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Negative ion formation in dissociative electron attachment to selected halogen derivatives of propane[☆]

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ABSTRACT

Dissociative electron attachment (DEA) to halogenated derivatives of propane: 1-bromo-3-chloropropane, 2-bromo-1-chloropropane, 3-bromo-1,1,1-trichloropropane and 1,3-dibromo-1,1-difluoropropane was studied in the gas phase at ambient temperature using a high resolution crossed electron/molecule beams technique. The negative ions formed via DEA reaction were identified using mass spectrometric technique and the anion yields were measured in the electron energy range from 0 to 10 eV. The absolute partial cross sections for DEA to the molecules were estimated using the relative flow technique.

1. Introduction

Dissociative electron attachment (DEA) reactions to the molecules play an important role in various fields of chemistry, physics and in large number of technological applications [1]. Chloro- and bromo-substituted hydrocarbons are of high importance for the atmospheric chemistry. These molecules which are either of anthropological or natural origin are sources of the atomic chlorine and bromine in the upper atmosphere and are responsible for the decomposition of the stratospheric ozone in a catalytic cycle [2,3]. To the most important sources of the chloro- and bromo-substituted hydrocarbons belong the human activities (organic and pharmaceutical synthesis) and there exists also natural sources (ocean) thus these molecules may exist in the atmosphere in considerable amounts [4]. Besides these environmental hazards it has been proved that the halogenated propanes have also genotoxic ability (damages to the DNA) and that this ability depends on the mutual position of the halogens in the molecules. The most toxic halogenated propanes contain vicinal bromines [5]. The environmental importance of the molecules, the genotoxic properties and also the fundamental interest in the competition of the several reaction channels in DEA reactions motivated present study. Additionally, the study of DEA to different isomers of chloro–bromo-propane is of fundamental interest as we are able to study the effects of the molecular structure on the fragmentation and the kinetics of the DEA reaction.

Our laboratory systematically deals with DEA to chloro- and bromo-substituted hydrocarbons [6–11]. The DEA to several isomers of methane revealed that the Br^- channel is dominant accounting for more then 90% of the products and rest the Cl^- anion. Interesting question in DEA to chloro- and bromo-substituted hydrocarbons is the formation of the molecular ions Cl_2^- and $ClBr^-$. These ions were observed in FALP (Flowing Afterglow Langmuir Probe) experiments to chloro- and bromo-substituted methanes [6], however in our crossed beams experiments we were not able to detect these anions [10]. Thus one of the questions in present experiment is if molecular negative ions are formed in DEA reaction with larger halo-hydrocarbons.

In present work we studied the reaction of the DEA to halogen substituted propanes:

$$e + M \rightarrow (M^{\#-}) \rightarrow X^- + (M - X) \quad (1)$$

$M^{\#-}$ represents the transient negative ion (TNI), X^- represents a halogen negative ion and $(M - X)$ a radical. The DEA reaction is a two step process. In the first step an unstable transient negative ion $M^{\#-}$ is formed, which either decays via autodetachment or decompose into fragment negative ion and neutral fragment or fragments.

The DEA to the chloro–bromo-propanes have been previously studied using swarm technique and crossed beams technique

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[☆] Dedicated to Professor Eugen Illenberger on the occasion of his 65th birthday.

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[12,13]. The rate coefficients for DEA to 2-bromo-1-chloropropane of $3.5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ and to 1-bromo-3-chloropropane of $2.5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$ have been measured in swarm experiment [12]. In the low resolution crossed beams experiment the Br^- and Cl^- ions as the main products have been detected. Significant differences in the ratio of the Cl^-/Br^- intensities have been observed, ranging from about 1 for 2-bromo-1-chloropropane to about 0.05 for 1-bromo-3-chloropropane [12]. The crossed beams experiment [12] has been carried out with low resolution electron beam (full width at half maximum (FWHM) of more then 1 eV) and thus the low energy resonances are not properly resolved. So far we are not aware of experimental cross beams studies to the molecules 1,3-dibromo-1,1-difluoropropane and 3-bromo-1,1,1-trichloropropane.

