The Electron Attachment to Nitromethane at Ambient Pressure

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Abstract. The electron attachment rate constant to nitromethane in nitrogen buffer gas was determined from the electron transmission through a drift tube using the Lambert-Beer law. The work was done at ambient pressure using a single shutter drift tube in the range of reduced electric field *E/n* from 0.5 Td to 2.0 Td. The concentration of nitromethane in the gas mixture varied from 4 ppm to 82 ppm. The electron attachment rate constant of 8.4×10^{-11} cm^3s^{-1} and 5.2×10^{-10} cm^3s^{-1} were determined at reduced electric field of 0.5 and 2.0 Td respectively.

Introduction

The detection of trace amounts of organic compounds in air is an important field of research today. A special group of compounds, nitrocompounds, may indicate presence of explosives and their detection is very important in the field of security. The nitrocompounds can be effectively detected using an ion mobility spectrometry (IMS) operated in negative ion mode. The knowledge of reaction rates of relevant electron-molecular and ion-molecular reactions under conditions valid in ion mobility spectrometers is necessary for better understanding of the processes involved and for estimation of the detection efficiency.

Several methods for measurement of electron attachment rates under conditions common in ion mobility spectrometers have been developed and reported. One method is based on the evaluation of the waveform of the ion current measured on the collector at the end of a drift tube [1]. This method allows determination of the electron attachment rate constant from a single IMS spectrum measurement, however, it can only be applied when a single type of ions is formed. Another approach is to measure the electron-transmittance through a drift tube containing an electron-attaching gas [2]. Here, formation of several anionic products or subsequent ion-molecular reactions do not hamper evaluation of the rate constant, however, the transmittance must be measured at several concentrations of electron attaching gas in the drift tube.

In the present work we have applied this approach to study the electron attachment rate constant to nitromethane in nitrogen buffer gas. The electron attachment to nitromethane proceeds via several reaction channels and results in formation of several anionic products [3]. It is therefore more suitable to determine the electron attachment rate from electron transmission through a drift tube. The reliability of this method has been previously verified by measurement of electron attachment to oxygen [4] and comparison of the results with previously reported values [5].

Experiment

The measurements were performed using a single shutter drift tube shown schematically in Figure 1. Free electrons were generated by a discharge in a point-to-plane geometry. The discharge was fed by pure nitrogen with a constant flow of 200 ml/minute. The electrons were transmitted through the aperture 1 in the plane electrode and subsequently through the aperture 2. The electrons were periodically released into drift tube in 100 μs pulses by a shutter grid formed by coplanar parallel wires according to Bradbury-Nielsen design [6]. In the drift tube, some electrons were attached and formed negative ions, the rest reached collector placed at the end of the drift tube. The collector was shielded by a metal mesh to prevent a charge induction by the approaching electrons. The electron current was amplified by a current/voltage amplifier (model DHPCA-100, FEMTO *Gmbh*) and recorded in a digital oscilloscope.

The drift tube was fed by a mixture of nitromethane vapour and nitrogen buffer gas. The constant flow of 500 ml/minute of nitrogen was controlled using MKS^{TM} mass flow controller. The flow of nitromethane vapour was controlled using a syringe pump with a syringe containing a small amount of liquid nitromethane. The number density of nitromethane vapour in the syringe at given temperature

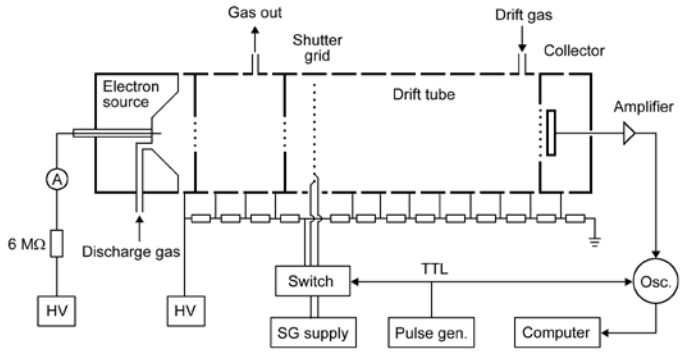

Figure 1. Schematic diagram of the experimental setup.

