MEASUREMENT OF ELECTRON ATTACHMENT RATE TO O_2 AT AMBIENT PRESSURE USING IMS

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Electron attachment rate constant to oxygen was measured in nitrogen buffer gas at ambient pressure using Ion Mobility Spectrometry (IMS) technique. The range of the values of the reduced electric field *E/n* varied from 0.5 to 2 Td and the content of O_2 in N_2/O_2 mixture was 0.1% to 1.6%. The rate constants for electron attachment were obtained using three different methods.

1. Introduction

The electron and ion processes in air attract attention of the scientist not only due to their importance for the environment, but also due to increasing importance of the atmospheric pressure discharges in various fields of application [1]. In the case of the electron attachment reactions in air an important role has molecular oxygen as the electronegative component of the air. At low pressure and intermediate electron energies, the dissociative electron attachment to O_2 is the dominant reaction.

$$e + O_2 \rightarrow O_2^{-\#} \rightarrow O^- + O \qquad (1)$$

This reaction has been studied in crossed beams experiment [2, 3, 4]. At elevates pressures and low electron energies, different attachment reaction is operative, the non-dissociative (three body) electron attachment.

$$e + O_2 \rightarrow O_2^{-\#} + M \rightarrow O_2^- + M \qquad (2)$$

where $O_2^{-\#}$ is the transient negative ion and M is the third particle (O_2, N_2,...). The third body stabilises the transient negative ion by the quenching of the excess energy. Most experiments devoted to the estimation of the kinetic data for reaction (2) have been carried out in drift tubes at lower pressures (~10 mbar) and the values of the rate constant were extrapolated toward high pressure [5, 6, 7, 8]. One exception is the experiment of McCorkle [9] which has been carried out in large range of pressures starting at 300 Torr up to 10^4 Torr. The three body electron attachment depends not only on the energy of the electrons, the density of the gas, the temperature of the gas, but also on the nature of the buffer gas (third body), which determines the electron energy distribution function and also has the stabilising effect on the molecular ion. Chanin et al. [5] refers that three body electron attachment to O_2 is the most efficient in O_2 and that the efficiency is decreasing in N_2 and even more in He. This paper presents three different methods based on the IMS technique, to measure the kinetics of the three body electron attachment reactions at atmospheric pressure.

2. Experiment

The work was performed using a home made ion mobility spectrometer. Detailed description of the instrument is given in [10]. The electrons are generated in discharge in a point-to-plate geometry (negative potential applied to point electrode) fed by pure nitrogen. In non-electronegative gases as N_2 the discharge current is conducted by electrons. The discharge current is measured on the tip electrode and it was found to be independent on oxygen concentration inside the drift tube. Most of electrons from discharge are collected on a mesh forming the plane electrode and only a fraction of them drift through the instrument. After passing an aperture with 6 mm diameter the electrons are released to drift tube in short pulses controlled by a shutter grid. The current of charged particles (electrons and negative ions) is measured on a collector with placed on the end of drift tube. it is amplified and recorded by an oscilloscope. The length of the drift tube is L=11.1 cm and it is fed by nitrogen buffer gas with small admixtures of O_2. Purity of both nitrogen and oxygen gas was 99.999%. The gas mixture is prepared using MKS® mass flow controllers.

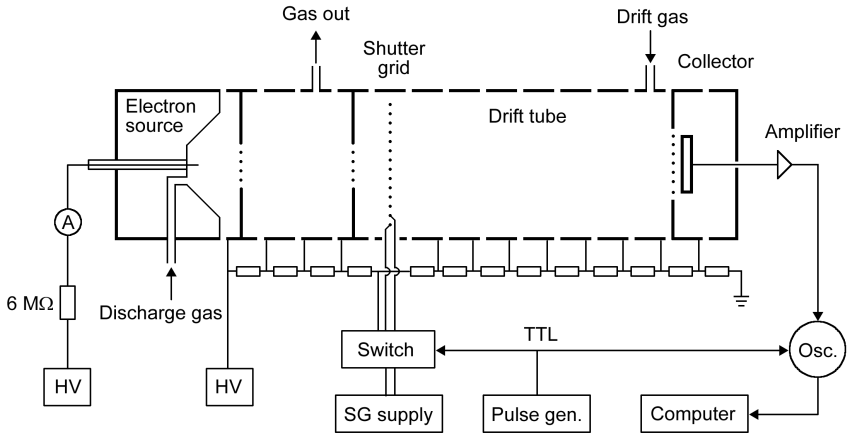

Fig. 1. The experimental setup.

The speed of a three body electron attachment reaction can be expressed as:

$$\frac{d[M^-]}{dt} = -\frac{d[e]}{dt} = k[M][e][X] \tag{3}$$

where [e], [M] and [X] are number densities of electrons, electron attaching gas (O_2) and neutral molecules (N_2 and O_2). [M^-] is the number density of negative ions formed in the reaction and k is the reaction rate constant. Due to the electron attachment reaction the amount of the electrons in the drift tube is decreasing with increasing distance from the shutter grid d according to following formula:

$$[e]_d = [e]_0 \exp\left(-\frac{k[M][X]d}{w_e}\right) \tag{4}$$

where w_e is electron drift velocity and $[e]_0$ is number density of the electrons just at shutter grid.