2. Experiment

Present study has been carried out using a crossed electron/molecular beams apparatus which has been described in detail in [14]; therefore we will give only a brief description. The electron beam is formed in a trochoidal electron monochromator (TEM) [15] with an electron energy resolution in present experiment of about 100 meV full width at half maximum. The molecular beam is formed by effusion of the molecules through a channel (4 mm long and 0.5 mm diameter). The molecular beam source is temperature controlled so the DEA reaction can be measured at different gas temperatures. The pressure in the molecular beam source (about 1 Pa) is measured by absolute pressure gauge (Baratron MKS). The negative ions are formed at the crossing point of the two beams. The ions are extracted by a weak electric field ($E < 0.2\,\mathrm{V\,cm^{-1}}$) into quadrupole mass spectrometer and the mass selected ions are detected as a function of the electron energy. Spatial discrimination of the ions exists in present experiment, i.e., only ions from a very small spatial angle are extracted into the mass spectrometer. This discrimination does not depend on the mass of the molecule and only weakly on the kinetic energy of the molecule. For this reason we do not expect discrimination effect concerning the Cl^-/Br^- ratio. Some discrimination of the ions is also possible in the mass spectrometer (transmission) and detector; however, according to our experience we may neglect these effects in this range of masses. The resolution of the mass spectrometer was sufficient to resolve the isotopes of Br and Cl (^{79}Br, ^{81}Br, ^{35}Cl, ^{37}Cl). The negative ion yields were measured for isotopes ^{35}Cl and ^{79}Br, however, the experimental intensities were corrected in order to get total $Br^-$and Cl^- ion yields. The calibration of the electron energy scale and the estimation of the electron energy distribution function of the electron in the electron beam were carried out through the measurement of the electron attachment (EA) process SF_6^-/SF_6, additionally, the electron attachment reaction SF_6^-/SF_6 has been used to estimate the cross sections for DEA to the studied molecules using the relative flow technique.

The cross section curves were obtained by data analysis of the experimental ion yields. The ion yield is a convolution of the cross section and the electron energy distribution function and also depends on the sensitivity of the apparatus. Measuring the ion yield for a reference molecule under well defined experimental conditions we are able to determine the electron energy distribution function $f(E,U)$ and the response function K of the apparatus. Using $f(E,U)$ and K we are able to determine cross sections for a molecule measured under identical conditions as the reference molecule (electron current, $f(E,U)$, pressure). We assume identical sensitivity of the apparatus K for the detection of the ions. In present experiment we have used SF_6 as a reference molecule. The cross section for EA to SF_6 has well-established values [17]. The DEA cross sections (Fig. 2) were obtained from the ion yields by a deconvolution procedure (see [16] for details).

The ion yields were measured in the electron energy range from 0 to about 9 eV. The molecules studied in present experiment are under normal conditions liquids and the purity of the samples has been 99%. No additional cleaning of the samples has been carried out. The gases were purified by the vacuum freeze–pump–thaw technique in order to remove impurities. Without this cleaning procedure of the gases the negative ions formed in DEA to the impurities present in the sample were dominant, however, also this cleaning technique could not remove all impurities from the sample.

3. Results and discussion

DEA to 2-bromo-1-chloropropane, 1-bromo-3-chloropropane was measured in the electron energy range from 0 up to 9 eV. The DEA to these derivatives of propane results in the formations of the ions Br^- and Cl^-. The measured ion yields for DEA to the 2-bromo-1-chloropropane, 1-bromo-3-chloropropane are presented in Figs. 1 and 2. The ion yields for all fragments exhibit a prominent peak at ~0 eV. The 0 eV peak is usually attributed to the capture of s-wave electrons and subsequent dissociation of the parent molecular anion. This process is typical for exothermic dissociative electron attachment channels. The structures and width of the 0 eV peaks for these molecules indicate additional low energy resonances present in the molecules at approximately 0.1 eV in 2-bromo-1-chloropropane and at about 0.5 eV in 1-bromo-3-chloropropane. In previous low resolution experiment [12] due to broad electron energy distribution function (about 1 eV FWHM) only one broad resonance was observed in both molecules located at 0.31 eV in 2-bromo-1-chloropropane and 0.37 eV in 1-

