TEMPERATURE DEPENDENCIES IN DISSOCIATIVE ELECTRON ATTACHMENT TO CCl_3Br

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The study of dissociative electron attachment (DEA) to CCl_3Br molecule has been performed in the electron energy range from 0 to about 2 eV and in the gas temperature range from 293 K to 478 K using a crossed electron-molecular beams apparatus with a temperature regulated, effusive molecular beam source. Strong enhancement of the negative ion production with the gas temperature has been observed for the overall negative ion yield and for Cl^-/CCl_3Br reaction channel at low electron energies (≈ 0 eV). Activation energies for dissociative electron attachment of (123 ± 20) meV and (65 ± 20) meV have been estimated for the overall negative ion formation and for the Cl^- reaction channel. The DEA cross section for Br^-/CCl_3Br reaction channel was at low electron energies temperature independent. At the 0.6 eV (Br^-/CCl_3Br) and 0.65 eV (Cl^-/CCl_3Br) resonances the cross-sections were temperature independent. At the elevated gas temperatures above 422 K, strong decrease of the negative ion yield has been observed for DEA CCl_3Br assigned to the catalytic thermal decomposition of molecules on the iron surface of the molecular beam source.

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1 Introduction

Electron attachment (EA)reactions to the molecules play important role in various fields of chemistry, physics, and in large number of technological applications [1]. For this reason EA reactions have attracted scientific attention and have been studied in many experiments using both beam and swarm techniques. Present paper is devoted to the study of the gas temperature effect on the dissociative electron attachment (DEA) to CCl_3Br molecule:

$$e + CCl_3Br \rightarrow Cl^- + CCl_2Br + 0.43 \, eV. \tag{1}$$
$$\rightarrow Br^- + CCl_3 + 0.83 \, eV. \tag{2}$$

The exothermicity of the reaction (2) was calculated from data available in [2], for the reaction (1) we were not able to calculate the exothermicity due to lack of data, but we assume, that the exothermicity is about the same as in the case Cl^-/CCl_4.

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Alajajian *et al.* [3] studied DEA to CCl_3Br using the krypton photoionisation method at room temperature and reported only observation of Br^- negative ion. The first gas temperature study of DEA to CCl_3Br (coordinated swarm and crossed beams study) was performed by Spanel *et al.* [4]. The swarm study showed that the overall rate coefficient of the electron attachment reaction depends on electron temperature (T_e) and on the temperature (T) and is strongly enhanced by T [4]. From the increase of the overall negative ion signal the activation energy of 55 meV have been estimated. The observed increase of the overall rate coefficient with T was due to enhancement of the Cl^- channel with T. The Br^- channel decreased slightly with T. The distribution of the product in the reaction channels (1) and (2), expressed in form of the branching ratio $R = Br^-/(Cl^- + Br^-)$, was also temperature dependent. At $T = T_e = 300$ K, the Br^- ion yield was about 80% of the overall negative ion signal, at elevated temperature $T = T_e = 540$ K the Br^- ion yield was only 20%. Moreover, in the swarm experiment also molecular negative ions $BrCl^-$ and Cl_2^- were observed at very low intensities.

In the crossed beams study of DEA to CCl_3Br the ion yields for Cl^- and Br^- as functions of electron energy E (from ≈ 0 to 2 eV) and gas temperature T (temperature range from 311 to 423 K) were measured. The Parathasarty *et al.* [5] studied DEA to CCl_3Br using the Rydberg Electron Transfer (RET) technique. Using this technique, they estimated the kinetic energy of the product ions Br^- and Cl^-, the life time of the TNI and described the mechanism of the reaction. In another study of Parathasarty *et al.* [6], the temperature effects in DEA to CCl_3Br were studied and temperature behaviour very similar to that published by Spanel *et al.* [4] was observed.

Schramm *et al.* [7] performed high resolution DEA study to CCl_3Br at room temperature using the Laser Photoelectron Attachment (LPA) technique in the electron energy range from threshold to 0.172 eV and the electron attachment spectroscopy in the electron energy range from threshold to about 2 eV. Using these two techniques, absolute cross sections for DEA to CCl_3Br were estimated. The value of the cross section for the overall negative ion formation trough DEA was $1 \times 10^{-19} \, m^2$ at ~ 0.6 eV resonance. They concluded that DA at energies below 0.15 eV was controlled by the ground state of CCl_3Br^- whereas at higher electron energies the first excited state becomes important and gives the peak located at about 0.6 eV.

