Scientific Report

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Title of the project: Electron attachment processes to chloro-bromo- derivatives of hydrocarbons

1. Purpose of the visit

The low energy electron attachment mechanism and the kinetics to a large number of holocarbons have been measured at the University of Podlasie using a high pressure electron swarm method [1-3]. Under these conditions electron attachment occurs both by individual molecules and by the van der Waals complexes. The electron attachment to haloethanes and halopropanes proceeds only via two-body mechanism. Using this technique, thermal electron attachment rate coefficients for electron attachment to the molecules have been measured. An important question for understanding the electron attachment reactions is the relation between the structure of the molecule and the mechanism and the rate constant of the process.

The aim of the visit was to study the electron attachment reactions to chloro-bromo-derivatives of hydrocarbons which have been already measured using the swarm technique at the University of Podlasie. These molecules have been measured during my visit using a different, crossed electron/molecules beams technique. The crossed beams apparatus at Department of Experimental Physics is equipped with trochoidal electron monochromator, quadrupole mass spectrometer and temperature controlled effusive molecular beams source [4]. 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.

The studied reactions are very important for understanding an electron-molecule interaction and negative ion formation in technological plasmas. Investigations of the electron attachment processes in the gas systems containing halocarbons are also important for environment, especially for investigating the processes occurring in the earth atmosphere.

2. Description of the work carried out during the visit

During the visit we have studied dissociative electron attachment reaction to the bromo-chloro hydrocarbons:

$$e + C_kH_lBr_mCl_n \rightarrow (C_kH_lBr_mCl_n)^- \rightarrow Br^- + C_kH_lBr_{m-1}Cl_n \quad (1)$$

$$(C_kH_lBr_mCl_n)^- \rightarrow Cl^- + C_kH_lBr_mCl_{n-1} \quad (2)$$

The DEA reaction is a two step process involving first formation of transient negative ion (TNI) followed by dissociation into thermodynamically stable fragments. The formation of the TNI is a resonant process in which the free electron is captured by the neutral molecule and a negative ion in its electronic ground or electronically excited state is formed. The thermodynamically unstable TNI decays then by an emission of the extra electron (autodetachment) or dissociation (DEA) into energetically accessible channels consisting of one negatively charged fragment and one or more neutral fragments. The TNI in case of DEA may dissociate in two reaction channels (1) and (2) [5,6]. The DEA is characterized by cross section which depends on electron energy and gas temperature.

During the visit in Bratislava we have studied the DEA to following molecules: $CH_3CH_2CH_2Br$, $CH_3CHBrCH_3$, $ClCH_2CH_2CH_2Br$, $CH_3CHBrCH_2Cl$, $ClCH_2CH_2Br$, $CHClFCF_2Br$, $CHBrClCF_3$, $CH_2BrCH_2CF_2Br$.

Using the experimental setup we have measured partial cross section for DEA to these molecules in the electron energy range from about 0 to 9 eV. We have also measured the gas temperature dependence of the partial cross sections to the molecules $CH_3CH_2CH_2Br$, $CH_3CHBrCH_3$, $ClCH_2CH_2CH_2Br$, $ClCH_2CH_2Br$, $CF_2ClCHFBr$ in the gas temperature range from 300 K to 500 K. In this case DEA reactions have been studied in the electron energy range 0 to about 2eV. We have studied the temperature dependence of DEA reactions for the Br^- and Cl^- reaction channel.

3. Description of the main results obtained

1-bromopropane and 2-bromopropane

In Figures 1 and 2 the Br^- ion yields for DEA to 1-bromopropane and 2-bromopropane measured at room temperature are presented. The ion yield for DEA to 1-bromopropane exhibits several resonances. The first one at about 0 eV, second one at 0.6 eV, third broad resonance above 6 eV consists of two narrow structures at 6.5 and 6.8 eV. Formation of Br^- ion occurs also above 8 eV.

