observations of Gardiner and Craggs [12] who registered at 4 kPa relatively high yield of O^- ions (comparable with $CO_4{}^-$ yields). The signal of O^- ions in our experiments was found to be considerably smaller than that of the $CO_4{}^-$ ions. Moreover, $CO_4{}^-$ was not observed in measurements [11,16,21,22].

To understand the results we must appreciate an important distinction between the glow region near the tip of the HV electrode and the drift region through which ions are transported towards the plane electrode. At high electric fields, typical for glow region (≈100 Td) the dissociative electron attachment reaction [27]:

$$e + O_2 \rightarrow O^- + O, \quad k_1 = f\left(\frac{E}{N}\right) \tag{1}$$

is the source of primary O^- ions. In the presence of carbon dioxide these are converted via the fast three body ion–molecule reaction to form $CO_3{}^-$ ions [28]:

$$O^- + CO_2 + M \rightarrow CO_3{}^- + M, \quad k_2 = 1 \times 10^{-29}\,\mathrm{cm^6/s} \tag{2}$$

Dissociative electron attachment to CO_2 molecules can be neglected because of the low concentration of carbon dioxide in air. If the concentration of ozone in the discharge gap is closed to zero, the three body process [27]:

$$O^- + O_2 + M \rightarrow O_3{}^- + M, \quad k_3 = 3.3 \times 10^{-31}\,\mathrm{cm^6/s} \tag{3}$$

is the only potential source of $O_3{}^-$ ions. The characteristic reaction time for processes (2) and (3) at the maximum working pressure in our experiment (27 kPa) is $1/k_2[CO_2][M] = 6.2\,\mu s$ and $1/k_3[O_2][M] = 0.3\,\mu s$, respectively. It is therefore evident that the O^- ions generated in the glow region would be predominately converted to $O_3{}^-$ ions in this region because the transport time of O^- ions trough the glow region is of order of microseconds.

There are several processes that may lead to $O_3{}^-$ decomposition [27] but only two are important in the current discharge conditions [27,28]:

$$O_3{}^- + CO_2 \rightarrow CO_3{}^- + O_2, \quad k_4 = 6 \times 10^{-10}\,\mathrm{cm^3/s} \tag{4}$$

$$O_3{}^- + M \rightarrow O_3 + M + e, \quad k_5 = 2.3 \times 10^{-11}\,\mathrm{cm^3/s} \tag{5}$$

In contrast, in the absence of nitrogen oxides, the $CO_3{}^-$ ion is very stable with the reaction [21]:

$$CO_3{}^- + O_2 \rightarrow CO_2 + O_3{}^-, \quad k_6 = 7 \times 10^{-14}\,\mathrm{cm^3/s} \tag{6}$$

being slow.

The following kinetic equations may be used for the estimation of an equilibrium value for the ratio of $O_3{}^-$ and $CO_3{}^-$ concentrations:

$$\begin{aligned}\frac{d[O_3{}^-]}{dt} &= k_3[O^-][O_2][M] + k_6[CO_3{}^-][O_2] \\ &\quad - k_4[O_3{}^-][CO_2] - k_5[O_3{}^-][M]\end{aligned} \tag{7}$$

$$\frac{d[CO_3^-]}{dt} = k_2[O^-][CO_2][M] + k_4[O_3^-][CO_2] - k_6[CO_3^-][O_2] \quad (8)$$

In equilibrium $d[O_3^-]/dt = d[CO_3^-]/dt = 0$. Hence:

$$\frac{[O_3^-]}{[CO_3^-]} = \frac{k_6(A+1)[O_2]}{k_4(A+1)[CO_2] + k_5[M]} \quad (9)$$

where $A = k_3[O_2]/k_2[CO_2]$.At a pressure of 27 kPa and with a standard concentration of carbon dioxide in air (approximately 300 ppm) the ratio $[O_3^-]/[CO_3^-]$ calculated from (9) is close to 0.01, hence no more than 1% of O_3^- ions should appear in the ionic yield. This is in excellent agreement with our experimental results. The high concentration of O_3^- ions found by Gardiner and Craggs [12] at pressures 1.33 and 2.66 kPa, confirmed also by Shahin [11], must then be explained by existence of a secondary source of O_3^- ions. If the concentration of ozone in the glow region is of range of 100 ppm the ion O_3^- can be formed via charge transfer reaction [27]:

$$O^- + O_3 \rightarrow O_3^- + O, \quad k_{10} = 5.3 \times 10^{-10}\ \mathrm{cm^3/s} \quad (10)$$