The present study was also motivated by our former experiments on DEA to the compounds CH_2ClBr and $CHClBr_2$ [8] [9]. In these studies we have measured the total DEA cross section its temperature dependence and the partitioning of the two exothermic reaction channels Br^- and Cl^-. In all these molecules the Br^- reaction channel was dominant independently of the temperature. These crossed beams results were in very good agreement with the swarm data on DEA to the same molecules by Spanel *et al.* [10]. A similar DEA study to a chloro-bromo derivative (1,4-chlorobromobenzene) has been performed by Rosa *et al.* [11] using a crossed beams experiment. Also for this type of molecule the Br^- channel was dominant at all gas temperatures. Unusual temperature behavior of the DEA reaction was observed, which resembles present thermal decomposition of the molecules at high temperatures.

2 Experiment

The present work has been carried out in the crossed electron/molecular beam apparatus. The apparatus has been described in detail in [12]; therefore we will give only a brief description.
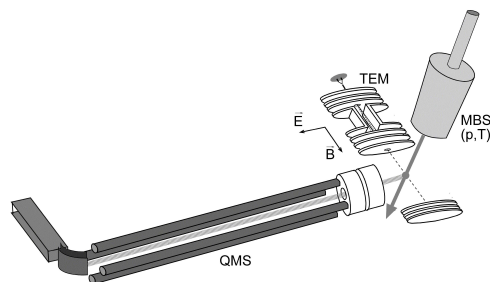
Fig. 1. Schematic view of the electron-molecular beam apparatus (TEM- trochoidal electron monochromator, EB- electron beam, MB-molecular beam, QMS-quadrupole mass spectrometer).

A schematic view of the apparatus is shown in the Fig. 1. The electron beam is formed in a trochoidal electron monochromator (TEM) [13] with an electron energy resolution of about 68 meV full width at half maximum (FWHM). The calibration of the electron energy scale and the estimation of the electron energy resolution were performed through measurement of the electron attachment (EA) process SF_6^-/SF_6.

The temperature regulated Effusive Molecular Beam Source consists of a heated stainless steel gas container (volume $\approx 10\,\mathrm{cm}^3$, inner surface $\approx 20\,\mathrm{cm}^2$) with a single 4 mm long cylindrical channel 0.5 mm diameter. The pressure inside the EMBS is measured with an absolute pressure sensor. A well defined molecular beam with a narrow angular distribution function is formed by effusion of the molecules trough this channel. An aperture with a diameter of 3 mm in a shielding is placed between the EMBS and the reaction chamber of the TEM in order to reduce the flow of the gas in the reaction chamber and the TEM. The EMBS is resistively heated (temperature range (293–650) K) using six heaters made from ceramic tubes and tungsten wire (diameter of 0.5 mm). The temperature of the EMBS is measured at two various positions by a pair of thermocouples (chromel-alumel). The gas inlet system of EMBS is working at higher pressure (typically $100-10^5$ Pa) and the gas is introduced to the EMBS through a precise diaphragm regulating valve, reducing the gas pressure to (0.1–7) Pa. At these pressures the mean free path of the molecules in the EMBS is much longer than the typical dimension of the EMBS and thus the collisions of the molecules with the walls are dominant ($\approx 10^4$ collisions). We assume that the molecules are in thermal equilibrium with the walls of the EMBS and thus the temperature of the molecules is equal to the temperature of the walls measured by the thermocouples. If the gas flow through the EMBS is constant, the density of the gas in the molecular beam n_0 varies with the temperature of EMBS (hence T) according to following expression:

$$n_0 \sim T^{-0.5}. \tag{3}$$

If a cross-section for DEA is independent on T, the ion yield will follow this dependence.