Formation of the Br^- via DEA to 2-bromopropane occurs at similar energies as in previous molecule. The 0 eV resonance, however, is not so strong, the second resonance is located at about 0.8 eV, the third one at about 6 eV. The third resonance does not show such structure as the 1-bromopropane molecule. Above 8 eV broad structure forming Br^- is present. We have also measured the ion yields for DEA to 1-bromopropane and 2-bromopropane at various gas temperatures from 300 to 500 K. The ion yields measured at different temperatures did not show any dependence on the gas temperature in the measured temperature range.

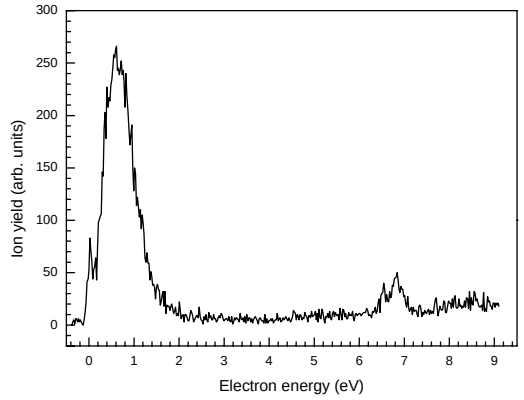

Fig.1 Ion yield for DEA reaction $Br^-/1\text{-}C_3H_7Br$

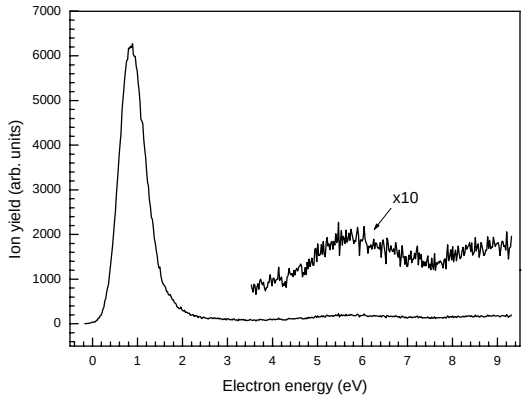

Fig.2 Ion yield for DEA reaction $Br^-/2\text{-}C_3H_7Br$

1-bromo-3-chloropropane and 2-bromo-1-chloropropane

The molecules $ClCH_2CH_2CH_2Br$, $CH_3CHBrCH_2Cl$ were subjected to the DEA. In the case of both isomers the Br^- and Cl^- ions were detected, additionally also molecular ions $ClBr^-$ and $HClBr^-$ were observed. In Figures 3 and 4 the Br^- and Cl^- ion yields for DEA measured at room temperature are presented. In Figures 5-8 the $ClBr^-$ and $HClBr^{--}$ ion yields for DEA measured at room temperature are presented.

The DEA yield for 1-bromo-3-chloropropane shows 0 eV peak both for Cl^- and Br^- ions. The low energy peak in the ion yields exhibits more structures. The ion yields for DEA to 2-bromo-1-chloropropane shows resonances at 0 eV for Br^- and 0 eV and 0.12 eV for Cl^-. Moreover, the Br^- reaction channel was dominant in both studied isomers at low electron energies.

In the case of these isomers we have observed very interesting results concerning the ratio Cl^-/Br^- ions at 0 eV. In the case of 1-bromo-3-chloropropane the ratio was about 1:100 but in the case of 1-chloro-2-bromopropane the ratio was only 1:20.

We have found also molecular ions $ClBr^-$ and $HClBr^-$. The production of these ions depends on the nature of the molecule. The molecular ion $ClBr^-$ was formed with higher intensities for 1-chloro-2-bromopropane while $HClBr^-$ for 1-bromo-3-chloropropane.

We have also studied the temperature dependence of DEA reactions for the Br^- and Cl^- to 1-bromo-3 chloropropane in the electron energy range from 0 to 2 eV. The ion yields did not show any dependence on the gas temperature in the measured temperature range.