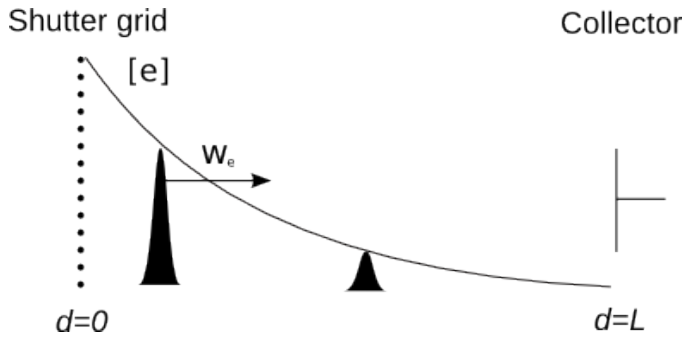

Fig. 2: Concentration of electrons in the drift tube.

The amount of produced negative ions is proportional to the amount of the electrons passing the given location

$$[M^-]_d = k\tau[M][X][e]_d \tag{5}$$

where τ is the shutter opening time. Electron and ion current measured on collector is given by

$$I_e = q_e[e]w_e S \quad \text{and} \quad I_i = q_e[M^-]v_i S \tag{6}$$

where q_e is the elementary charge, v_i ion drift velocity and S cross section of electron and ion beam. Given equations do not account spreading of the electron and ion beam due to diffusion and space charge effects. Typical oscillographic record of the electron and ion current on collector is shown in the figure 3.

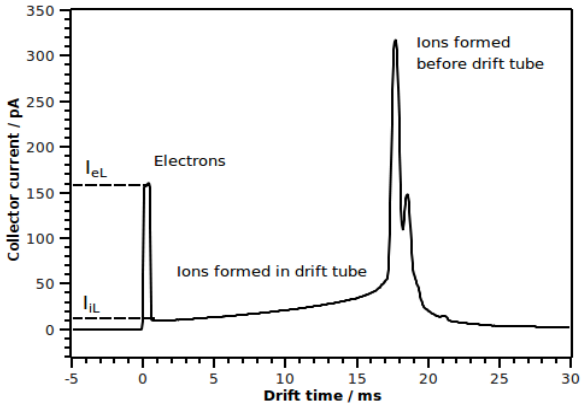

Fig. 3. Oscillographic record of electron and ion current on collector. At $t = 0$ shutter grid is open for 500 μs.

The first peak at very short drift time originates from the electrons. The next part with increasing exponential shape represents the ions formed inside the drift tube due to the electron attachment reaction. The ions formed close to collector arrive first and the ions formed just behind the shutter grid arrive as last. Finally, we see the ion peaks, which consists of ions formed before the shutter grid and which have passed the whole drift tube with fixed drift velocity v_i. In the figure shown we see several peaks which we associate with different types of the ions. This oscillographic record gives us possibility to determine the electron attachment rate constant k using several methods.

3. Evaluation methods

a)

Electron attachment rate constant is calculated from the electron current measured at collector I_{eL} and the current of ions formed just before the collector I_{iL}. Combinig equations (5) and (6) we can calculate k as :

$$k = \frac{I_{iL}}{I_{eL}} \frac{w_e}{v_i} \frac{1}{[M][X]\tau} \tag{7}$$

Ion drift velocity v_i was determined from ion drift time t_d over drift tube $v_i = L/t_d$ and the values of w_e were taken from [11].

b)

The second method for determination of k was previously published by Tabrizchi et al. [12]. The ions formed along the drift tube drift to the collector with velocity v_i. At time t measured from opening of the shutter grid the collector registers ions initially formed at distance:

$$d = L - v_i t \tag{8}$$

from the shutter grid. The concentration profile of negative ions formed along the drift tube is therefore mirrored in the oscilloscopic record of the ion current on collector. Using the equations (4), (5) and (8) the shape of ion current waveform is obtained:

$$I_i \propto \exp\left(k[M][X]\frac{v_i}{w_e}t\right) \tag{9}$$

The attachment reaction rate constant is calculated from the fit of an exponential function to the relevant part of recorded ion current waveform.

c)

The electron attachment rate constant is calculated using the Lambert-Beer law for electron transmittance through the drift tube containing electron attaching gas at various concentrations. If I_0 is electron current transmitted when drift tube is filled with pure N_2 and $I_{[M]}$ when number density of electron attaching gas is [M] the rate constant of electron attachment reaction can be expressed as

$$k = \frac{w_e}{L[M][X]} \ln \frac{I_0}{I_{[M]}} \tag{10}$$

The electrons were released into drift tube in pulses so that electron and ion current on collector could be distinguished. Unlike in previous two methods where k could be determined from a single measurement, at least two measurements at different concentration of electronegative gas are necessary.

