



Temperature dependencies in dissociative electron attachment to chloro-bromo methanes

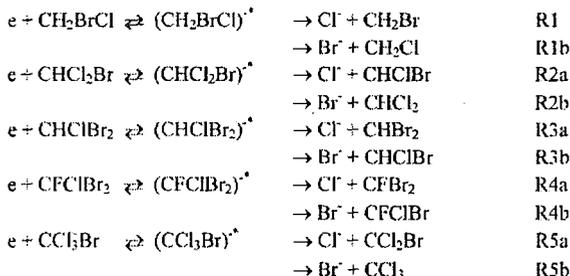
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I. Introduction

Electron attachment reactions play important role in various fields of chemistry and physics and in a large number of technological applications (gas dielectrics in high-voltage devices, certain types of discharges and plasma) [1]. Due to this, EA reactions have attracted scientific attention and have been studied in many experiments. Previous EA studies to large number of molecules demonstrated that the electron attachment reactions depend strongly on the kinetic energy of electrons. In many cases EA to the molecules is strong enhanced by heating the attaching gas to higher gas temperatures (T_g) [2].

The present work is devoted to the study of the gas temperature effect on the dissociative electron attachment (DEA) to the chloro-bromo-methanes:



This study has been performed in the electron energy range from 0 to 2 eV and in the gas temperature range from about 300 K to about 500 K using a new crossed electron-molecular beams apparatus with a temperature regulated, effusive molecular beam source.

The gas temperature studies of DEA to these molecules are of fundamental interest. The DEA reactions R1a-R5b are exothermic reactions, with a competition between two separate reaction channels (Cl^- and Br^-). For some of these molecules the overall DEA rate coefficients have been measured by Sunagawa and Shimamori [3] and the temperature dependencies of the rate coefficients for particular reaction channels have been measured by Smith and Spanel [4]. In present contribution, the distribution of the reaction products into these two channels has been studied as a function of the electron energy and the gas temperature.

II. Experiment

The present study has been carried out using a new high-resolution electron-molecular beam apparatus [5]. The electron beam formed by a Trochoidal Electron Monochromator (TEM) is perpendicular crossed by a molecular beam formed by an Effusive Molecular Beam Source (EMBS). The negative ions produced in the reaction chamber are extracted by a weak electric field from the reaction chamber and focused into the entrance of a Quadrupole Mass Spectrometer (QMS). The intensity of a selected negative ion is then measured as a function of the electron energy E and the gas temperature T_g . The electron energy distribution function

of the electrons in the electron beam (measured as a Full Width at Half Maximum FWHM) of around 70 meV has been used in the present experiment. The EMBS consists of a heatable stainless steel container, gas inlet system, heaters and a pair of thermocouples. The pressure in EMBS is measured using an absolute pressure gauge (MKS Barratron, pressure range 0-7Pa). The gas is effusing from the EMBS through a single channel (5mm long, 0.5mm diameter). The molecular beam is formed by the effusion of the molecules through the channel. The EMBS was resistively heated (temperature range 300 K– 500 K). The temperature of the EMBS was measured using a pair of thermocouples (chromel, alumel). The gas inlet system of the EMBS was working at higher pressure (typically 10^5 - 10^2 Pa). The reacting gas was introduced to the EMBS using a precise diaphragm-regulating valve, reducing the gas pressure to 0.1-7 Pa. For the temperature dependent studies it is important to know, the variation of the gas number density in the molecular beam with the gas temperature. The number density of the molecule in the molecular beam is decreasing with the increasing T_g :

$$n_0 \sim T_g^{-0.5} \quad (1)$$

providing the gas flow through the EMBS is constant [5]. If the cross section for a DEA reaction does not depend on T_g , the ion signal should decrease with T_g as the $T_g^{-0.5}$.