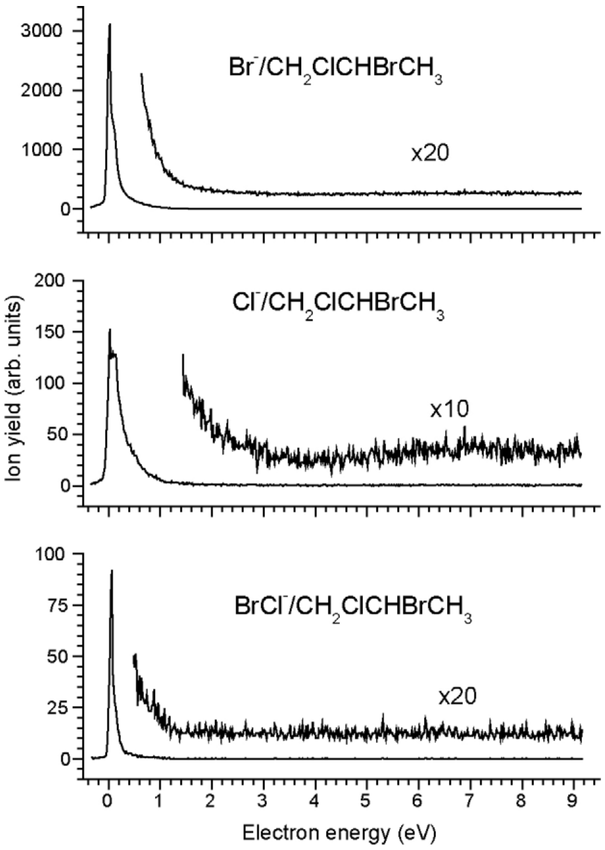

Fig. 1. The ion yields of the ions formed in DEA to 2-bromo-1-chloropropane.

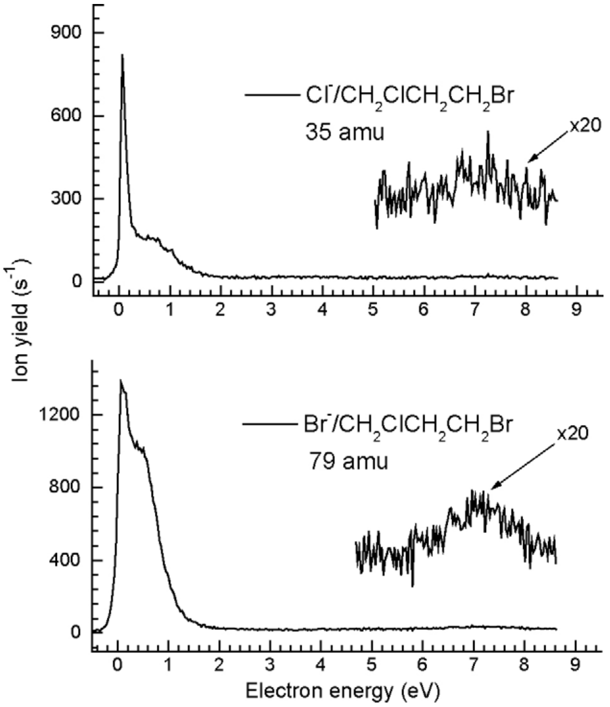

Fig. 2. The ion yields of the ions formed in DEA to 1-bromo-3-chloropropane.

bromo-3-chloropropane. The positions of the resonances of all studied molecules are listed in Table 1. A weak most probably core excited resonance is present at approximately 7 eV in 1-bromo-3-chloropropane, this resonance is present for both negative ions Cl^- and Br^-. In the case of 2-bromo-1-chloropropane, there is some indication of similar high energy resonance, however, this resonance is very weak and just above the noise level. The sensitivity of the apparatus was not sufficient to detect this resonance more clearly. Using relative flow technique (reference reactions $SF_6{}^-/SF_6$, the cross section for this reaction was taken from [17]) we have roughly estimated the values of the partial cross sections. The values of the cross sections for DEA to 2-bromo-1-chloropropane are $2 \times 10^{-16}\,cm^2$ (Br^- at 0.12 eV) and $2 \times 10^{-17}\,cm^2$ (Cl^- at 0.1 eV). In the case of DEA to 1-bromo-3-chloropropane the values are $3 \times 10^{-17}\,cm^2$, $1 \times 10^{-18}\,cm^2$ (Br^- at 0.47 eV, respectively 7 eV) and 5×10^{-18}, $6 \times 10^{-19}\,cm^2$ (Cl^- at 0.57 eV, respectively 7 eV). The accuracy of the present cross sections is limited with relative accuracy of about 20%. In the low electron energy range (at 0 eV peak) the accuracy of the cross sections is deteriorated by the presence of impurities in the samples, the cross sections at higher electron energies are not influenced by the impurities. In the paper [12] besides the low resolution crossed beam study also a quantitative swarm study was presented. The values of the total rate constants for DEA to several chloro–bromo-substituted hydrocarbons were measured. In the case of 2-bromo-1-chloropropane and 1-bromo-3-chloropropane the values were $3.5 \times 10^{-10}\,cm^3\,s^{-1}$, respectively $2.5 \times 10^{-10}\,cm^3\,s^{-1}$. The integration of the present deconvoluted partial cross section gives values of rate coefficients of 3×10^{-9} and $8 \times 10^{-10}\,cm^3\,s^{-1}$ which exceed the values obtained in the swarm experiment. The experiments to the molecules with inefficient dissociative electron attachment are very sensitive to the impurities. Already trace amounts (less then 1%) of impurities (in the sample, the gas inlet system or the apparatus) with large cross sections for DEA (e.g., CCl_4, CCl_3Br, ...) present in the sample may affect the apparent rate of the reaction. This is probably also problem in the present DEA studies to 1-bromo-3-chloropropane and 2-bromo-1-chloropropane and may explain the difference in the reaction rates in present and the former experiment. The trace amounts of impurities were confirmed also by positive mass spectra of the compounds, however in the positive mass spectra the impurities were very weak.

