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# Temperature dependence of electron attachment to CH<sub>2</sub>ClBr: competition between Cl<sup>-</sup> and Br<sup>-</sup> formation

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#### Abstract

Dissociative electron attachment (DEA) to CH<sub>2</sub>ClBr has been studied in a crossed electron/molecular beams experiment in the electron energy range between 0 and 2 eV and in the gas temperature range between 328 and 449 K. In this electron energy range we find the two negative fragment ions Cl<sup>-</sup> and Br<sup>-</sup> which are both formed from a prominent low energy resonant feature ( $\approx 0$  eV). While the Br<sup>-</sup> ion yield (recorded at  $\approx 0$  eV) considerably increases with the temperature, that of Cl<sup>-</sup> slightly decreases resulting in an overall increase of ion formation at low electron energy. The temperature dependence is interpreted by the relative disposition of the involved potential energy surfaces. For the exothermic Br<sup>-</sup> channel an activation energy of  $107 \pm 10$  meV for the DEA reaction is obtained. Using absolute rates from swarm data the total cross section for the DEA to CH<sub>2</sub>ClBr has been calibrated to absolute values leading to  $5 \times 10^{-21}$  m<sup>2</sup> at 0.5 eV.

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# 1. Introduction

It is well known that the halo-methanes (with the exception of some fluorocarbons) undergo effective dissociative electron attachment (DEA). In the past, electron capture by these molecules has extensively been studied using electron swarm and crossed electron-molecular beams techniques [1,2]. Previous studies on compounds with one single exothermic DEA channel [3–5] have demonstrated that the cross sections can strongly depend on both

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the kinetic energy of the electrons and the gas temperature (i.e., rotational and vibrational excitation of the target molecules). While the electron energy dependence is explained by the resonant nature of the attachment process and the associated Franck–Condon transition (with its limitations in the very low energy region), the increase of the DEA cross section with temperature (as observed for the systems CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> [3–7]) was attributed to the existence of an energy barrier for DEA. On the other hand, there also exist exothermic DEA reactions (CCl<sub>4</sub>, CHBr<sub>3</sub>) where the cross section is independent on the gas temperature as reported from beam experiments [4,5] and also swarm experiments [8–10].

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The study of temperature effects becomes particularly interesting in cases where competitive exothermic reaction channels are available. Spanel et al. [11] performed a coordinated swarm/crossed beams study on the compound CCl<sub>3</sub>Br with respect to the temperature effect for the total DEA cross section but also that for the two competitive channels Cl<sup>-</sup> and Br<sup>-</sup> with a very good agreement between the beam and swarm experiments. A further swarm study of DEA to the chloro-bromo methanes CHCl<sub>2</sub>Br, CHClBr<sub>2</sub> and CCl<sub>2</sub>Br<sub>2</sub> revealed interesting effects concerning the temperature dependence of the rate coefficient and also the product ion distribution [12].

In this contribution we study DEA to the chloro-bromo methane  $CH_2ClBr$  in the electron energy range from about 0 to 2 eV and in the gas temperature range from 328 to 449 K. We have chosen  $CH_2ClBr$  since the relevant DEA channels

e (0 eV) + CH<sub>2</sub>ClBr 
$$\rightarrow$$
 Cl<sup>-</sup> + CH<sub>2</sub>Br  
+ 0.18 eV (1)

$$e (0 eV) + CH_2ClBr \rightarrow Br^- + CH_2Cl + 0.41 eV$$
(2)

are exothermic by 0.18 and 0.41 eV, respectively. These values are obtained from the bond dissociation energies  $D(\text{Cl-CH}_2\text{Br}) = 3.43$  eV and  $D(\text{Br-CH}_2\text{Cl}) = 2.95$  eV [13], and the well known electron affinities EA(Cl) = 3.61 eV and EA(Br) = 3.36 eV [14].

In the literature we find an electron attachment study to CH<sub>2</sub>ClBr using a swarm technique by Sunagawa et al. [15], however, without mass spectrometric identification of the products. The overall rate coefficient for DEA was measured as a function of the mean electron energy applying the microwave pulsed radiolysis method. The thermal attachment rate coefficient was estimated as  $7.1(\pm 0.2) \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>. Using a deconvolution procedure the total value for the DEA cross section was obtained as  $4.4 \times 10^{-20}$  m<sup>2</sup> at 0.1 eV [14]. To our knowledge no crossed beams studies for this molecule are available in the literature so far.

# 2. Experimental

The present experiments were performed on the newly established crossed electron/molecular beam apparatus at Bratislava. The experimental setup has previously been described in detail [5] 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 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. In the case of CH<sub>2</sub>BrCl the vapour is introduced into the EMBS via a precision leak valve. The vapour 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 [5]

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

and 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  $(1 \text{ V m}^{-1})$  and focused onto a quadrupole mass spectrometer (QMS). The mass analysed 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 very small spatial angle are extracted into mass spectrometer. This discrimination does not depend on the mass of the molecule and on the kinetic energy of the molecule. For this reason we do not expect discrimination effect concerning ration  $Cl^{-}/Br^{-}$ .