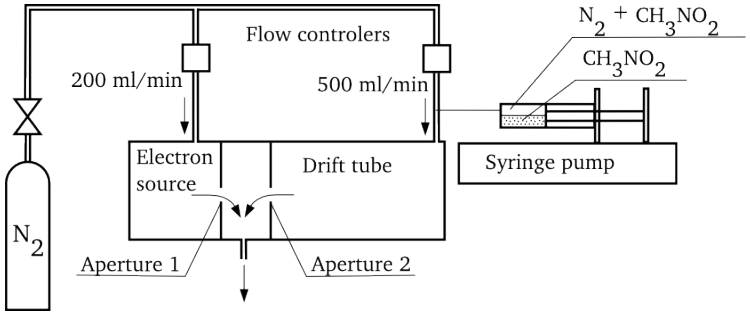

Figure 2. The schematic view of the gas feeding system.

and pressure was calculated using the equation of state and the data from [7]. The concentration of nitromethane in the mixture fed into the drift tube varied from 4 ppm to 83 ppm. The schematic view of the gas feeding system is shown in Figure 2.

The method

Electron attachment rate constant to nitromethane was determined from electron transmission through the drift tube containing an electron attaching gas at different concentrations.

If we consider following electron attachment reaction:

$$e + M \rightarrow M^- \tag{1}$$

the rate of reaction can be expressed as

$$\frac{d[M^-]}{dt} = -\frac{d[e]}{dt} = k[M][e] \tag{2}$$

where $[M^-]$, [e], [M] is number density of negative ions, electrons and electron attaching molecules respectively and k is the electron attachment rate constant. The amount of electrons in the package released into drift tube is decreasing with time t according to

$$[e]_t = [e]_0 \exp(-k[M]t) \,. \tag{3}$$

Knowing the electron drift velocity w_e we can rewrite this equation as

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

where d is the distance from the shutter grid. The values of w_e were taken from [8]. The profile of the electron concentration in the drift tube is shown in Figure 3.

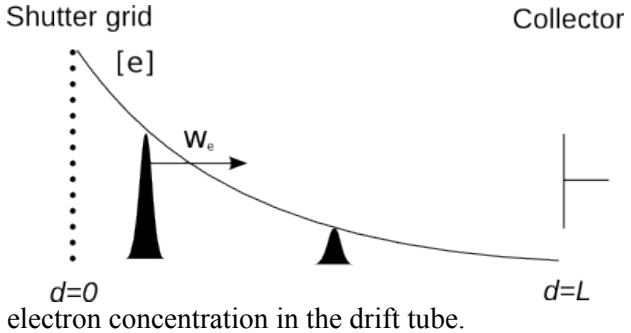

Figure 3. Profile of the electron concentration in the drift tube.

The electron current registered on the collector at a distance L from the shutter grid can be expressed as

$$I_{[M]} = I_0 \exp\left(-\frac{kL[M]}{w_e}\right), \tag{5}$$

where I_0 is electron current entering the drift tube. If there is no electron-attaching gas inside the drift tube, the electron current at collector is given by I_0. If we plot the values of the electron current as $ln(I_{[M]}/I_0)$ versus the concentration [M], the rate constant can be calculated using a linear fit according to

$$ln\left(\frac{I_{[M]}}{I_0}\right) = -\frac{kL[M]}{w_e}. \tag{6}$$

In our experiment, however, the electrons are already attached between the electron source (aperture 1) and the shutter grid. To take this into account the rate constant was calculated using an effective length L_{ef} in the equation (6).

$$ln\left(\frac{I_{[M]}}{I_0}\right) = -\frac{kL_{ef}[M]}{w_e}. \tag{7}$$

L_{ef} is given by the sum of the distance from aperture 2 to collector and by 5/7 of the distance between apertures 1 and 2. The ratio 5/7 is given by the flow of gas mixture from the drift tube (500 ml/min) and the total flow of gas to this area (700 ml/min). The concentration of the electron attaching gas between the apertures is therefore 5/7 of [M], while its concentration between the aperture and the collector is [M].

Results

The electron attachment rate constant was determined for different values of the reduced electric field in range from 0.5 to 2.0 Td. For each value of the *E/n* the current of electrons passing the drift tube was measured as a function of nitromethane concentration. The measured values of the electron current and linear fits according to (7) are shown in Figure 4a–d.

For all studied values of *E/n* the logarithm of electron current decreasing linearly with increasing concentration of the electron attaching gas. Therefore, the rate constant k is calculated by a linear fit to these data and using the equation (6). The calculated values of k are shown in Figure 5.

The electron attachment rate constant for nitromethane continuously increases with *E/n* in the range of *E/n* studied. The increase is very significant from 8.4×10^{-11} cm^3s^{-1} at 0.5 Td to 5.2×10^{-10} cm^3s^{-1} at 2 Td (corresponding to the electron energy range from 0.3 to 0.7 eV [8]).