With decreasing pressure reaction (10) prevails. In our experiment, conducted in flowing regime, the ozone concentration in the discharge gap was very low, close to zero, due to intensive airflow through the discharge reactor, while in experiments conducted by Gardiner and Craggs [12] the flow rate was limited only by leaking air through the extraction orifice. Hence one can presume that the concentration of ozone was considerably higher in the experiments of Gardiner and Craggs due to the substantially longer retention time of air in the discharge gap. The production of O_3^- ions is then expected to increase with increasing discharge current.

The second most dominant ion detected in our experiments as well as in experiments performed by Gardiner and Craggs [12], is CO_4^-. The ion CO_4^- is formed from O_2^-, which is generated in the negative corona discharge in air, especially in the drift region [27]:

$$e + O_2 + M \rightarrow O_2^- + M, \quad k_{11} = f\left(\frac{E}{N}\right) \quad (11)$$

It should be noted that number of such ions is considerably smaller in comparison with O^- ions generated in glow region, because most of the free electrons are lost via dissociative attachment (1). The ions CO_4^- are formed via three-body process [21]:

$$O_2^- + CO_2 + M \rightarrow CO_4^- + M, \quad k_{12} = 1 \times 10^{-29}\ \mathrm{cm^6/s} \quad (12)$$

This is competitive with another three-body process producing O_4^- [21]:

$$O_2^- + O_2 + M \rightarrow O_4^- + M, \quad k_{13} = 5.1 \times 10^{-31}\ \mathrm{cm^6/s} \quad (13)$$

If ozone and NO_2 are produced in the discharge gap the O_2^- ions can be also depleted via the two binary reactions [21,27]:

$$O_2^- + O_3 \rightarrow O_3^- + O_2, \quad k_{14} = 3 \times 10^{-10}\ \mathrm{cm^3/s} \quad (14)$$

$$O_2^- + NO_2 \rightarrow NO_2^- + O_2, \quad k_{15} = 2 \times 10^{-9}\ \mathrm{cm^3/s} \quad (15)$$

At a pressure of 27 kPa the rate of reactions (13–15) are comparable if $[O_3] > 2500$ ppm and $[NO_2] > 380$ ppm, respectively. Both values are relatively high and should not be reached in our discharge operating under the fast flow conditions. As it follows from results published recently by Ross and Bell [29], concentration of ozone produced in point-to-plain negative corona discharge was much higher (approximately by factor of 10) than the total concentration of nitrous oxides. If we presume linear increase of ozone concentration with discharge current the ozone concentration at current of 100 μA should be below 1000 ppm in conditions of Ross and Bell. The flow rate in our flowing conditions was considerably higher; hence the ozone concentration should have been substantially below the value of 1000 ppm. Therefore the contribution of processes (14) and (15) in O_2^- balance is only marginal.

The ion O_4^- is not stable and is effectively converted to CO_4^- [28]:

$$O_4^- + CO_2 \rightarrow CO_4^- + O_2, \quad k_{16} = 4.8 \times 10^{-10}\ \mathrm{cm^3/s} \quad (16)$$

or is decomposed back to the parent ion O_2^- [21]:

$$O_4^- + M \rightarrow O_2^- + O_2 + M, \quad k_{17} = 4.8 \times 10^{-10}\ \mathrm{cm^3/s} \quad (17)$$

The last process is faster and represents the destruction of cluster ions $O_2^-{\cdot}O_2$ in collisions with neutral gas due to acceleration of such negative clusters in electric field. The rate constant k_{17} corresponds to ions at thermal equilibrium. One can easily surmise that this rate must increase dramatically with increasing electric field. This may explain the fact why only traces of O_4^- ion were experimentally observed [16].

