

Ion Mobility Spectrometry Study of Negative Corona Discharge in N₂/O₂ Mixtures in N₂ Drift Gas*

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Abstract: The negative ions formed in negative corona discharge in the point to plain geometry in the mixtures N₂/O₂ have been analysed using the Ion Mobility Spectrometry (IMS) technique. The formation of the negative ions was studied as a function of the N₂/O₂ mixture. Negative ions NO₂⁻·(H₂O), NO₃⁻·(H₂O), CO₃⁻·(H₂O) have been identified on the base of their known ion mobilities. Additionally, an unknown negative ion with reduced ion mobility of 1.94 cm²·V⁻¹·s⁻¹ has been detected. The structure of this ion is unknown. However, we assume on the basis of its behaviour with increasing O₂ density that it is a negative cluster ion (most probably N_xO_y⁻·(H₂O)_z, x = 2 and y = 3).

1. Introduction

The Ion Mobility Spectrometry (IMS) is an ion separation method based on the phenomenon that different ions have different drift velocities in a drift gas and homogeneous electric field. The IMS technique has been developed and introduced in 1970 under the name plasma chromatography [1]. Since then a variety of different devices working on this principle were developed, mainly for detection of trace organic compounds in air [2, 3]. In the 80's a huge progress was achieved in the field of the ion - molecule reactions at atmospheric pressure and the IMS was rediscovered as a powerful analytical method [3, 4].

Generally, the IMS consists of the ionization source, the reaction region, the shutter grid and the drift tube. The most common ionization source is ⁶³Ni (γ -radiation) radioactive source, which is suitable for many applications because of its stability, low cost and low weight. Unfortunately, this source is radioactive and there is tendency to replace the radioactive source from environmental reasons. Several ionization sources using UV ionization, multi-photon laser ionization, electrospray ionization or corona discharge [2, 3] were tested in the past. The ionization efficiency of the corona discharge is very high and it can be used for production of both positive and negative ions [5]. The ions formed in the ion source are called primary ions. These ions react with the sample gas which is introduced into reaction region of the spectrometer. The sample molecules are ionized by ion-molecular reactions with primary ions. In the case of positive ions the reaction involved is mainly proton transfer and, as a result, the proton will stick to the compounds

*) Dedicated to Professor Peter Lukáč on the occasion of his 70th birthday.

with the highest proton affinity. High electron affinity and charge transfer reactions are usually decisive for negative ions formation. In both polarities the ionization processes are very selective and, as a result, the ion mobility spectrometry is a very sensitive technique for detection of certain compounds.

The ions are separated at ambient pressure as they drift in weak electric field through a gas (oxygen in this case). The velocity v of a drifting ion is proportional to the electric field E and the constant K called the mobility:

$$K E \quad (1)$$

The mobility of certain ion in a drift gas depends on several parameters and can be expressed as

$$K = \frac{3q}{16n} \sqrt{\frac{2}{k_b T}} \sqrt{\frac{m_g m_i}{m_g m_i}} \frac{1}{\sigma}, \quad (2)$$

where q is the charge of an ion, n is the neutral gas density, T is the temperature of the gas, m_g and m_i is the mass of gas molecules and ions, respectively, and σ is the collisional cross-section. As the mobility depends on the collisions of the ion with the drift gas, it depends also on the density of the drift gas. Therefore a correction to the standard conditions ($T_0 = 273$ K, $p_0 = 101.3$ kPa) is made and the resulting value is reported as reduced mobility K_0 given by the formula:

$$K_0 = K \frac{T_0}{T} \frac{p}{p_0}, \quad (3)$$

The most common gas which is used in the commercial IMS instruments as a drift gas is dry purified air. The same gas is usually used in the ion source, where primary ions are formed. Formation of negative ions in air by corona discharge has been studied using mass spectrometry by several authors.