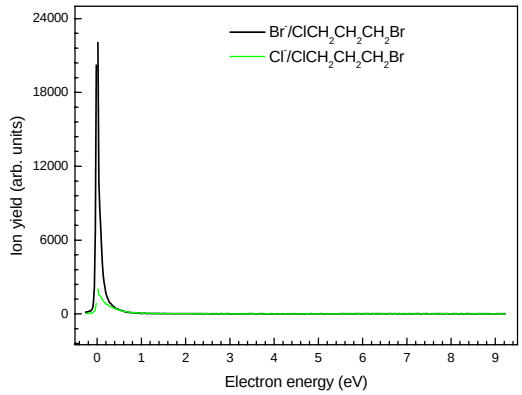

Fig.3 Ion yield for DEA reaction $Br^-/ClCH_2CH_2CH_2Br$ and $Cl^-/ ClCH_2CH_2CH_2Br$

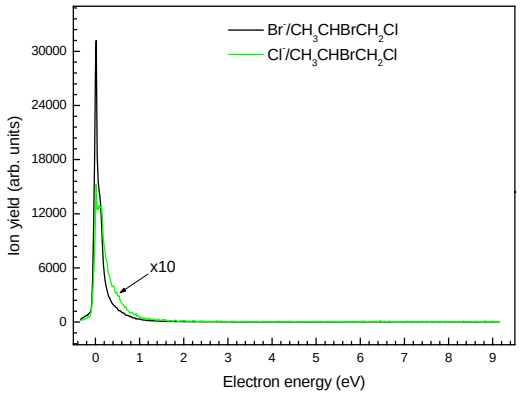

Fig.4 Ion yield for DEA reaction $Br^-/ CH_3CHBrCH_2Cl$ and $Cl^-/ CH_3CHBrCH_2Cl$