The negative ions formed in the intersection between the electron and the molecular beams are extracted by a weak electric field ($1\,\mathrm{Vm^{-1}}$) into a Quadrupole Mass Spectrometer (QMS). The mass spectroscopically analysed negative ion signal as a function of the electron energy has been measured.
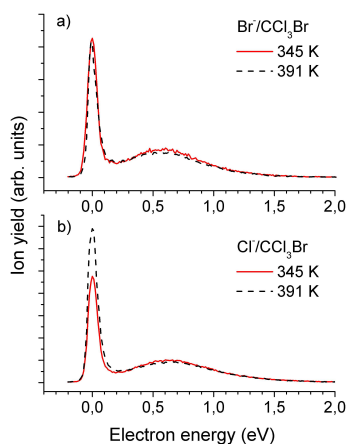
Fig. 2. Ion yield curve for a) DEA reaction Br^-/CCl_3Br as a function of electron energy, b) DEA reaction Cl^-/CCl_3Br as a function of electron energy, measured at two different temperatures 345 and 391 K.

3 Results and discussion

In present experiment we have measured ion yield curves for the reaction channels (1) and (2) for DEA to CCl_3Br in the electron energy range from $0\,eV$ to $1.8\,eV$ and in the temperature range from 293 K to 460 K. In the Fig. 2 a) and b) the ion yields for Br^- and Cl^- negative ions are presented for two gas temperatures 345 and 391 K. The shapes of the ion yields as a function of electron energy are in very good agreement with previous crossed beams study by Spanel *et al.* [4]. The first peak is located at zero electron energy ($\approx 0\,eV$) for both Br^- and Cl^- channels. The second broad peak can be found at about $0.60\,eV$ for Br^- and at about $0.65\,eV$ for Cl^- reaction channel. The Cl^- peak occurs at slightly higher energy than the Br^- peak. This can be attributed to a larger survival factor for the lighter fragment, leading to a smaller redshift of the Cl^- DEA peak relative to the resonance energy [7].

In case of Br^- we see in Fig. 2a, only little difference in the ion yields measured at two different temperatures. This difference is produced by decrease of the molecular density in the molecular beam with increasing T (3). In case of Cl^- ion (Fig. 2b), the increase of ion yield at $\approx 0\,eV$ peak is observed, at higher electron energies the ion yield decreases slowly according to (3).

In the Fig. 3 a) b) the gas temperature dependences of the Br^- and Cl^- ion yields measured at first and second peaks are shown. The Br^- ion yield decreases slowly with T in the temperature range (293–422 K) (Fig. 3a) and 3b). At the gas temperatures above 420 K more pronounced decrease of the Br^- signal with T is observed; very similar dependence of the ion yield dependence on T is observed also for the $0.6\,eV$ peak. The slow decrease of the Br^- signal with T for both peaks is only due to the decrease in the gas number density of the molecular beam with T and thus follows the $T^{-0.5}$ law (3). For this reason it can be concluded, that the cross-section for the Br^- channel does not depend on T in the temperature range 293–422 K. In the beam experiment published by Spanel *et al.* [4], slow decrease of Br^- signal has been reported, this observation however was in contradiction to the swarm experiment in Spanel *et al.* [4], where
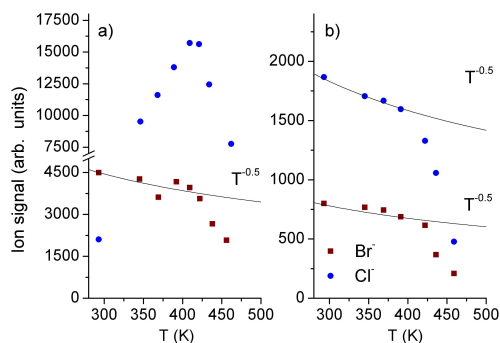
Fig. 3. The temperature variations of Br^-/CCl_3Br and Cl^-/CCl_3Br ion yields a) for the ≈ 0 eV and b) 0.6 eV and 0.65 eV peak, as functions of T. The $T^{-0.5}$ dependence of the ion signals are indicated by the solid line.

Br^- is temperature independent and also with present observation of temperature independent cross section for Br^-/CCl_3Br DEA reaction channel.