Skalny et al. [6] studied the negative ions formed in a negative corona discharge using both dry and 'wet' air at pressures between 5 and 27 kPa. In the dry air the dominant ion was CO_3^- . In presence of water this was converted to cluster ions containing one or more water molecules. If ozone and nitrogen oxides were added, or were produced in discharge in sufficient concentrations, NO_3^- ions and NO_3^- hydrated clusters were formed. Nagato et al. [7] studied ions in the negative corona in air at ambient pressure at different reaction times, 1 ms and 10 ms. They observed that after 10 ms the number of ions is significantly reduced and the only significant intensity appears at masses 62, 124 and 125 amu. They attributed these masses to NO_3^- , $\text{HCO}_3^- \text{HNO}_3$ and $\text{NO}_3^- \text{HNO}_3$ ions. When the humidity was limited to 25 ppm of H_2O the only ion observed was the NO_3^- . Gravendeel and Hogg [8] studied mass spectrometrically negative corona in N_2/O_2 mixture with ratio 5 to 1. Although they used high purity gases with less than 5 ppm H_2O and 0.1 ppm CO_2 they observed numerous negative ions with O_3^- , OH^- , NO_3^- and CO_3^- being the most intense

ones. In this case, however, the time between formation of ions and their entrance to the vacuum was in order of 10^{-5} s and the reactions might not have been completed.

As we can see the types and relative intensity of the ions observed in these studies differ significantly. The results are very sensitive to many parameters. This includes humidity, concentration of O_3 , NO_x and other molecules. It depends also on the reaction time for which the ions are present in gaseous environment before they enter vacuum to be mass analysed.

In the present work we have applied the IMS technique to study the ion formation in the negative corona discharge in the N_2/O_2 mixtures in N_2 drift gas. One of the major advantages of the IMS technique is that, in contrast to the mass spectroscopic techniques, it avoids the generation of the high vacuum. The transport of the ions from ambient pressure into the vacuum is associated with negative effects, which may change the nature of the ions (clustering, collision induced dissociation). One of the main drawbacks of the IMS technique is the lack of data concerning the ion mobilities in the particular drift gases and, thus, the difficulties with the identification of ions.

In the present experiment we used the N_2 drift gas in the IMS. There are only several works [8–11] dealing with ion mobilities of the negative ions in N_2 drift gas, however, also in this case there is relatively large uncertainty in the values of the ion mobilities.

2. Experiment

The work was performed on a home made ion mobility spectrometer schematically shown in Fig. 1. The ions are formed in the negative corona discharge in a point to plane geometry. The point electrode is made of a thin tungsten wire with $100\ \mu\text{m}$ diameter. It is situated 14 mm from a brass aperture with 5 mm diameter, which serves as a plane electrode. The discharge chamber is made of PTFE and it has a gas inlet in the proximity of coronating electrode.

The reaction region is located between the ion source and the drift tube. It is equipped with an independent gas inlet. The molecules introduced to this region react with primary ions formed in the ion source. The reaction region is separated from the drift tube by an

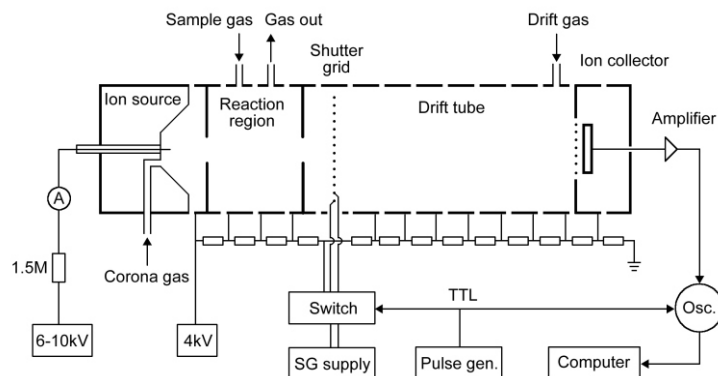


Fig. 1. The schematic view of the ion mobility spectrometer.

aperture with 5 mm diameter. The aperture is necessary to maintain high purity of the gas in the drift tube. The reaction region contains also gas outlet from the spectrometer. The ions in the drift tube are separated according to their individual mobilities. The ions enter the drift tube in short 150 ns pulses controlled by a shutter grid (SG). The shutter grid is built according to Bradbury-Nielsen design [12].

The drift tube consists of identical brass rings separated by the PTFE Teflon rings. The inner diameter of the brass ring is 50 mm and the length is 9 mm. The distance between two rings is 1 mm. The brass rings are connected to a voltage divider. The drift tube length (shutter to collector) is 110 mm and the electric field along the drift tube is 278 V/cm. The field strength corresponds to reduced electric field $E/N = 1.1$ Td. The drift tube is terminated with an ion collector. The ion collector consists of aperture grid, collector and shielding. The collector is made of stainless steel and its diameter is 16 mm. The collector is shielded from the front side by an aperture grid and from other sides by a brass body. The aperture grid is made of a fine Ni mesh. The distance from the collector to the aperture grid is 1 mm. The ion current is amplified by a home made current/voltage amplifier with amplification 10^8 and is averaged and recorded by a Tektronix TDS 220 oscilloscope.

