EIPAM - Short Visit Grant

Scientific Report

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Title: **DISSOCIATIVE ELECTRON ATTACHMENT TO THE CHLORO-BROMOPROPANES**

Purpose of the visit

The purpose of the visit was to study dissociative electron attachment to chloro-bromopropanes. The study was a continuation of our program of measurements of a rate of an electron attachment processes to chloro-bromo derivatives of hydrocarbons which have been already measured using the swarm technique at the University of Podlasie.

The study was conducted in the gas phase using the crossed electron/molecules beams apparatus in Bratislava. In contrast to the swarm method we were able to extend the electron energy range up to 10 eV and we were also able to analyse the products of the reactions using the mass spectrometer.

Dissociative electron attachment in halocarbons have been investigated very intensively using different experimental techniques but data from various laboratories sometime differ strongly, for example in the case of swarm experiment the difference in the rate constants quite often is of more than one hundred percent and some were measured only once. So there is a need for seeking a method which helps to verify these values as well as to find connection between the structure of the molecule and its ability to capture an electron.
We hope that investigations of a big homologus grup of compounds, where the small changes in the molecule can change both the effectiveness and the mechanism of the negative ions formation process, could be a very good tool for finding some general rules controlling the attachment process.

Description of the work carried out

During the visit we have studied dissociative electron attachment (DEA) to following molecules: $CH_2BrCH_2CCl_3$, $CH_2BrCH_2CF_2Br$, $ClCH_2CH_2CH_2Br$.

The experimental work has been carried out at the crossed electron/molecular beam apparatus at the Department of Experimental Physics in Bratislava.

The crossed beams apparatus is equipped with trochoidal electron monochromator, quadrupole mass spectrometer and temperature controlled effusive molecular beams source.

The electron beam is formed in a trochoidal electron monochromator. The molecular beam is produced in an effusive molecular beam source. The beam is formed by effusing the gas through a channel (0.5 mm diameter and 4 mm long) and an external aperture. Negative ions formed within the intersection between the electron beam and the molecular beam are extracted by a weak electric field ($1Vm^{-1}$) and focused into a Quadrupole Mass Spectrometer. The mass analyzed negative ion signal is then detected as a function of the electron energy.

The main interest of our investigation was the measurements of the ion yields of the negative ions formed in the DEA to the molecules. The ion yields were measured in the electron energy range from 0 to about 9 eV. In this energy range we recorded the electron energy dependency of fragments with the mass to ratio (m/Z): 158, 79, 70, 63, 35, 19. Additionally the negative ion mass spectra of the molecules at different electron energies have been studied.

Description of the main results obtained

3-bromo-1,1,1-trichloropropane

The DEA to $CH_2BrCH_2CCl_3$ have been measured in the energy range from 0 to about 9 eV incident electron energy and a gas temperature of 333 K. In this energy range four fragment negative ions (Cl^-, Cl_2^-, $C_2H_4Cl^-$ and Br^-) were observed. Figure 1 present the ion yield curves of negative ions obtained from electron attachment to single $CH_2BrCH_2CCl_3$. This ion yield shows two resonances in the case Cl^- the first one at about 0.1 eV, second one at about 6.9 eV (but not so strong). The formation of the Br^- occurs at similar energies. The first resonance is located at 0.13 eV, the second one at about 6.6 eV. We have found also molecular ions Cl_2^- and $C_2H_4Cl^-$. The negative ion Cl_2^- is formed at a resonance peaking at 0 eV and formation of $C_2H_4Cl^-$ ion occurs about 0.1 eV

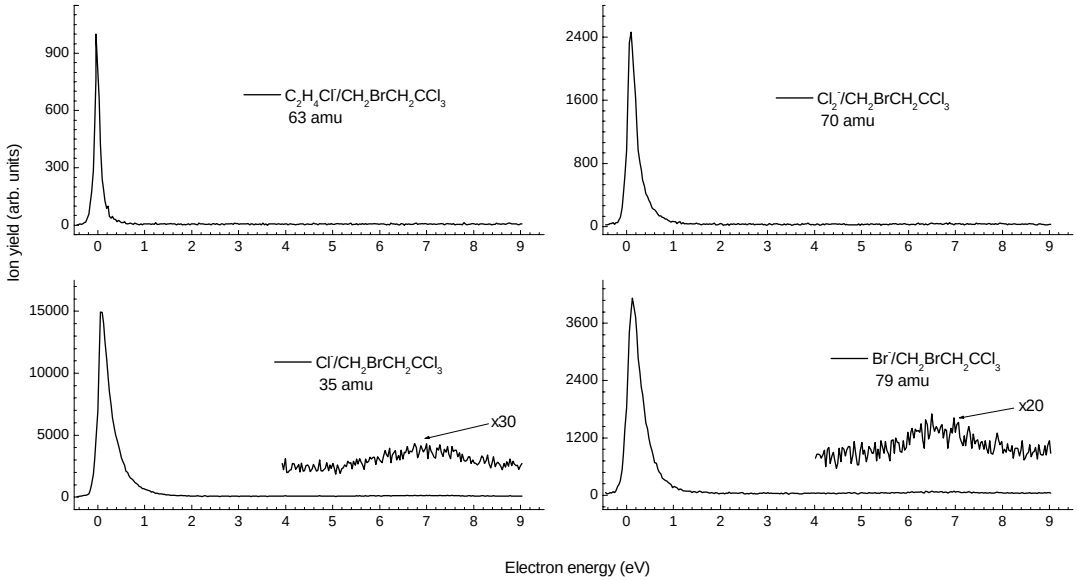

Fig. 1. Cl_2^-, Cl^-, $C_2H_4Cl^-$ and Br^- ion yields for DEA to $CH_2BrCH_2CCl_3$

1,3-dibromo-1,1-difluoropropane

The $CH_2BrCH_2CF_2Br$ molecule was also subject our investigations.

