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Temperature dependence of electron attachment to $CHCLBr_2$: crossed beams study

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Dedicated to Professor Tilmann D. Märk on the occasion of his 60th birthday

Abstract

Dissociative electron attachment (DEA) to $CHClBr_2$ has been studied in a crossed electron/molecular beams experiment in the electron energy range between 0 and 8 eV and in the gas temperature range from 321 to 475 K. In this electron energy range we have found two negative fragment ions Cl^- and Br^- which are formed from a prominent low energy resonant feature (∼0 eV) and at resonances at about 0.4 and 4.7 eV. The molecular ion $ClBr^-$, in contrast to the swarm experiment, was not observed in the beam experiment. The total absolute cross-section for DEA has a value of $1.4(\pm0.2) \times 10^{-20}$ m^2 at 0.4 eV and $5(\pm2) \times 10^{-22}$ m^2 at 4.7 eV. The total DEA cross-section and the DEA cross-section for Br^- reaction channel are temperature independent at low electron energies (∼0 eV). The cross-section for Cl^- reaction channel at ∼0 eV increases with the gas temperature and for this reaction channel we have derived activation energy of 42(±15) meV. The enthalpies of the DEA reaction and C–Cl and C–Br bonds have been calculated at G2MP2 and G2 level of theory. The DEA reaction has been found exothermic for both reaction channels.

Keywords: Dissociative electron attachment; Gas temperature dependence; $CHCLBr_2$; Crossed beams study

1. Introduction

The dissociative electron attachment reactions become particularly interesting in cases where competitive exothermic reaction channels are available. Spanel et al. [1] performed a coordinated swarm/crossed beams study on the compound CCl_3Br with respect to the temperature effect for the total dissociative electron attachment (DEA) cross-section but also that for the two competitive channels Cl^- and Br^- with a very good agreement between the beam and swarm experiments. Further swarm study of DEA to the chloro–bromo methanes $CHCl_2Br$, $CHClBr_2$, and CCl_2Br_2 revealed interesting effects concerning the temperature dependence of the rate coefficient and also the product ion distribution [2].

In this contribution we study DEA to $CHClBr_2$ in the electron energy range from about 0 to 8 eV and in the gas temperature range from 321 to 475 K. The reactions

$$e^-\ (0\,\text{eV}) + CHClBr_2 \rightarrow Cl^- + CHBr_2 + 0.27\,\text{eV} \quad (1)$$

$$e^-\ (0\,\text{eV}) + CHClBr_2 \rightarrow Br^- + CHClBr + 0.68\,\text{eV} \quad (2)$$

are according to present quantum–chemical calculations exothermic (see later).

The present study follows our recent experimental study concerning DEA to CH_2ClBr molecule [3]. In the case of CH_2ClBr molecule, the Br^- reaction channel was dominant at all temperatures and energies. The total DEA cross-section at low electron energies was temperature independent, however, slow increase of the Cl^- reaction channel with gas temperature was observed.

Swarm technique has been used to study electron attachment to $CHClBr_2$ (Sunagawa and Shimamori [4]). The overall rate coefficient for DEA was measured as a function of mean electron energy applying the microwave pulsed radiolysis method. The thermal attachment rate coefficient was estimated as $1.2(\pm0.1) \times 10^{-7}$ cm^3 s^{-1}. This experiment has been carried out without mass-spectrometric identification

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of the ions. Using a deconvolution procedure they derived the total DEA cross-section with a value $2 \times 10^{-19}\,m^2$ at 0.1 eV [4].

Spanel and Smith [2] studied this molecule in the flowing afterglow Langmuir probe (FALP) experiment. They measured overall rate coefficient for the DEA to $CHClBr_2$ molecule as a function of electron and gas temperature. The rate coefficient at 300 K of $3 \times 10^{-8}(\pm 15\%)\,cm^3\,s^{-1}$ was almost one order of magnitude below the value of Sunagawa and Shimamori [4]. Using mass-spectrometer Spanel and Smith [2] identified product ions. Beside the Br^- and Cl^- ions they detected also significant fraction of molecular ions $BrCl^-$. At gas temperature of 540 K moderate increase of the rate coefficient was observed and drastic change in the product distribution was observed (significant increase of the $BrCl^-$ ions).

Parthasarathy et al. [5] studied dissociative electron attachment to $CHClBr_2$ using Rydberg electron transfer technique with velocity selected Rydberg atoms. This experiment was restricted only to very low electron energies. In contrast to FALP experiment, they detected only the Br^- ions. The absence of Cl^- ion was explained on basis of the endothermicity of the $Cl^-/CHClBr_2$ DEA reaction.