The gas flows were measured by flow meters and were kept constant in present measurements. The drift tube was fed by pure nitrogen with flow 400 ml/min. The ion source was fed by pure oxygen or by nitrogen/oxygen mixture with total flow of 200 ml/min. The purity of both oxygen and nitrogen gas was 5.0 (Linde). The measurements were performed at ambient temperature and pressure. The mobility of ions is calculated using the formula:

$$K = \frac{l_d}{t_d E}, \quad (4)$$

where l_d is the length of the drift tube and t_d is the drift time of the ions. The reduced mobility K_0 is calculated using Equation 3. The uncertainty in calculated K_0 values is believed to be 4%.

3. Results

Pure N₂

The IMS spectrum of the negative ions formed in the negative corona-like discharge in pure N₂ is shown in Fig. 2. One has to mention, that N₂ has negative electron affinity gas and thus is not able to form negative ions. The IMS spectrum is dominated by a strong peak at low drift time, which we attribute to the drifting electrons. The large width of this peak is due to slow response of the preamplifier. The negative ions present in the IMS spectrum are due to impurities present in the N₂ gas. According to the information from the producer the H₂O and O₂ are the main impurities at concentrations less than 7 ppm.

The spectrum shows one peak at 11.5 ms drift time, which corresponds to the reduced mobility $2.27 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This ion could be NO₂⁻ the next ions with reduced mobilities 2.21 and 2.12 could be NO₃⁻ and CO₃⁻, respectively. We make the assignment only tenta-

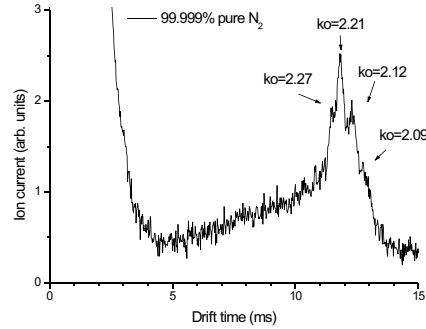
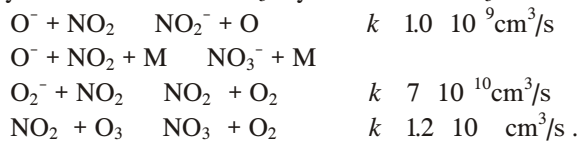


Fig. 2. Ion mobility spectrum of the ions formed in the negative corona discharge in N_2 .

tively as there exists no reliable data on the ion mobilities of such ions in N_2 , thus, this assignment was done in analogy with our previous study of formation of negative ions in N_2/O_2 mixtures in pure O_2 drift gas [13].

N_2/O_2 mixture

The negative corona discharge in the mixture of N_2 with O_2 results in formation of nitrogen oxides N_xO_y . Many of these molecules possess a positive electron affinity. The electrons and the primary negative ions O^- and O_2^- react with NO_2 and form NO_2^- which may be converted into NO_3^- by reaction with O_3



The electron affinity of both NO_2 (2.27 eV) and NO_3 (3.93 eV) exceeds that of O_3 (2.10 eV). The NO_3^- has also been observed to be the terminal negative ion in dry air [7].

In the present study the corona discharge was fed by the mixtures of N_2 with O_2 while drift gas was still pure N_2 . The concentration of N_2 in the mixture varied from 10% to 50%. Fig. 3 shows the ion mobility spectra with 1.25%, 3.75% and 25% concentration of O_2 in ($N_2 + O_2$) in the corona discharge. We have observed ions with reduced mobility 2.21, 2.13 and 2.09 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The intensity of the produced ions as a function of O_2 concentration is plotted in the Fig. 4. We see that with increasing concentration of O_2 from 1.25% to 3.75% the intensity of the ion with reduced mobility 2.21 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ significantly increases, further increase of the O_2 density results in decrease of the intensity of this ion. The ion with $K_0 = 2.13 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ has similar behaviour and the maximum intensity is in mixture with 3.75% O_2 concentration. Above this O_2 concentration its intensity is slightly decreasing. The maximum and the decrease are not so pronounced as it was in the ion with $K_0 = 2.21 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The ion with $K_0 = 1.94 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ is dominant at O_2 concentration exceeding 10%.