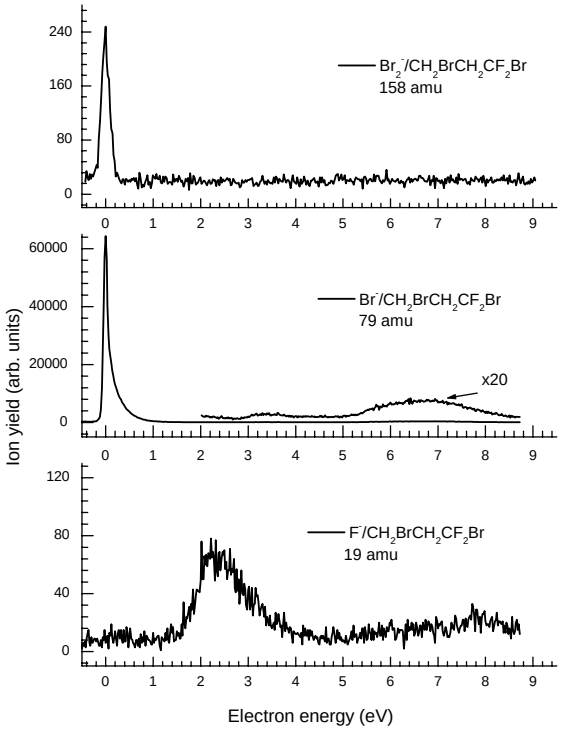

Fig. 2. Br_2^-, Br^- and F^- ion yields for DEA to $CH_2BrCH_2CF_2Br$.

In figure 2 the Br_2^-, Br^- and F^- ion yields for DEA to $CH_2BrCH_2CF_2Br$ are presented. The dominant ion is Br^-. In this case the ion yield shows three resonances, first one at 0 eV, second one at about 3.5 eV and third one at about 6.9 eV. The ion yield F^-/ $CH_2BrCH_2CF_2Br$ exhibits one dominant peak at about 2.4 eV.

We have found also molecular ion Br_2^-. This ion was formed at much lower intensity than Br^- with resonance peaking at about 0 eV.

1-bromo-3-chloropropane

The molecule $ClCH_2CH_2CH_2Br$ was subject of our earlier investigation. The DEA yield for this molecule shown only 0 eV peak both for Cl^- and Br^- ion. On the basis of analysis obtained results we have found that the partial cross sections for DEA reactions have been inflated.

However, the zero energy peaks may also originate from impurities (such as CCl_4, CBr_3Cl) which have extremely high cross sections for DEA at 0 eV and already trace amounts may substantially contribute to the ion yield at low electron energies. For this reason decided to repeat our measurements using new samples.

Figure 3 presents the ion yield curves of the two fragments observed in electron attachment to single $ClCH_2CH_2CH_2Br$ molecules.

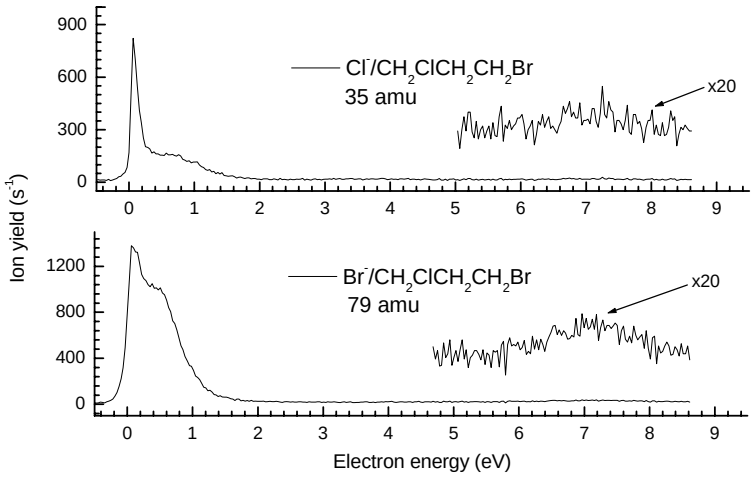

Fig. 3 Ion yield for DEA reaction Cl^-/ $CH_2ClCH_2CH_2Br$ and Br^-/$CH_2Cl\,CH_2CH_2Br$

In the case formation both Cl^- and Br^- ion, the ion yield shows a prominent 0 eV peak. The strong electron attachment at about 0 eV (so as previously) is due to presence of an impurity in the present sample (purity 99%). In the present experiment (in contrast to previous) we have observed also other resonance. The Cl^- ion was formed also at about 0.6 eV and at about

7.2 eV, in the case Br^- we have observed two additional resonances, first at about 0.4 eV and the second one at about 7.2 eV.

Future collaboration

We are going to continue our collaboration on the field of the DEA studies. The advantage of the swarm experiment at the University of Podlasie is the possibility to measure absolute rate coefficients for DEA. The base for further collaboration with the Department of Experimental Physics at Comenius University in Bratislava is the fact that we may compare the results obtained by the swarm experiment obtained under different experimental conditions with the crossed beams data. Further, we are able to compare the values of the rate coefficients with the cross section estimated in the crossed beams experiment.

Projected publications

The results obtained during the visit in Bratislava will be published in scientific papers.