2. Experimental

The present experiments were performed on the crossed electron/molecular beam apparatus in Bratislava. The experimental setup has previously been described in detail [6] and only a brief description will be given here. The electron beam is formed by means of a trochoidal electron monochromator (TEM). In the course of the present experiments the instrument was operated at an electron energy resolution of about 60 meV. Calibration of the electron energy scale, cross-section and estimation of the electron energy resolution was established using the well known electron attachment process SF_6^-/SF_6.

The molecular beam was produced in an effusive molecular beam source (EMBS) which is temperature controlled. The beam is formed by effusing the gas through a channel (0.5 mm diameter and 4 mm long) and an external aperture. The vapor of $CHClBr_2$ is introduced into the EMBS via a precision leak valve. The vapor pressure inside the EMBS (typically 1 Pa) is measured by an absolute pressure gauge. For this molecular beam source we know the variation of the gas density in the beam with the gas temperature [6],

$$n \sim T^{-0.5} \tag{3}$$

and therefore the temperature dependencies of the cross-section have to be corrected accordingly. The profile of the molecular beam does not change with the temperature in the present experiment.

Negative ions formed within the intersection between the electron beam and the molecular beam are extracted by a weak electric field ($1\,V\,m^{-1}$) and focused onto a quadrupole mass spectrometer (QMS). The mass analyzed negative ion signal is then detected as a function of the electron energy at different target gas temperatures. A 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.

3. Results and discussions

The Br^- and Cl^- ions are the only negative ions observable from $CHClBr_2$ in present experiment in the electron energy range from 0 to 8 eV. Fig. 1 presents the ion yields for both negative ions recorded at the gas temperature of 321 K. The intensities are in arbitrary units but within the same scale for both fragment ions. The ion yields peak at energies close to 0 eV. Both curves exhibit apparent shoulder near 0.4 eV. It should be noted that near threshold) (0 eV the shape of the ion yields is strongly affected by the electron energy distribution function: the measured ion yield is a convolution of the electron energy distribution function $f(E,U)$ and the cross-section $\sigma(E)$:

$$I(U) = K \int_0^\infty \sigma(E)\, f(E, U)\, \mathrm{d}E \tag{4}$$

where $I(U)$ is the ion yield at the acceleration voltage U; $\sigma(E)$, cross-section for the DEA reaction; $f(E,U)$, distribution

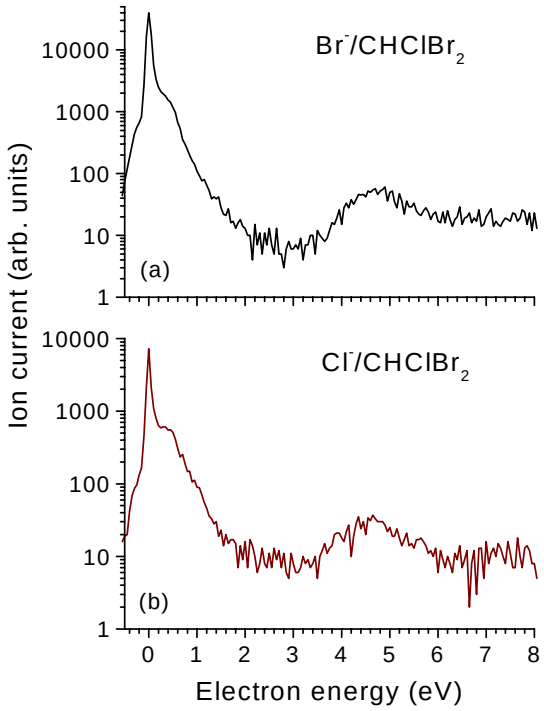

Fig. 1. The Br^- (a) and Cl^- (b) ion yields for DEA to $CHClBr_2$ measured at $T = 321$.

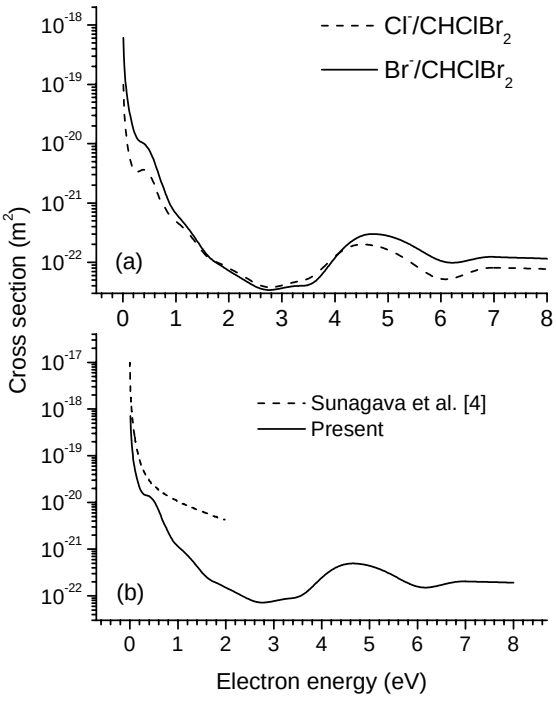

Fig. 2. (a) Partial cross-sections for DEA to $CHClBr_2$. (b) Total DEA cross-section to $CHClBr_2$.

function for the electron energy which is directly related to the acceleration voltage U and K express efficiency of the extraction, transmission and detection of the ions. The next resonance was observed at 4.7 eV for Br^- and at 4.5 eV in Cl^-.