In case of Cl^- ion, the variations of the ion yield of the first and the second peak with T are plotted in the Fig. 3a and 3b. The Cl^- ion yield at ≈ 0 eV increases with T in the temperature range 293–422 K. This increase of the signal is attributed to the activation energy (EA) for the Cl^- reaction channel. At higher gas temperatures however a decrease of the ion yield with T is observed. This effect is ascribed to the thermal decomposition of CCl_3Br. The Cl^- ion yield of the second peak decreases with T according to $T^{-0.5}$ law (in the temperature range 293–422 K). Therefore one can surmise that the second peak of DEA cross-section to CCl_3Br does not depend on T in this temperature range. Above 422 K strong decrease of the ion yield due to thermal decomposition of the molecules in the EMBS is observed.

A considerable decrease in the Br^- and Cl^- ion intensity at temperatures above 422 K is most probably due to surface catalysed thermal decomposition of CCl_3Br in the EMBS. Analogous effects have been observed in the DEA studies to CH_3Cl, C_2H_5Cl and C_3H_7Cl by Pearl *et al.* [10] and by Matejčík *et al.* [12] in case of CCl_4, $CHCl_3$ and $CHBr_3$.

An Arrhenius plot for Cl^- and for overall negative ion yield for DEA to CCl_3Br molecule is presented in Fig. 4. From the slope of the Arrhenius plot the activation energy for DEA reaction can be estimated. From the slopes of Arrhenius plots presented in Fig. 4 we have derived a value of the activation energy for Cl^- channel of $113(\pm 20)$ meV and for the overall negative ion yield of $65(\pm 20)$ meV. For comparison, Spanel *et al.* [4] gives overall activation energy for DEA to CCl_3Br estimated from swarm experiment of 55 meV. They did not estimate the activation energy for the Cl^- channel, but using their published swarm data we have derived for this channel activation energy of 123 meV. Parathasarty *et al.* [6] measured temperature dependence of DEA to CCl_3Br using the RET technique and from their published data we have derived an activation energy of 93 meV for Cl^- channel. The present values of activation energies both for Cl^- channel and overall ion yield are in satisfactory agreement with the values derived from swarm experiment and RET experiments.

In Fig. 5 branching ratios R as functions of electron energy and gas temperature at 293 and 422 K are presented. From the branching ratio at 293 K we are able to deduce that at low electron
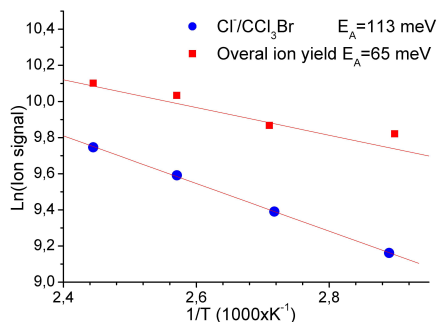
Fig. 4. Arrhenius plots for DEA to CCl_3Br, for overall negative ion formation and for the reaction channel Cl^-/CCl_3Br.
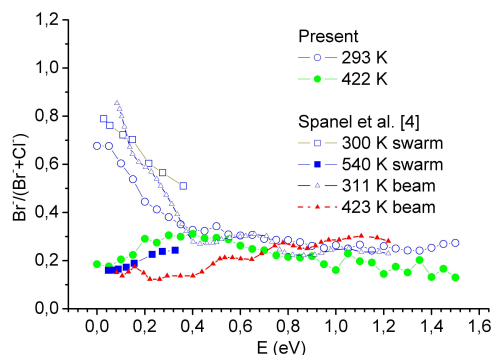
Fig. 5. Branching ratios measured at 293 and 422 K. For a comparison branching ratio from Spanel *et al.* [4] obtained using swarm and crossed beams techniques are presented.

energies $\approx 0\,eV$ formation of Br^- is dominant (almost 70% of the products is Br^-), at higher electron energies R is close to statistical value of 25%. Similar behaviour was observed also by Spanel *et al.* [4] in the swarm and the beam experiments. The branching ratio at high 422 K has different character. In whole electron energy range Cl^- channel is dominant and the branching ration is nearly statistical ($\approx$25%). This observation is in very good agreement with the swarm and beam data of Spanel *et al.* [4].

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