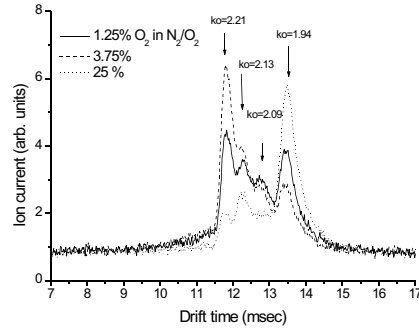


Fig. 3. Mobility spectra of negative ions formed in corona discharge in N_2/O_2 mixture with 1.25%, 3.75% and 25% concentration of O_2 . Mobility values are in $cm^2 V^{-1} s^{-1}$.

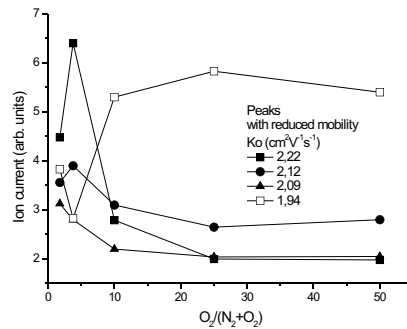


Fig. 4. Intensity of observed ions as a function of relative O_2 concentration in the corona discharge.

Clear identification of the observed ions is problematic due to the lack of data concerning ion mobilities. The mobility of negative ions in O_2^- in N_2 has not been measured so far. The mobility of O_3^- in N_2 has been measured by McDaniel et al. [9].

The most relevant work concerning the negative ion mobility in N_2 is the work of Eisele et al. [10]. They performed measurements of ion mobilities of negative ions with water: $NO_2^-(H_2O)$, $NO_3^-(H_2O)$, $CO_3^-(H_2O)$ and $CO_4^-(H_2O)$. The ions were identified using mass spectrometry. The determined values of the ion mobilities were 2.29, 2.21, 2.11 (at 257 K) and $2.14 cm^2 V^{-1} s^{-1}$. Viehland et al. [11] published also the reduced mobility of negative ions in N_2 for NO_2^- and NO_3^- 2.53 and $2.33 cm^2 V^{-1} s^{-1}$. In the present experiment the pure N_2 contains approximately 7 ppm H_2O and this H_2O density is sufficient to form water clusters at the negative ions. Therefore we have assigned the peaks observed to the ions $NO_3^-(H_2O)$, $CO_4^-(H_2O)$ and $CO_3^-(H_2O)$, according to Eisele et al. [10]. Similar assignment was possible also for the negative ions formed in negative corona discharge in N_2/O_2 mixtures, whereas the ion with $2.27 cm^2 V^{-1} s^{-1}$ assigned to $NO_2^-(H_2O)$ was not detected anymore. Most probably this ion was converted into the more stable $NO_3^-(H_2O)$ ion. New important negative ion with the reduced mobility of $1.94 cm^2 V^{-1} s^{-1}$ appears in the IMS spectra. There exists no data so far in the literature for ions with this reduced mobility. We may conclude from the kinetic behaviour (the

increase of its intensity with the O₂ density) we may conclude, that this is most probably some N_xO_y⁻·(H₂O)_z (x = 2, y = 3 and z = 1) clusters. Similar cluster ions were observed in the IMS spectra of negative corona discharge in N₂/O₂ mixtures measured in the O₂ drift gas [13].

Summary

Formation of negative ions in the negative corona in N₂/O₂ mixtures has been investigated using ion mobility spectrometry in the nitrogen drift gas. Negative corona in the pure N₂ results in detection of electrons at the end of the drift tube and only small amounts of anionic products from the impurities present in N₂. Negative corona discharge in N₂/O₂ mixtures results in formation of several negative ions. The ions with mobility 2.21 and 2.13 cm²V⁻¹s⁻¹ were identified as the NO₃⁻·(H₂O) and CO₄⁻·(H₂O). The nature of the most intense ion with reduced mobility 1.94 cm²V⁻¹s⁻¹ remains unclear.

Acknowledgment

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