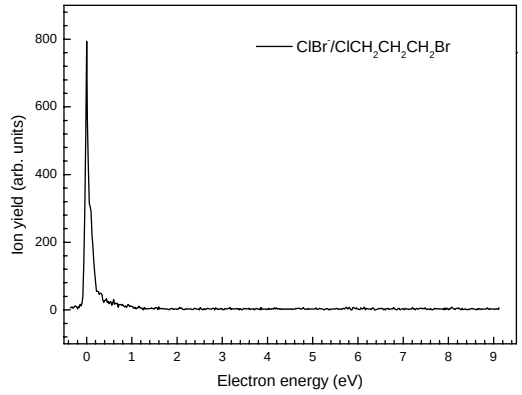

Fig.5 Ion yield for DEA reaction $ClBr^-/ClCH_2CH_2CH_2Br$

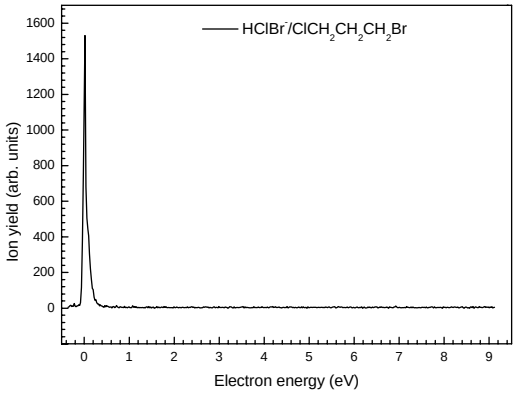

Fig.6 Ion yield for DEA reaction $HClBr^- /ClCH_2CH_2CH_2Br$

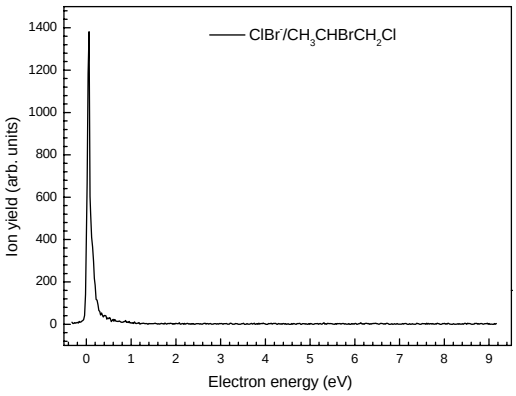

Fig.7 Ion yield for DEA reaction
$ClBr^-/ CH_3CHBrCH_2Cl$

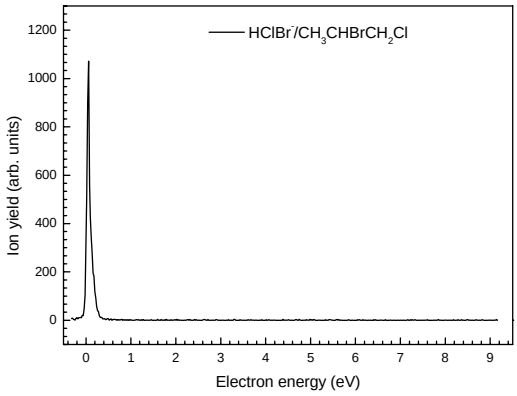

Fig.8 Ion yield for DEA reaction
$HClBr^- / CH_3CHBrCH_2Cl$

1-bromo-2-chloroethane

In Figure 9 Br^- and Cl^- ion yields for DEA to 1-bromo- 2-chloroethane measured at room temperature are presented. The ion yields were measured in the electron energy range from 0 to about 9 eV. This ion yield for DEA to 1-bromo- 2-chloroethane shows two resonances in the case Br^- the first one at about 0 eV, second one at 6.5 eV. The Cl^- ion was formed with lower intensities at resonance peaking at about 0 eV. Additionally the molecular ion $ClBr^-$ has been also observed in present experiment.

We have also studied the temperature dependence of DEA reactions for the Br^- and Cl^- to 1-bromo- 2-chloroethane in the electron energy range from 0 to 2 eV. We have found slow increase of the DEA reaction with the temperature.

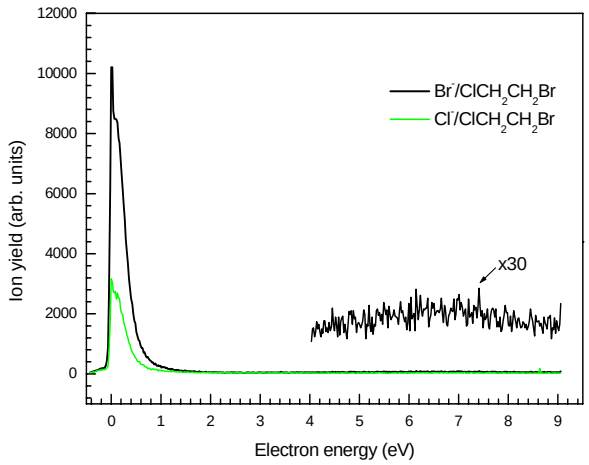

Fig.9 Ion yield for DEA reaction $Br^-/ClCH_2CH_2Br$ and $Cl^-/ ClCH_2CH_2Br$

1-bromo-2-chloro-1,1,2-trifluoroethane

The DEA to 1-bromo-2-chloro-1,1,2-trifluoroethane have been measured in the electron energy range from about 0 to about 9 eV. The ion yields for Cl^- and Br^- ions is presented in Figure 10. The dominant ion is Br^-. The molecular ions $ClBr^-$ and $HClBr^-$ and F^- ion have been not observed in present experiment. The cross section for F^- is so low that the sensitivity of the apparatus was not sufficient to detect F^- ion.

We have studied lso the temperature dependence of DEA reactions for the Br^- and Cl^- reaction channel. The 1-bromo-2-chloro-1,1,2-trifluoroethane did not show any dependence on the temperature.