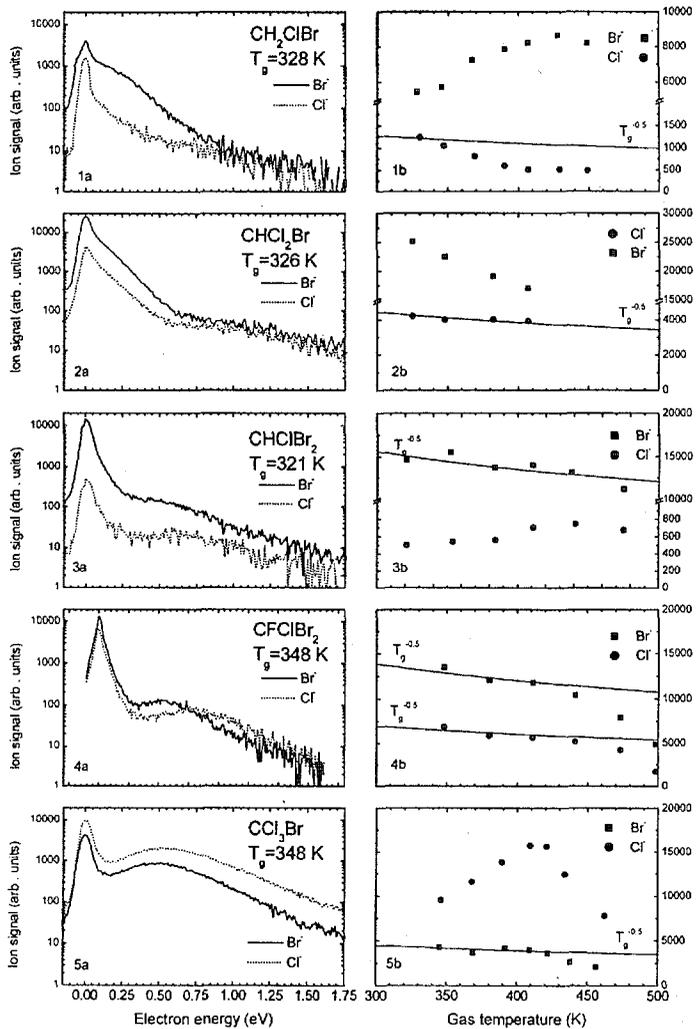
III. Results

In the Figures 1a-5a are presented the measured ion yields for the reactions R1-R5 as the functions of the kinetic energy of the electrons in the electron energy range 0-1.75 eV. The Cl⁻ and Br⁻ ions yields have been measured at the gas temperatures indicated in the graph. The intensities of Cl⁻ and Br⁻ ions measured at the zero electron energy as functions of the gas temperature are shown in the Figures 1b-5b.

In the case of the molecule CH₂ClBr (Fig.1a, 1b), the Br⁻ ion is the dominant reaction product in the whole electron energy range from 0 to 1.75 eV. The ion yield for Br⁻ has a peak at 0 eV and a shoulder between 100 meV and 500 meV indicating a second resonance in this region. The ion yield for Cl⁻ channel has a peak at 0 eV and then signal decreases monotonically in the whole electron energy range. With the increasing gas temperature the Br⁻ ion signal at 0 eV electron energy is increasing and is becoming even more dominant product (Fig. 1b). The intensity of the Cl⁻ ion is decreasing with the increasing gas temperature. The $T_g^{-0.5}$ function in the Figure 1b represents the decrease of the ion signal, due to the decrease of the gas number density of the molecules in the molecular beam with increasing T_g . The Cl⁻ signal decreases more rapidly with T_g as the $T_g^{-0.5}$ function. This indicates the decrease of the partial cross section at 0 eV with the gas temperature.

The ion yields for Br⁻ and Cl⁻ channels (Fig. 2a) for DEA to CHCl₂Br have very similar shape, the maximum at 0 eV and then a monotone decrease in the whole electron energy range from 0 eV up to 1.75 eV. In the electron energy range from 0 eV to about 0.5 eV is the decrease exponential. The Br⁻ ion is dominant in the whole measured electron energy range. With the increasing gas temperature is Br⁻ intensity decreasing more rapidly than $T_g^{-0.5}$, indicating the decrease of the partial cross section at 0 eV with increasing T_g . The Cl⁻ intensity at 0 eV decreases as $T_g^{-0.5}$. This indicates, that the cross section for this reactions channel does not depend on T_g .

The ion yields for DEA to CHClBr₂ are presented in the Fig. 3a. The Br⁻ channel has a maximum at 0 eV and the second resonance is at about 0.5 eV. The Cl⁻ channel has a maximum at 0 eV and the second resonance is at about 0.6 eV. The Br⁻ is the dominant product in the whole electron energy range and also at all gas temperature. The Fig. 3b indicates, that the cross section for the Br⁻ channel at 0 eV is constant with T_g and that the cross section for Cl⁻ channel is increasing with increasing T_g .



Figures 1a-5b

The ion yields for DEA to CFCIBr₂ are presented in the Fig. 4a. For the Br⁻ reaction channel the first peak can be found at 0 eV and the second resonance at about 0.6 eV. The ion yield for Cl⁻ reaction channel has first peak at 0 eV and the second at about 0.8 eV. At the electron energies below 0.75 eV Br⁻ is the dominant ion and above 0.75 eV Cl⁻ is the dominant ion. The temperature dependencies of the 0 eV peaks show monotone ($T_g^{-0.5}$) decrease of the Br⁻ and Cl⁻ signals with increasing T_g in the gas temperature range from 348 K up to 440 K. This indicates, that the cross sections at low electron energies for both reaction channels do not depend on T_g . At the gas temperatures above 440 K the decrease of the Cl⁻ and Br⁻ signals is stronger than $T_g^{-0.5}$. This is most probably due to thermal decomposition of CFCIBr₂. Due to thermal decomposition of the molecules in the EMBS, the number density of the molecules in the molecular beam decreases more rapidly than predicted by (1) and therefore also ion signals are decreasing. Similar effects have been observed in [5] for other molecules.

In the reactions R1-R4 dominant product of the reactions has been found Br⁻. In the case of CCl₃Br is the situation different. At the gas temperatures above 348 K is Cl⁻ ion the dominant product in the whole electron energy range. Spanel et al. [6] observed that at 297 K the dominant ion is Br⁻, but in the present experiment it was not possible to measure this reaction at such low temperature. The Br⁻ ion yield curve has two peaks, the first one at 0 eV and the second one at about 0.5 eV. The Cl⁻ ion yield has also two peaks, the first one at 0 eV and the second at about 0.6 eV. Spanel et al. observed the second peaks at slightly different electron energies. With the increasing gas temperature the Cl⁻ signal at 0 eV is increasing rapidly, but at the gas temperature above 420 K strong decrease of the signal is observed. This decrease is attributed to the thermal decomposition of CCl₃Br molecule in the EMBS. This effect can be observed also for the Br⁻ ion. The Br⁻ signal is decreasing with the increasing gas temperature according to $T_g^{-0.5}$ law (indicates temperature independent cross section), but at the gas temperatures above 420 K strong decrease of the Br⁻ signal is observed, this decrease is attributed to thermal decomposition.

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Track structure calculations

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