Ross and Bell using the IMS technique [29] have recently confirmed the formation of CO_4^- ions in negative corona discharge fed by air. They have shown that the abundance of such ion is very sensitive to the presence of ozone. If ozone is removed from the discharge gap the CO_4^- ion dominates the spectrum [29]. As shown in Fig. 2 the yield of CO_4^- ions is dramatically reduced with increasing discharge current. The increase in discharge current leads to increase in ozone concentration therefore reduction in CO_4^- ionic yield. The ions CO_4^- are removed from ionic spectrum via the fast process [28]:

$$CO_4^- + O_3 \rightarrow O_3^- + CO_2 + O_2, \quad k_{18} = 1.3 \times 10^{-10}\ \mathrm{cm^3/s} \quad (18)$$

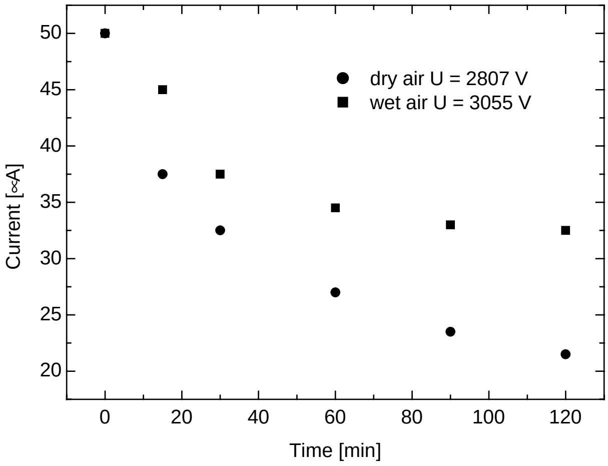

Fig. 3. The time dependence of discharge currents in flow-stopped regime in dry and wet air at $P = 27$ kPa.

There is a second effect of the increasing discharge current on abundance of CO_4^- ions. These (presumably having the cluster form $O_2^-\cdot CO_2$), are decomposed due to drift in high electric field by process analogous to (17). The electric field in the drift region is increasing with increasing discharge current. Therefore both the first and the second mechanisms most likely contribute to destruction of CO_4^- ions and accelerate the destruction of these.

The effect of gaseous impurities produced in the discharge gap is even more pronounced in a static regime. In such circumstances the neutral chemical products formed in the discharge will accumulate within the discharge tube. Under static conditions the discharge current was found to decreases in time at constant voltage on electrodes both in dry and wet air (Fig. 3). The decrease was more pronounced in dry air. This phenomenon has been described earlier [30–32]. This decrease in total discharge current is due to the density of free electrons in the drift region being reduced due to increasing role of dissociative electron attachment to ozone formed in discharge [33–35]:

$$e + O_3 \rightarrow O^- + O_2, \quad k_{19} = f\left(\frac{E}{N}\right) \tag{19}$$

$$e + O_3 \rightarrow O_2^- + O, \quad k_{20} = f\left(\frac{E}{N}\right) \tag{20}$$

The processes (19) and (20) are additional to (11), which otherwise determinates the concentration of free electrons in drift region in the case of ozone-free air. The concentration of ozone in the discharge tube in static regime increases in time practically exponentially from nearly zero (less than 50 ppb), to reach a saturated value, which is determined by the total volume of the discharge tube as well as by properties of material of wall [30]. Therefore with increasing ozone concentration in discharge gap the number of free electrons is reduced and the total discharge current decreases to saturated value. This is stabilised when ozone concentration is reached the saturated value.

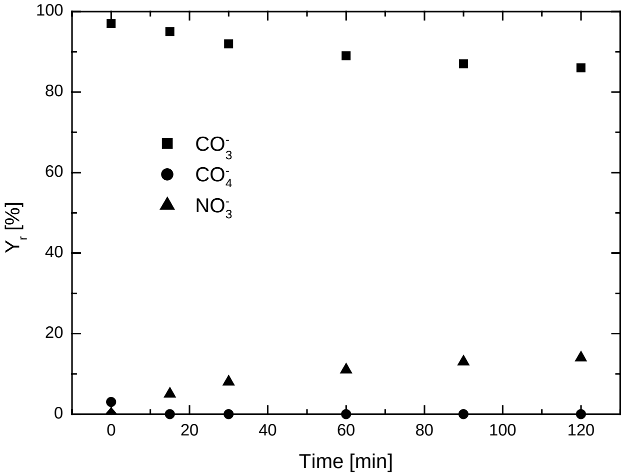

Fig. 4. The time dependence of relative yields of individual ions in flow-stopped regime negative corona discharge in dry air at $P = 27$ kPa.

The ion yield extracted from the discharge changes in time in the static regime due to changes in concentration of compounds generated by the negative corona discharge. In addition to ozone nitrogen oxides may also be produced in the static discharge. NO oxide is formed from nitrogen and oxygen atoms produced by electron impact dissociation. NO_2 is then produced by oxidation of NO [36,37]. The concentration of nitrogen oxide is however at least one order smaller than the ozone concentration as it was already mentioned [29].