Valuable information about reactions with two or more reaction channels gives quantity called "branching ratio" (R). This quantity describes the relative distribution of the ions into the reaction channels R defined as follows ($R_{Br} = Br^-/(Br^- + Cl^- + BrCl^-)$, $R_{Cl} = Cl^-/(Br^- + Cl^- + BrCl^-)$). There exist characteristic difference in the branching ration between 2-bromo-1-chloropropane and 1-bromo-3-chloropropane. Whereas in 2-bromo-1-chloropropane the branching ratio R_{Br} is about 90% (almost constant in whole measured electron energy range) in 1-bromo-3-chloropropane the R_{Br} depends strong on the electron energy (62% at 0 eV, 87% at 0.47 eV and about 60% at higher electron energies (above 1 eV)). If we compare the present branching ratio results with those published in [12] we may conclude that there is reasonable agreement between these two experiments.

The DEA reaction to 3-bromo-1,1,1-trichloropropane results in four different reaction channels (within the sensitivity of present apparatus). We have detected the products Cl^-, Br^-, $Cl_2{}^-$ and $C_2H_4Cl^-$. The ion yields of these products are visible in Fig. 3. The dominant product at ~0 eV is Cl^- which is stronger than the Br^- anion. This is unusual result as in the previously studied chloro–bromo-substituted hydrocarbons, the dominant ion was always Br^-. The high efficiency of the Cl^- channel is most probably due to the fact that first carbon is highly substituted with Cl. The high substitution of this carbon results in a weak C–Cl bond and thus high exothermicity of the Cl^- channel. Using similar procedure as mentioned above we have estimated the values of the partial cross sections for DEA: $2 \times 10^{-17}\,cm^2$ at 1 eV and $6 \times 10^{-18}\,cm^2$ at 6.8 eV for Cl^-, $6 \times 10^{-18}\,cm^2$ at 1 eV and $3 \times 10^{-18}\,cm^2$ at 6.5 eV for Br^-. The molecular ions $Cl_2{}^-$ and $C_2H_4Cl^-$ were formed only at 0 eV resonances and the magnitude of the ion yield was one order, respectively three orders of magnitude lower then the magnitude of the Cl^- peak. Using the present cross section data we were able to calculate the rate constant for DEA to 1,1,1Cl-3Br-propane. The value of the total rate constant (including Cl^- and Br^- channel) was $1 \times 10^{-8}\,cm^3\,s^{-1}$ for gas temperature $T_g = 300\,K$ and electron temperature $T_e = 300\,K$.

Electron attachment to 1,3-dibromo-1,1-difluoropropane results in formation of three different negative ions (Fig. 4). The main product is Br^- which is effectively formed already at ~0 eV. It is well known that in the brominated hydrocarbons this reaction channel is exothermic and this ~0 eV peak is most probably result of

Table 1
The position of the resonances as observed for particular molecules

Molecules	Resonances (eV)										
	Cl^-			Br^-						F^-	
$CH_2ClCH_2CH_2Br$	0	0.57	7.0	0	0.47				7.0	–	
$CH_2ClCHBrCH_3$	0	0.10	7.0	0	0.12				–	–	
$CH_2BrCH_2CCl_3$		0.10	6.8	0	0.13				6.5	–	
$CH_2BrCH_2CF_2Br$	–			0		2.0	3.3	5.6	6.82	2.16	7.8