## 3. Results and discussions

In the energy range from about 0 to 2 eV the fragment ions Br<sup>-</sup> and Cl<sup>-</sup> are the only negative ions observable from CH<sub>2</sub>ClBr. Fig. 1 presents the ion yields for both negative ions recorded at a gas temperature of 328 and 449 K. Note the logarithmic scale for the ion intensity. The intensities are in arbitrary units but within the same scale for both fragment ions and temperatures. From Fig. 1 it is immediately obvious that at very low energies (close to 0 eV) the intensity of the Br<sup>-</sup> signal increases and that of the Cl<sup>-</sup> signal decreases upon heating. The total ion yield, on the other hand, increases with temperature. Both ion yields peak at energies close to 0 eV. The shape of the Br<sup>-</sup> curve exhibits an additional shoulder near 0.1 eV. The thermal cracking studied by positive ion mass spectrometry (reported in [5] for molecules CCl<sub>4</sub> and CHCl<sub>3</sub>) was not observed for CH<sub>2</sub>ClBr in the measured temperature range.

It should be noted that near threshold (0 eV), the shape of the ion yields are strongly affected by



Fig. 1. (a)  $Br^-$  and (b)  $Cl^-$  ion yields for DEA to  $CH_2ClBr$  measured at the two different temperatures 328 and 449 K.

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  $\sigma(E)$ 

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

where I(U) is the ion yield at the acceleration voltage U,  $\sigma(E)$  is the cross section for the DEA reaction and f(E, U) is the distribution function for the electron energy which is directly connected to the acceleration voltage U.

Fig. 2 compares the energy dependence of the total DEA cross section obtained from the swarm technique with the present results. The absolute values of the total DEA cross section was obtained from the pulse radiolysis swarm experiment [15] by measuring the rate constant at different electron temperatures and applying a deconvolution procedure. The cross section curve from the present experiment was obtained by taking the sum of Cland Br<sup>-</sup> formation at a gas temperature of 328 K (which approximately corresponds to that in the swarm experiment). The present cross section curve was then calibrated to the absolute value at E = 0.1 eV. Fig. 2 indicates that the beam experiment exhibits a weaker energy dependence resulting in a lower value at energies below the calibration point and vice versa. Apart from the



Fig. 2. The overall cross sections for DEA to  $CH_2ClBr$  by Sunagawa and Shimamori [15] and present study. The error bars of the present data are equivalent to the size of the data points at low electron energies and to the statistical scatter of the data at higher electron energies.

deviation at the highest electron energy, the agreement is reasonable. At that point it should be noted that in comparing cross sections between beam and swarm experiments one has to be aware of the totally different conditions under which both experiments are carried out. While the swarm experiment 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. 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. Further problems may arise from discrimination effects in the mass spectrometer but also the deconvolution procedure, which was used to obtain the cross section from the rate coefficient.

Returning to Fig. 1 it can be seen that by increasing the gas temperature from 328 to 449 K the Br<sup>-</sup> ion yield at the low energy peak (close to 0 eV) is increased by almost three times from 4000 to 11 000 U. In contrast to that the Cl<sup>-</sup> intensity decreases from 1570 to 600 U resulting in an overall increase of the ion intensity. These temperature dependences over the entire range are explicitly shown in Figs. 3a and b, note that the experimental points are not corrected for the temperature dependence of the gas density.

The temperature dependence of the DEA cross section can be explained by the relative disposition of the potential energy surfaces involved in DEA. For the present system CH<sub>2</sub>ClBr electron capture generates the transitory ion in a repulsive state along the C–Br and C–Cl axis. This is directly related to the virtual molecular orbital (MO) involved in low energy electron capture having  $\sigma^*$ (C–Cl) and  $\sigma^*$ (C–Br) antibonding character. We may thus approximate DEA into Br<sup>-</sup> and Cl<sup>-</sup> by means of two dimensional potential energy curves. The temperature dependence can then be described by the population of vibrational levels and the competition between dissociation and autodetachment in the transient negative ion [8,9].

In the case where the potential curve of the anion crosses that of the neutral at distances larger than the equilibrium distance of the neutral



Fig. 3. The temperature dependencies of the (a) overall and  $Br^-$  ion yield (b) Cl<sup>-</sup> ion yield at low electron energies. The signal is not corrected on the decrease of the gas number density with the temperature.

transitions from vibrationally excited states extend the Franck–Condon region thus allowing transitions to the repulsive ionic potential energy curve at *lower* electron energies and hence *higher* dissociation probabilities. This results in the appearance of a threshold peak and an increase of the cross section. This effect is the more pronounced the stronger autodetachment competes to dissociation in the transient anion. From a thermodynamic point of view the energy of the crossing point  $R_c$  can be viewed as the *activation energy* for the dissociative attachment of thermal electrons.

On the other hand, if the ionic potential energy curve crosses left of the equilibrium distance, one expects an decrease of the DEA cross section with temperature. In this case, the negative ion is no longer accessible from vibrationally excited states and the ground state is depopulated upon heating. This situation is analogous to that of the *inverted region* in electron transfer reactions [16].