The temporal development of ions produced in the static regime having relative abundance higher than 1% is shown in Fig. 4. Traces of O_2^-, O_3^- and NO_2^- were observed before the flow was stopped but were not present after 15 min of static operation. Also after 15 min of a static regime the signal of CO_4^- ions completely disappeared. This effect is ascribed to the fast process (18). In contrast the yield of NO_3^- ions (mass 62) grew after 15 min. NO_3^- ions were not observed in the flowing regime in any measurable concentrations.

There are several possible reactions that may lead to formation of NO_3^- ions. Since the NO_3^-yield increases as the CO_3^- yield simultaneously decreases we can presume that the most probable process for forming NO_3^- is [28]:

$$CO_3^- + NO_2 \rightarrow CO_2 + NO_3^-, \quad k_{21} = 1 \times 10^{-10}\,\mathrm{cm^3/s} \tag{21}$$

If the concentration $[NO_2] \approx 100$ ppm the characteristic time for process (21) is of 14 μs at a pressure 27 kPa. This is comparable with the transport time of CO_3^- across the drift region. Three other reactions of involving O_3^-, O_4^-, and CO_4^- may also produce NO_3^- ions [28]:

$$O_4^- + NO \rightarrow NO_3^- + O_2, \quad k_{22} = 2.5 \times 10^{-10}\,\mathrm{cm^3/s} \tag{22}$$

$$CO_4^- + NO \rightarrow NO_3^- + CO_2, \quad k_{23} = 5 \times 10^{-11}\,cm^3/s \tag{23}$$

$$O_3^- + NO \rightarrow NO_3^- + O, \quad k_{24} = 1 \times 10^{-11}\,cm^3/s \tag{24}$$

The contribution of these, however, is only marginal because according Ross and Bell [29] the concentration of NO in negative corona discharge in air is constant and low. The efficiency of reactions (22–24) is relatively very low because at experimental conditions typical for our experiment the characteristic time of these is comparable with the transport time of O_3^-, O_4^-, and CO_4^- ions only if the [NO] > 1000 ppm. The last value cannot be reached at the low discharge currents used in our experiment.

3.2. Results in ‘wet’ air

Ambient air having the relative humidity within the range 40–55% was used in experiment in both flowing and static regimes. In the flowing regime in contrast to experiments performed in dry air only the traces of single ion CO_3^- was observed in recorded spectra instead the dominant signals observed were the cluster ions $CO_3^-{\cdot}(H_2O)_n$. The data obtained in flowing regime are shown in Fig. 5 at time $t = 0$. All other data shown in Fig. 5 were obtained in static regime when the flow of air was stopped. Due to the limited mass range of the mass spectrometer only the ions having the specific mass smaller than 100 were studied, hence only ions $CO_3^-{\cdot}(H_2O)$ and $CO_3^-{\cdot}(H_2O)_2$ were analysed. The data shown in Fig. 5 were obtained with an initial discharge current of 50 μA, detected in flowing regime before the airflow was stopped. If the current was reduced the yield of hydrated ions increased. All other ions observed in flowing regime at $I = 50\,\mu A$ were observable only in cluster forms. It is interesting that ions $O_2^-{\cdot}(H_2O)_n$ ($n = 1, 2, 3$) were present at relatively high concentrations although in dry the single O_2^- ion was not detected (Fig. 2). $O_2^-{\cdot}(H_2O)_n$ clusters may be formed through the reaction [21]:

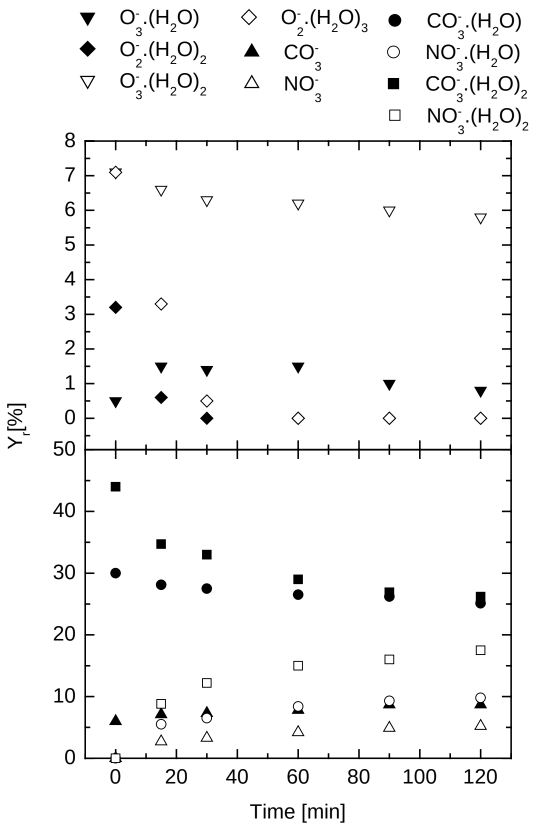

Fig. 5. The time dependence of relative yields of individual ions in flow-stopped regime of negative corona discharge in wet air at $P = 27$ kPa.

$$O_2^- + H_2O + M \rightarrow O_2^- \cdot H_2O + M, \quad k_{25} = 2 \times 10^{-28}\,cm^6/s \tag{25}$$

This reaction in wet air is two orders of magnitude higher than the rate for process (12) and (13). The absence of CO_4^- and O_4^- ions in spectra even at low discharge current is an evidence for such statement. Moreover, if some CO_4^- ions are formed these are efficiently decomposed by the process [36]:

$$CO_4^- + H_2O \rightarrow O_2^- \cdot H_2O + CO_2, \quad k_{26}\ \text{(from equilibrium constant)} \tag{26}$$

If the gas flow is stopped the ozone and nitrogen oxides are generated in the discharge gap, hence the concentration of these species increases with time. The mass spectra are changed considerably for wet air in a static regime. The relative yields of clusters $CO_3^-{\cdot}(H_2O)$ and $CO_3^-{\cdot}(H_2O)_2$ are found to decrease with time probably due to role of reactions similar to (21) performed between cluster forms of CO_3^- ions with NO_2. Hence the processes:

$$CO_3^- \cdot (H_2O)_n + NO_2 \rightarrow NO_3^- \cdot (H_2O)_n + CO_2 \quad (n = 1, 2, \ldots), \quad k_{27} = ? \tag{27}$$

are most likely active in production of cluster ions $NO_3^-{\cdot}(H_2O)_n$ ($n = 1, 2, \ldots$). The increase in relative yield of such ions is evident from Fig. 5. Unfortunately there are no direct data on such types of reactions.

The hydrated forms of O_2^- ion also react very fast with ozone molecules and produce single O_3^- and cluster ions $O_3^-{\cdot}(H_2O)_n$ [21]:

$$O_2^- \cdot H_2O + O_3 \rightarrow O_3^- + O_2 + H_2O, \quad k_{28} = 8 \times 10^{-10}\,cm^3/s \tag{28}$$

$$O_2^- \cdot (H_2O)_2 + O_3 \rightarrow O_3^- \cdot H_2O + O_2 + H_2O, \quad k_{29} = 7.8 \times 10^{-10}\,cm^3/s \tag{29}$$

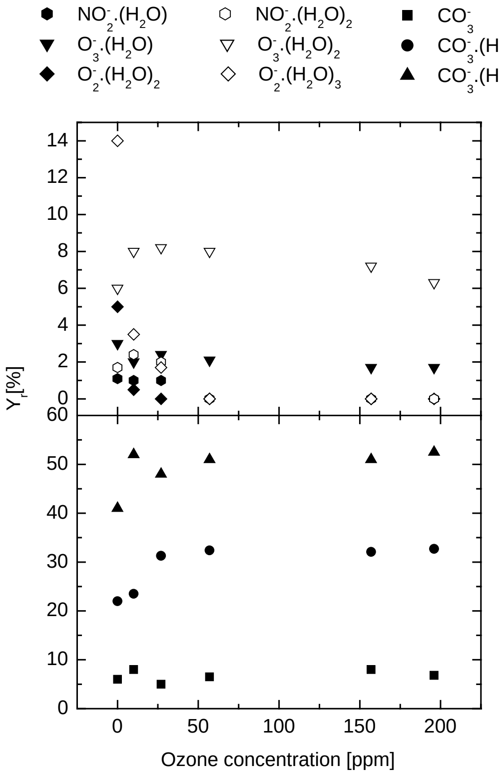

Fig. 6. The dependence of relative yields of individual negative ions in flowing regime of negative corona discharge in wet air on ozone concentration at $P = 27\,\mathrm{kPa}$.