Fig. 2a presents absolute cross-sections for reactions (1) and (2). The cross-section curves were obtained by data analysis of the experimental ion yields measured at 321 K (Fig. 1). As mentioned above (Eq. (4)) 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. 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 also 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 is well known [7]. The DEA cross-sections (Fig. 2a) were obtained from the ion yields by a deconvolution procedure (see [8] for details, based on the Fourier transformation). Present total cross-section (sum of the cross-sections for Br^- and Cl^-) is compared with the total DEA cross-section from the pulse radiolysis swarm experiment in Fig. 2b (Sunagawa and Shimamori [4]). Our cross-section is in the whole electron energy range below the cross-section of Sunagawa and Shimamori [4] (the value of the cross-section at 0.4 eV is $1.4(\pm0.2)\times10^{-20}$ m^2 in present experiment and 2.9×10^{-20} m^2 in [4]). We have used present cross-section to calculate DEA rate coefficient. The value of the rate coefficient at $T_e = 321$ K is 2.7×10^{-8} cm^3 s^{-1}. This value is in agreement with the rate coefficient determined by Spanel and Smith [2] in FALP experiment ($3\times10^{-8}(\pm15\%)$ cm^3 s^{-1}). The discrepancy between present (and also FALP [2]) value of the rate coefficient and the value in [4] exists most probably due to different experimental condition in the experiments. It should be noted that in comparing cross-sections (and rate coefficients) between beam and swarm experiments one has to be aware of the totally different conditions under which both experiments are carried out. While the experiment [4] was performed under a gas pressure of about 100 mbar (corresponding to a collision frequency of the order of 10^9 per single molecule), the present beam experiment operates under true single collision conditions. In the high pressure experiment the collisions between the molecules give access to stabilization routes for the temporary negative ion. This can affect, e.g., its autodetachment lifetime which itself depends on the electron energy.

Fig. 3 presents the dependence of the ion yields at ~0 eV as a function of the gas temperature in the temperature range from 321 to 475 K. The Br^- ion yield shows slow decrease with the increasing temperature. On other hand Cl^- ion yield increases with increasing temperature. The overall ion intensity is, however, decreasing due to decrease of the Br^- signal which dominates. The experimental points in Fig. 3 are not corrected for the temperature dependence of the gas density and thus the decrease of the Br^- ion yield and total ion yield corresponds to the decrease of the gas number density in the molecular beam with increasing temperature. This indicates that the cross-section for Br^- formation at ~0 eV is temperature independent. The thermal cracking studied by positive ion mass-spectrometry (reported in [5] for molecules CCl_4 and $CHCl_3$) was also observed for $CHClBr_2$ at the highest temperature of 475 K. The temperature dependence of the Cl^- yield in the ln(I) versus T^{-1} representation (Arhenius

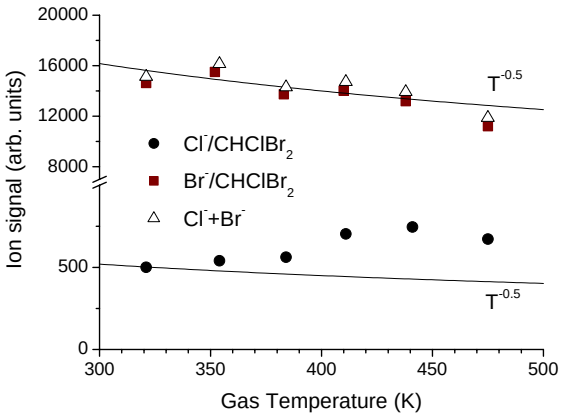

Fig. 3. The temperature dependencies of the overall and Br^- ion yield; Cl^- ion yield at low electron energies (~0 eV). The ion yields are not corrected for the temperature dependence of the gas density $T^{-0.5}$ which are indicated by the full lines.