In this spirit we interpret the present results by means of DEA via the schematic potential energy curves shown in Fig. 4. Both negative ion curves indicate bound states although the existence of a parent negative ion CH<sub>2</sub>ClBr<sup>-</sup> has not been reported so far. If bound states exists observation of CH<sub>2</sub>ClBr<sup>-</sup> is unlikely under collision free conditions (lack of effective stabilization mechanisms) but electron attachment to CH<sub>2</sub>ClBr clusters can give access to the stabilized parent anion. The shoulder near 0.1 eV on the Br- yield can be interpreted as a Franck-Condon transition near the equilibrium distance and the 0 eV peak due to a transition from a vibrational excited state near the level of the crossing point between the two potential curves (hot band transition). Note that the intensity of the 0 eV peak can reach appreciable values in spite of a moderate population of excited vibrational levels. This is due to the reciprocal energy dependence of the attachment cross section and also the autodetachment lifetime which strongly varies with the electron energy.

Fig. 5 shows that the temperature dependence of the Br<sup>-</sup> yield in the  $\ln(I)/T^{-1}$  representation shows a reasonably linear behaviour (Arhenius plot). From the slope of the line we derive the activation energy for Br<sup>-</sup> formation as  $E_a(Br^-) =$  $107 \pm 10$  meV.

It should be mentioned that the above interpretation is based on the Born–Oppenheimer approximation i.e., the use of localized potential



Fig. 4. Schematic two dimensional potential energy curves for the exothermic DEA channels in  $CH_2ClBr$  (see the text).



Fig. 5. Arhenius plot for the  $Br^-$  channel to obtain the activation energy for the DEA reaction.

energy surfaces and the application of the Franck– Condon principle. This picture has its limitations in the case of very low electron energies.

We hence mention a further mechanism, which can generate structures in low energy ion yields. In a collaborative research using the high-resolution laser photoelectron attachment (LPA) technique und the present beam technique [17] DEA to CH<sub>2</sub>Br<sub>2</sub> resembled a sharp peak at an energy near 72 MeV. This is close to the onset for excitation of one quantum of the symmetric CBr<sub>2</sub> stretch vibration  $v_3 = 1$ , spectroscopically located at 72.9(5) MeV. Similarly at the onset for the asymmetric CBr<sub>2</sub> stretch vibration  $v_9$  (at  $81.0 \pm 2$  meV) a weak upward cusp was observed. The structures in the DEA cross section of the CH<sub>2</sub>Br<sub>2</sub> molecule at the thresholds for vibrational excitation were consequently interpreted as a vibrational Feshbach resonance (VFR) [5], i.e., coupling of the attachment process with the inelastic scattering channels. We can hence not exclude that the presently observed structure is related to a VFR.

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#### References

- L.G. Christophorou (Ed.), Electron–Molecules Interactions and their Applications, Academic, Orlando, 1984.
- [2] L.G. Christophorou, J.K. Olthoff, M.V.V.S. Rao, J. Phys. Chem. Ref. Data 26 (1997) 1.
- [3] A. Kiendler, Š. Matejčík, J.D. Skalný, A. Stamatovic, T.D. Märk, J. Phys. B 29 (1996) 6217.
- [4] S. Matejcik, G. Senn, P. Scheier, A. Kiendler, A. Stamatovic, T.D. Märk, J. Phys. Chem. 107 (1997) 8955.
- [5] S. Matejcık, V. Foltin, M. Stano, J.D. Skalny, Int. J. Mass Spect. 223–224 (2003) 9.
- [6] Hahndorf, L. Lehr, E. Illenberger, J. Manz, Chem. Phys. Lett. 231 (1994) 460.
- [7] I. Hahndorf, E. Illenberger, Int. J. Mass Spect. Ion Proc. 167/168 (1997) 87.
- [8] L.M. Warman, M.C. Sauer, Int. J. Radiat. Phys. Chem. 3 (1971) 273.

- [9] D. Smith, N.G. Adams, E. Alge, J. Phys. B: At. Mol. Opt. Phys. 17 (1984) 461.
- [10] L.G. Christophorou, J.K. Olthoff, Adv. Atom. Mol. Opt. Phys. 44 (1999) 155.
- [11] P. Španěl, D. Smith, Š. Matejčík, A. Kindler, T.D. Märk, Int. J. Mass. Spect. Ion. Proc. 167/168 (1997) 1.
- [12] P. Spanel, D. Smith, Int. J. Mass Spect. 205 (2001) 243.
- [13] S.-H. Lee, Y.-J. Jung, K.-H. Jung, Chem. Phys. 260 (2000) 143.
- [14] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 78th edition, CRC Press, Boca Raton, New York, 1997–1998.
- [15] T. Sunagawa, H. Shimamori, J. Chem. Phys. 107 (1997) 7876.
- [16] R.A. Marcus, Angew. Chem. 105 (1993) 1161.
- [17] A. Schramm, M.-W. Ruf, M. Stano, S. Matejcik, I.I. Fabrikant, H. Hotop, J. Phys. B: At. Mol. Opt. Phys. 35 (2002) 1.