$$O_2^- \cdot (H_2O)_3 + O_3 \rightarrow O_3^- \cdot (H_2O)_2 + O_2 + H_2O, \quad k_{30} = 6.4 \times 10^{-10}\,\mathrm{cm^3/s} \tag{30}$$

All hydrated forms are partially converted to CO_3^- ions in single and cluster forms [21]:

$$O_3^- \cdot (H_2O)_n + CO_2 \rightarrow CO_3^- \cdot (H_2O)_{n-1} + O_2 + H_2O, \quad k_{31} < 1 \times 10^{-10}\,\mathrm{cm^3/s} \tag{31}$$

that are transferred to NO_3^- ion and its clusters (28).

In order to quantify the role of ozone in such static discharges a final set of experiments was performed in which ozonised air (formed in ozoniser) was passed through the negative corona discharge in a flowing regime with a flow rate $50\,\mathrm{cm^3/s}$. The results are shown in Fig. 6. In contrast to experiments performed in the static flow regime only traces of NO_3^- were found (concentrations below 1%). The absence of NO_3^- ions and its clusters in spectrum is most likely due to low concentration of nitrogen oxides in ozonised air. Nitrogen oxides are generated in ozoniser with ozone but the concentration of these is more than one order smaller than ozone concentration. Moreover, during the transport of ozonised air through duct connecting the ozoniser with the discharge tube (approximately 1 m) great part of nitrogen oxides is decomposed via neutral chemical reactions with ozone molecules [37]:

$$O_3 + NO \rightarrow NO_2 + O_2, \quad k_{32} = 1.8 \times 10^{-14}\,\mathrm{cm^3/s} \tag{32}$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2, \quad k_{33} = 3.2 \times 10^{-17}\,\mathrm{cm^3/s} \tag{33}$$

If the concentration of ozone is of order 100 ppm the characteristic time for reaction (32) is substantially shorter than the transport time in the duct. Thus the NO is completely decomposed in the duct. The NO_2 concentration is low because of high flow rate through the ozoniser and also is decomposed in the duct connecting the ozoniser and the discharge tube. Hence the existence of NO_3^- ions and its clusters in the static regime is an evidence that the concentration of nitrogen oxide in the discharge gap should be considerably higher than it is in the ozonised air introduced into discharge tube.

The observed decrease of relative yield of O_3^- clusters at higher ozone concentrations is caused by reaction of O_3^- clusters with CO_2 molecules (31). Single O_2^- ions were absent both with and without ozone in air. The O_2^- clusters were found to disappear if ozone concentrations were higher than 25 ppm. The mechanism of depletion is expected to similar to that described in the static regime. Also processes (28–30) are the effective sink of such ions.

4. Conclusions

The yield of negative ions produced in a negative corona discharge using both dry and 'wet' air is strongly affected by trace concentrations of ozone, nitrogen oxides and water vapours. In dry air the dominant ion is CO_3^-. In presence of water this is converted very efficiently to form hydrated cluster ions. If ozone and nitrogen oxides are added to the air, or are produced in discharge in with sufficient amounts, NO_3^- ions in single and hydrated forms are produced and may come to dominate the ion yields. The high sensitivity of the negative ion yield to the concentration of trace gases and humidity of the ambient air may therefore explain the discrepancies in ionic spectra reported by earlier authors and reveal the complexity of using such discharges in commercial and manufacturing industries. Careful control of the gas preparation and input into corona discharge is necessary if reproducible results are to be obtained.