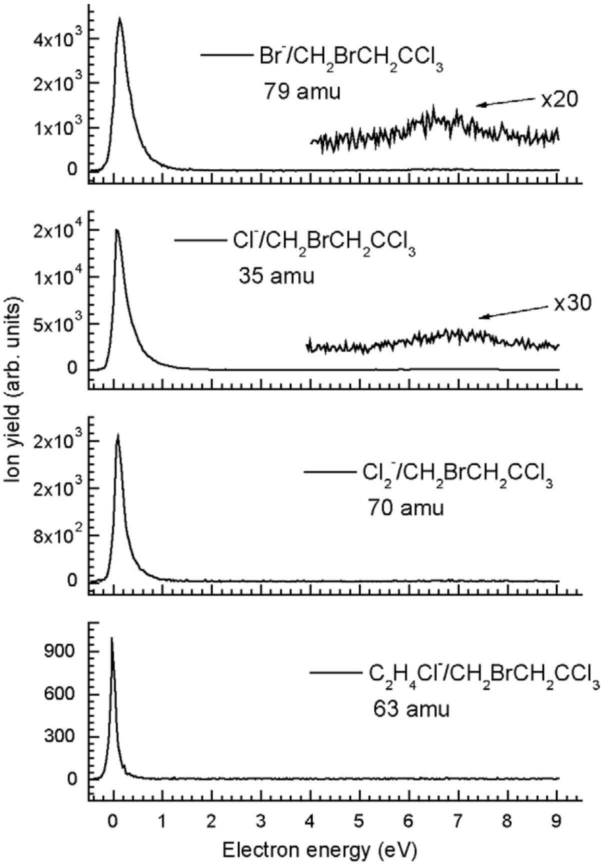

Fig. 3. The ion yields of the ions formed in DEA to 3-bromo-1,1,1-trichloropropane.

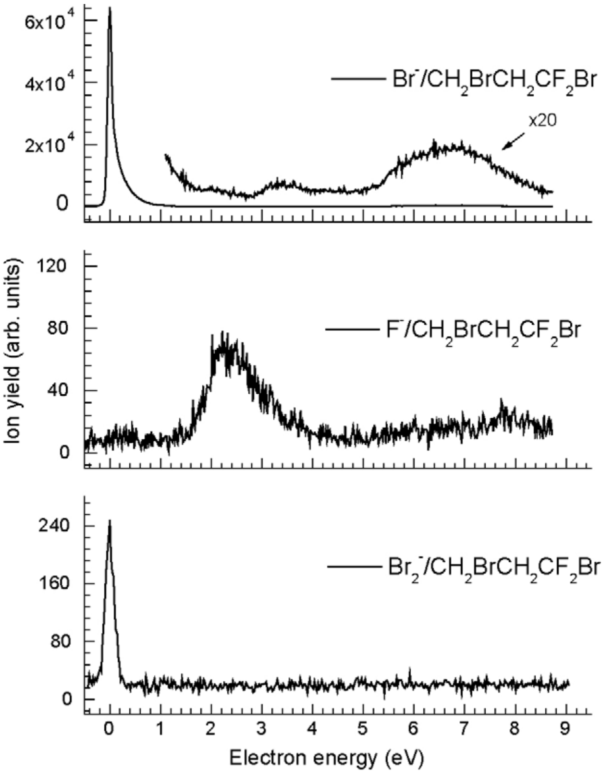

Fig. 4. The ion yields of the ions formed in DEA to 1,3-dibromo-1,1-difluoropropane.

the s-wave electron capture to the molecule, which for exothermic channel results in fast dissociation. Four additional resonances are present at electron energies of 2, 3.3, 5.6 and 6.8 eV. The last two resonances form a broad peak at energies above 5 eV. The 2 eV resonances has a cross of about 3×10^{-18} cm^2. The 3.3 eV resonance is most probably shape resonance (cross section $\sim4\times10^{-18}$ cm^2) while the 5.8 and 6.8 eV resonances could be core excited (cross sections $\sim1\times10^{-17}$ cm^2). Additionally, at low electron energies the molecular anion Br_2^- is formed, however its intensity in comparison to Br^- is more then two order of magnitude lower. The DEA channel resulting in F^- formation is weak, estimated cross section of about 2×10^{-18} cm^2. As the F^- channel is endothermic, there is a threshold for formation of this ion of about 1.5 eV. The peak of the resonance is located at about 2.2 eV. Additional resonance at about 8 eV is also present in ion yield curves. Using the present cross section we have calculated the rate constant for DEA to 1,3-dibromo-1,1-difluoropropane. The value of 2×10^{-8} cm^3 s^{-1} was obtained for gas temperature $T_g = 300$ K and electron temperature $T_e = 300$ K. This value is in very good according to that obtained in the swarm experiment which is equal to 1.8×10^{-8} cm^3 s^{-1} [18].

4. Conclusions

Using high resolution crossed electron–molecule beams technique we have measured the relative partial cross sections to four different halogen-derivatives of propane (1Cl-2Br-propane, 1Cl-3Br-propane, 1,1,1Cl-3Br-propane, 1,1Br-1,3F-propane). We have identified the products of the DEA reactions, the resonant energies present in the ion yields of particular products and estimated the values of the DEA cross sections to these molecules.

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