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Dissociative electron attachment to the volatile anaesthetics enflurane and isoflurane and the chlorinated ethanes pentachloroethane and hexachloroethane

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ABSTRACT

Negative ion formation through dissociative electron attachment to the gas-phase volatile anaesthetics enflurane and isoflurane ($C_3H_2ClF_5O$) and to two chlorinated ethanes, pentachloroethane (C_2HCl_5) and hexachloroethane (C_2Cl_6), have been studied in a crossed electron-molecular beam two sector field mass spectrometer experiment. Anion efficiency curves for the negatively charged fragments have been measured over an electron energy range of approximately 0–17 eV, with an energy resolution of ~1 eV. For the chlorinated ethanes, resonance features were generally found at ~0 eV and at 7.5 eV. For the volatile anaesthetics, no zero energy resonances were observed. Instead, product anions were detected mainly in the 2–3 eV and 9 eV energy regions, with the exception of Cl^-, whose dominant resonance occurs at approximately 0.6 eV and 0.9 eV for isoflurane and enflurane, respectively. To aid in the interpretation of the experimental results, quantum chemical calculations providing thermochemical thresholds of anion formation are also presented.

1. Introduction

Chlorinated molecules may be used in ion-mobility spectrometers as possible dopants to manipulate the ion-chemistry and hence to improve specificity of detection. A recent ion mobility spectrometric study by us investigating four chlorinated compounds showed that within the electron swarm environment of an ion mobility spectrometer (IMS) system, resulting in a mean electron energy of approximately 0.3 eV, electron attachment to pentachloroethane and hexachloroethane is very efficient, whereas that to the isoflurane and enflurane is not, despite their calculated electron affinities (DFT calculations using the B3LYP functional and the 6-31+G(d,p) basis set) being positive, 1.2 and 1.9 eV, respectively [1]. Chloride ion production following electron attachment was also calculated to be exothermic. We postulate that this unexpected behaviour may be due to the strongly positive Vertical Attachment Energies (VAE) calculated for isoflurane and enflurane to be 0.62 and 0.77 eV, respectively. To test this hypothesis we decided to investigate the electron attachment of the above molecules in more detail. The goal of this work is to determine the energy resonances and anion efficiencies of electron attachment, which to our knowledge have not been previously reported.

The present study represents a new experimental contribution for the measurement of negative ion yields for enflurane ($CHFCl–CF_2–O–CHF_2$), isoflurane ($CF_3–CHCl–O–CHF_2$), pentachloroethane (C_2HCl_5) and hexachloroethane (C_2Cl_6) molecules upon low-energy electron attachment. Although for an explanation of the IMS results energy resonances at less than 1 eV are of key importance, with the apparatus available we have taken the opportunity to investigate electron attachment to the above molecules over an electron energy range of 0–17 eV, which is of fundamental interest. To complement the experimental results, we have also carried out quantum chemical calculations on the electronic properties of all molecules studied in the present work. In the following sections we provide details on the experimental apparatus and the measurement techniques that have been used. This will be followed

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by a brief discussion on the computational methods adopted and a presentation and discussion of the experimental results.

2. Experimental details

Dissociative electron attachment (DEA) to the volatile anaesthetics and chlorinated ethanes was investigated by means of a crossed electron-molecular beam set-up utilizing a double focusing two-sector field mass spectrometer equipped with a standard Nier-type ion source [2]. The electron energy resolution close to 0 eV is about 1 eV full width at half maximum (FWHM). This low electron energy resolution is compensated by the high sensitivity that is available owing to the large electron current. The electron current is regulated to 10 μA, which is achieved for electron energies higher than 2 eV. Below 2 eV the electron current decreases linearly down to a value of approximately 2 μA at 0 eV. This reduction in current must be considered when comparing peak intensities below 2 eV to those above 2 eV for any particular energy scan for a given product anion. An effusive molecular beam emerges from an orifice of 3 mm diameter which is crossed with an electron beam to generate anions. A voltage drop of 6 kV accelerates product anions from the ion source towards the sector fields. Negative ion yields are obtained as a function of the electron beam energy. The electron energy scale and the electron energy resolution are calibrated to within ±0.2 eV using the well-known SF_6^-/SF_6 signal near 0 eV and the resonances of the F^-/SF_6 and F_2^-/SF_6 anions at higher electron energies.

Enflurane was purchased from Chempur. All other samples were purchased from Sigma-Aldrich with a minimum stated purity of 99%. Enflurane, isoflurane and pentachloroethane are liquid at room temperature and were degassed by a repeated freeze–pump–thaw cycle prior to experiments. Hexachloroethane is solid at room temperature but with a sufficient vapour pressure for it to be admitted into vacuum without the need for heating.