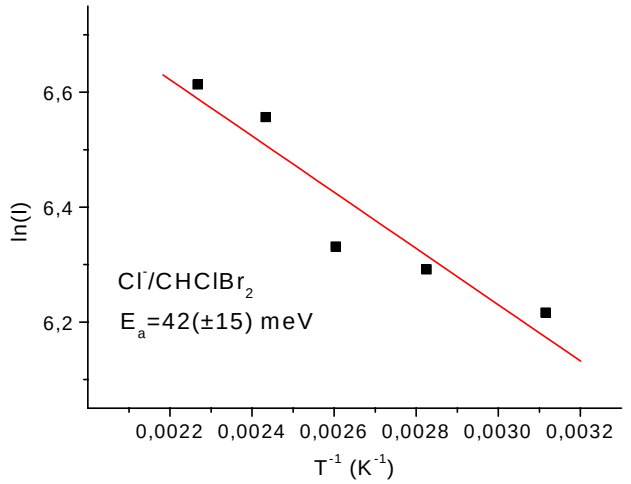

Fig. 4. The Arhenius plot for Cl^- ion yield. The Cl^- signal was corrected on the decrease of the gas number density with the temperature.

plot Fig. 4) shows a reasonably linear behavior. From the slope of the line we derive the activation energy for Cl^- formation as $E_a(Cl^-) = 42 \pm 15$ meV. The activation energy for Cl^- from the FALP [2] experiment has a value of 131 meV and exceeds present value by factor 3.

The branching ratios R ($R = Br^-/Cl^- + Br^-$ where Br^- and Cl^- are the ion yields of the ions Br^- and Cl^-) are shown in Fig. 5 as functions of the electron energy and the gas temperature at 321 and 439 K. The branching ratio at 321 K indicates that Br^- is the dominant product ion. The R obtained by Spanel and Smith [2] in the FALP experiment at 300 K is in very good agreement with the present results. At 440 K we observe slight decrease of the branching ratio in comparison to 321 K, however, in the whole electron energy range Br^- ion is still dominant product. The FALP branching ratio at 540 K is substantially lower than the present branching ratio at 440 K. This difference in the branching ratios at high temperatures can not be explained only by the fact that

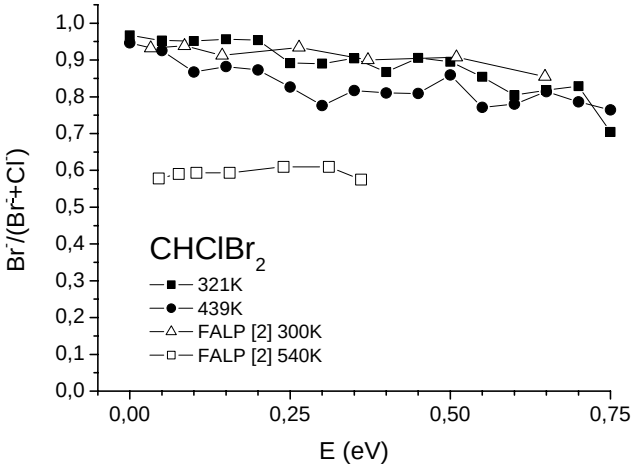

Fig. 5. The branching ratio $R = (Br^-/Br^- + Cl^-)$ as a function of electron energy and gas temperature. For a comparison the branching ratios from FALP experiment [2] are indicated.

in the FALP experiment the branching ratio was measured at higher temperature. The low value of the FALP branching ratio is due to a strong increase of the Cl^- and $ClBr^-$ ion yields at 540 K. The total attachment rate coefficient in the FALP experiment also effectively increased with the temperature. This is in contrast to the present experiment, where total cross-section is temperature independent. The differences between the present high temperature results and the high temperature data from the FALP experiment indicate that collisional effects (collisions of the transient negative ions with the buffer gas) could play an important role in the FALP experiment at higher gas temperatures.

The experimental enthalpy of formation, enthalpies of DEA reaction and bond dissociation energies (C–Cl and C–Br) for $CHClBr_2$ are not available in databases [9,10]. For this reason we have performed theoretical calculations to estimate some of these quantities. Theoretical predictions of reaction enthalpies for both channels (reactions (1) and (2)) were calculated at the standard G2 and G2MP2 levels [11,12] of theory, using GAUSSIAN98 set of programs [13]. According to present calculations reactions (1) and (2) are exothermic by 0.278 and 0.684 eV at G2 level, or by 0.251 and 0.639 eV at G2MP2 level. These results are in contrast with previous calculations in [5] where reaction (1) was predicted to be endothermic by ~0.4 eV on the basis of calculated C–Cl bond energy and known electron affinity of Cl. The source of this discrepancy can be ascribed to too high value of the C–Cl bond energy (4.05 eV) calculated at local-spin density approximation of the density-functional theory. According to present G2 calculations the C–Cl bond has a value of 3.323 eV and corresponding bond energy for C–Br bond is 2.795 eV. The exothermicity of the reaction (1) is also supported by present experimental observation of the Cl^- ion ~0 eV.

Acknowledgements

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