We associate the increase of the rate coefficient with the formation of the negative ions in the low energy range. In crossed beam experiments, dissociative electron attachment to nitromethane was observed [8,9], where at low electron energies the formation of NO_2^- is a dominant channel with cross section increasing with the electron energy and reaching a maximum at 0.62 eV [9]. The present data show similar energy dependence and increase with the electron energy.

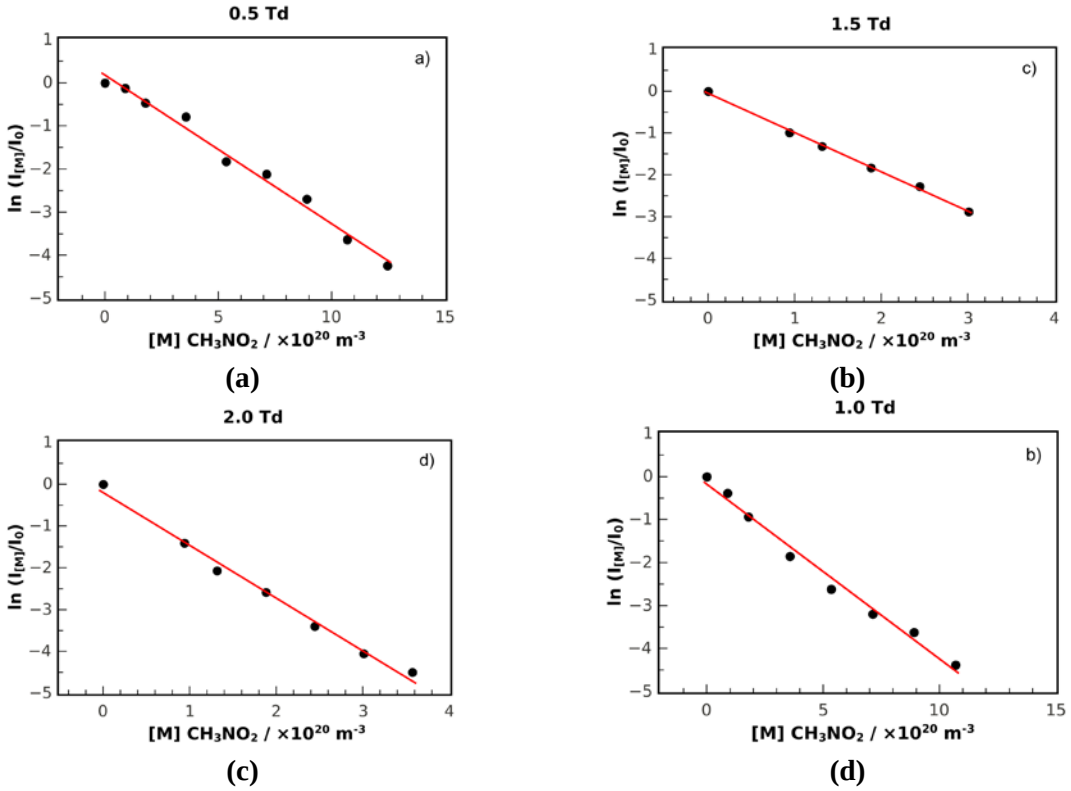

Figure 4. (a–d) The variation of the electron current intensity with nitromethane density for different values of reduced electric fields *E/n*.

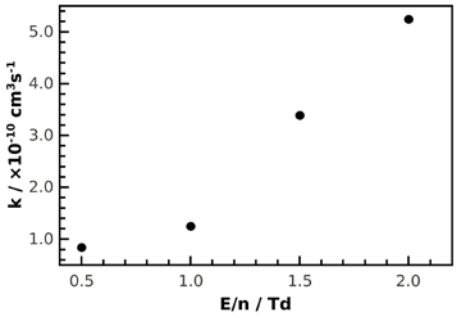

Figure 5. Electron attachment rate constant at different values of *E/n*.

The average cross section for electron attachment to nitromethane σ_{avg} at 1 Td, corresponding to 0.4 eV mean electron energy E_{mean}, was estimated using the equation

$$\sigma_{avg} = k\sqrt{\frac{m_e}{2E_{mean}}} \tag{8}$$

to be 4×10^{-18} cm^2. This value exceeds the cross section for dissociative electron attachment to nitromethane of 1×10^{-19} cm^2 at 0.62 eV as reported in [9].

Conclusion

Electron attachment rate to nitromethane in nitrogen buffer gas was for the first time determined in swarm experiment at *E/n* ranging from 0.5 to 2 Td. It was observed that the rate constant strongly increases with *E/n* in the range of *E/n* studied.

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