4. Results

The rate constants for electron attachment to oxygen obtained using the three methods described above are shown in the figures 4 and 5. The rate constant can be evaluated only if some electrons survive the drift and reach the collector. This limits the maximal O_2 concentration to 0.2% at 0.5 Td, 1.4% at 1 Td and 1.6% at 2 Td. The results obtained using different methods at the same conditions differ by up to factor of 4. The highest differences are at very low concentration of O_2 while agreement becomes better with increasing concentration of O_2. Most of present values are higher than previously reported values [5, 9] at given *E/n* or at corresponding mean electron energy, see the Table 1. In agreement with previous studies the average rate constant is decreasing with increasing *E/n* in the studied range.

Differences in values obtained by different methods indicate their relatively low accuracy. The results of all three methods can therefore be considered as approximate values only. The inaccuracies may result from several effects depending on the method used. If electron current is higher than ion current by several orders of magnitude, the ion current waveform may be deformed by the tail of electron peak. The use of methods a) and b) is limited in such situation. The problem can be suppressed by choosing a lower amplification and a higher bandwidth of the amplifier. However, the amplification must be still sufficient to measure the ion current. The inaccuracies may also arise from diffusion and coulomb repulsion of the electron and ion beam. Although these effects don't influence the results of the method a) their role in the method c) based on the Lambert-Beer law needs further investigation.

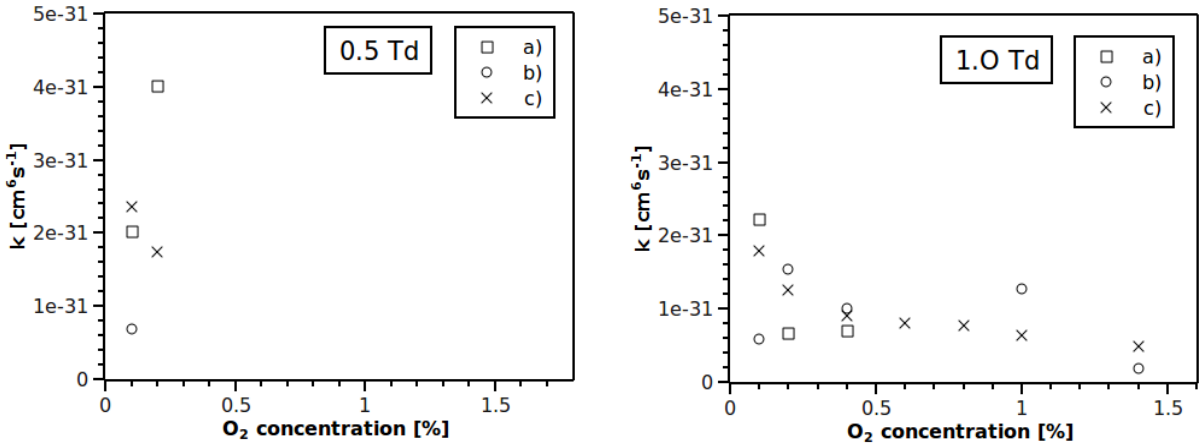

Fig. 4. Rate constants for electron attachment to O_2 at 0.5 Td (left) and 1 Td (right) obtained using methods a) b) and c).

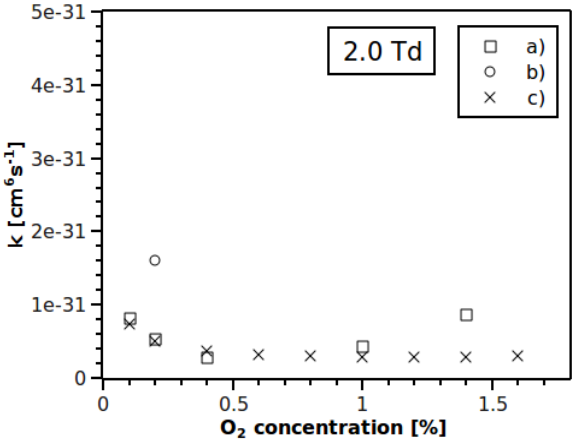

Fig. 5. Rate constants for electron attachment to O_2 at 2 Td obtained using different methods.

Tab. 1. Rate constants of electron attachment for O_2 in N_2 buffer gas.

E/n, Td	k, cm^6s^{-1} Method a)	k, cm^6s^{-1} Method b)	k, cm^6s^{-1} Method c)	<e>, eV [11, 13]	k, cm^6s^{-1} [5]	k, cm^6s^{-1} [9]
0,5	3.0×10^{-31}	6.3×10^{-32}	$2.0\times E^{-31}$	0,19	$9,7\times10^{-32}$	$\sim5\times10^{-32}$
1	1.2×10^{-31}	1.3×10^{-31}	$9.5\times E^{-32}$	0,36	$4,6\times10^{-32}$	$3,2\times10^{-32}$
2	5.8×10^{-32}	2.1×10^{-31}	$3.8\times E^{-32}$	0,6	$2,0\times10^{-32}$	- - -

Acknowledgement

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