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References

[1] P. Coxon, G. Canadas, Int. J. Mass Spectrom. Ion Phys. 37 (1981) 177.
[2] J. Skalny, Acta Phys. Univ. Comen. 29 (1989) 89.
[3] R.S. Sigmond, Proceedings of the Third Intenational Symposium on Gaseous Dielectrics, Knoxwille, 1982, p. 92.
[4] P.S. Gardiner, J.D. Craggs, Proceedings of the Fifth International Conference on Gas Discharges and their Applications, Liverpool, 1978, p. 81.
[5] P.S. Gardiner, J.L. Moruzzi, J.D. Craggs, J. Phys. D: Appl. Phys. 11 (1978) 237.
[6] R.S. Sigmond, T. Sigmond, Proceedings of the Ninth International Conference on Gas Discharges and their Applications, Venezia, 1988, p. 212.
[7] I. Sauers, Proceedings of the Ninth International Conference on Gas Discharges and their Applications, Venezia, 1988, p. 589.
[8] I. Sauers, G. Hartman, J. Phys. D: Appl. Phys. 25 (1992) 761.
[9] I. Sauers, G. Hartman, J. Phys. D: Appl. Phys. 25 (1992) 774.
[10] S.R. Hunter, L.G. Christophorou, D.L. McCorke, I. Sauers, H.W. Ellis, D.R. James, J. Phys. D: Appl. Phys. 16 (1983) 573.
[11] M.M. Shahin, Appl. Opt. Suppl. Electrophotogr. 3 (1969) 106.
[12] P.S. Gardiner, J.D. Craggs, J. Phys. D: Appl. Phys. 10 (1977) 1003.
[13] N.L. Allen, P. Coxon, R. Peyrous, Y. Teisseyre, J. Phys. D: Appl. Phys. 14 (1981) L207.
[14] R.S. Sigmond, J. Skalny, Book of Contributed Papers of the 16th ICPIG, Düsseldorf, 1983, p. 182.
[15] J. Skalny, R.S. Sigmond, Book of Contributed Papers of the 16th ICPIG, Düsseldorf, 1983, p. 554.
[16] C.A.M. de Vries, F.J. de Hoog, D.C. Schram, Proceedings of the Sixth ISPC, Montreal, 1983, p. 317.
[17] J. Skalny, Conference Abstracts of Sixth ESCAMPIG, Greifswald, 1986, p. C-13.
[18] R. Peyrous, P. Coxon, J. Moruzzi, Proceedings of the Seventh International Conference on Gas Discharges and their Applications, London, 1982, p. 169.
[19] V. Kotasek, Negative Ion/molecule reactions in a Negative Corona Discharge, Dissertation, UTIAS Technical Note No. 230, CN ISSN 0082-5263, Toronto, 1981.
[20] J. Skalny, Acta Phys. Univ. Comen. 27 (1987) 161.
[21] B. Gravendeel, Negative Corona Discharges a Fundamental Study, Dissertation, Technical University Eindhoven, Eindhoven, 1987.
[22] B. Gravendeel, F.J. de Hoog, J. Phys. B: At. Mol. Phys. 20 (1987) 6337.
[23] B. Held, R. Peyrous, Czech. J. Phys. 49 (1999) 301.
[24] S. Sakata, T. Okada, J. Aerosol Sci. 25 (1994) 879.
[25] M. Tabrizchi, T. Khayamian, N. Taj, Rev. Sci. Instrum. 71 (2000) 2321.
[26] M. Pavlik, J.D. Skalny, Rapid Commun. Mass Spectrom. 11 (1997) 1757.
[27] B. Elliason, Electrical Discharge in Oxygen. Part 1. Basic Data, Rate Coefficients and Cross Sections, Report KLR 83/40 C, Brown Boveri Forschungszentrum, Baden-Dättwil, 1985.
[28] H. Hokazono, M. Obara, K. Midorikawa, H. Tashiro, J. Appl. Phys. 69 (1991) 6850.
[29] S.K. Ross, A.J. Bell, Int. J. Mass Spectrom. 218 (2002) L1.
[30] A. Schwab, R. Zentner, ETZ-A 89 (1968) 294.
[31] A.G. Gagarin, Elektronnaya Obrabotka Materialov 3 (1984) 54.
[32] M. Černák, J. Skalný, S. Veis, Acta Phys. Slov. 29 (1979) 31.
[33] M. Černák, J. Skalný, S. Veis, D. Dindošová, Acta Phys. Slov. 29 (1979) 97.
[34] J. Ráhel', M. Pavlík, L. Holubčík, V. Sobek, J.D. Skalný, Contrib. Plasma Phys. 39 (1999) 502.
[35] P. Cicman, M. Francis, J.D. Skalny, S. Matejcik, T.D. Märk, Czech. J. Phys. 53 (2003) 181.
[36] D.L. Albriton, At. Data Nuclear Data Tables 22 (1978) 58.
[37] R. Atkinson, D.L. Baulch, R.F. Hampson, J.A. Kerr, M.T. Rossi, T. Troe, J. Phys. Chem. Ref. Data 26 (1997) 521.