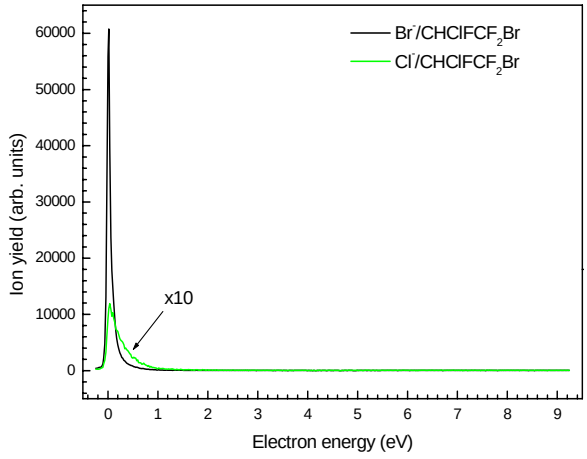

Fig.10 Ion yield for DEA reaction $Br^-/CHClFCF_2Br$ and $Cl^-/CHClFCF_2Br$

2-bromo-2-chloro-1,1,1-trifluoroethane

In Figure 11 Br^- and Cl^- ion yields for DEA to 2-bromo- 2-chloro-1,1,1-trifluoroethane measured at room temperature are presented. The ion yields were measured in the electron energy range from 0 to about 9 eV. This ion yields for DEA to 2-bromo- 2-chloro-1,1,1- trifluoroethane show two resonances in the case Br^- the first one at about 0.24 eV second one at 6.8 eV, in the case Cl^- the first one at about 0.18eV, second one at 6.8 eV.

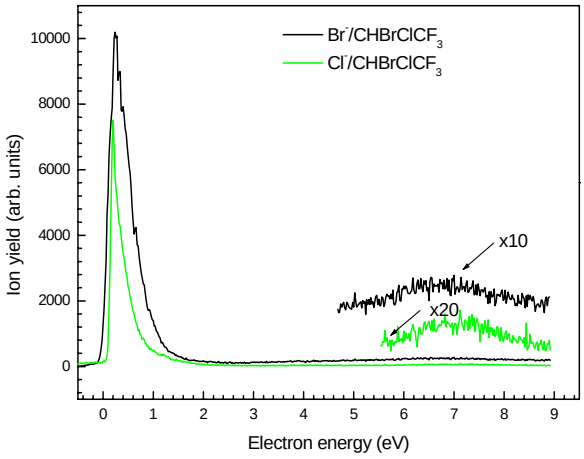

Fig.10 Ion yield for DEA reaction $Br^-/CHBrClCF_3$ and $Cl^-/CHBrClCF_3$

1,3-dibromo-1,1-difluoropropane

The yields of the ions formed via DEA to 1,3-bromo-1,1-difluoropropane are presented in Figure 11. The dominant ion formed is the Br^- with resonances observed at 0, 3.2 and 6.8 eV. The F^- ion was formed at much lower intensities with resonance peaking at 2.4 eV.

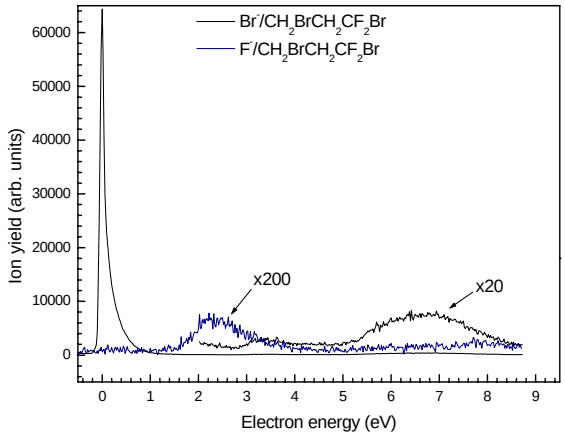

Fig.11 Ion yield for DEA reaction $Br^-/CH_2BrCH_2CF_2Br$ and $F^-/CH_2BrCH_2CF_2Br$

4. Future collaboration

We are going to continue our collaboration on the field of the DEA studies to the molecules. The advantage of the swarm experiment at the University of Podlasie is the

possibility to measure absolute rate coefficients for DEA to the molecules. 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.

5. Projected publications

The results obtained during the visit in Bratislava will be published in scientific papers. The paper should deal with the DEA to 1-bromo-3-chloropropane and 2-bromo-1-chloropropane 1-bromo-2-chloroethane, 1-bromo-2-chloro-1,1,2-trifluoroethane, 2-bromo- 2-chloro-1,1,1 -trifluoroethane.

Second paper could present the data obtained on DEA studies to 1-bromopropane, 2-bromopropane, 1,3-dibromo-1,1-difluoropropane.

6. References

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