3. Computational details

To aid in the interpretation of the experimental results, we have used several high-level extrapolation schemes for the determination of diverse quantum chemical properties, such as binding energies, (adiabatic) electron affinities and reaction thresholds. In particular we compare results from G3(MP2) [3], G4(MP2) [4] and CBS-4M [5,6] which yield similar accuracy. CBS-4M yields a mean absolute deviation (MAD) of 2.0 kcal/mol for the G2 test set [7], G3(MP2) yields a MAD of 1.3 kcal/mol for the G2/97 test set [8,9], whereas G4(MP2) yields the lowest MAD of 1.04 kcal/mol for the G3/05 test set [10]. A comparison of different extrapolation schemes is often valuable as they might yield worse performance in individual cases than reflected by the average accuracy evaluated for selected systems in the respective test sets. For instance, it is well-known that G3(MP2) is (on average) more suitable for the hydrogen bonded complexes in the G3/05 test set. In general, it is found that G3(MP2) and G4(MP2) energies are very similar, whereas CBS-4M exhibits convergence problems for a few fragments under consideration. Therefore we shall restrict ourselves to reporting energies from G4(MP2) level of theory. In the case of isomers we take the one providing the lowest energy. Note, for comparison of the theoretically derived values with the experimental data, the former corresponds to the threshold of a resonance rather than the position of its maxima.

In addition to the above we employed the MP2/6-311++G(3df,2p) level of theory and its density to visualize the natural orbitals of the parent transient negative ions (TNIs). All calculations were performed using the Gaussian 09 suite of programs [11].

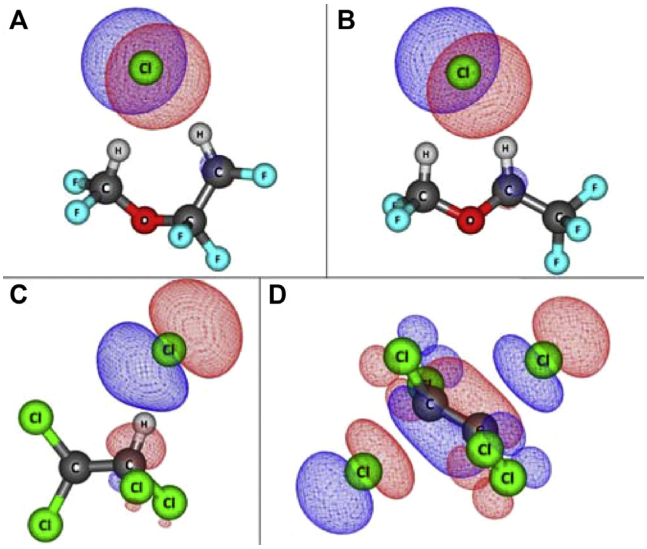

Fig. 1. Highest occupied natural orbitals for the anionic states of (A) enflurane, (B) isoflurane, (C) pentachloroethane, and (D) hexachloroethane. Visualization of the natural orbitals obtained using MP2/6-311++G(3df,2p) density.

4. Results and discussion

Electron capture by a polyatomic molecule generates a TNI, which is seen as a quasi-bound state embedded in the autodetachment continuum and unstable towards the loss of the extra electron. Therefore, the TNI may either be subject to autodetachment or fragmentation (DEA). In the latter case, the TNI can decompose via single bond cleavages or undergo structural rearrangement. Symbolically these two processes can be written as:

$$e^- + ABC \rightarrow (ABC)^{*-} \rightarrow AB + C^-, \quad (1)$$

$$e^- + ABC \rightarrow (ABC)^{*-} \rightarrow AC + B^-, \quad (2)$$

where $(ABC)^{*-}$ represents the TNI. In the case of isoflurane, enflurane and pentachloroethane, the computational work shows that optimization of the anionic state results in significant geometrical changes compared to the neutral molecule promoting the formation of a chloride ion and a neutral fragment rather than a single covalently bound anionic compound as can be seen in Fig. 1A–C. In contrast, for the optimized anionic hexachloroethane the excess charge is distributed over two distant chlorine atoms in para position. The highest occupied natural orbitals (HONOs) plotted in Fig. 1A–C correspond nicely to the HONO of an isolated chloride ion. However, for hexachloroethane we observe a much delocalized HONO, see Fig. 1D. The two previously mentioned distant chlorine atoms (left- and right-chlorine atoms in Fig. 1D) show σ* like bonding character, whereas the other chlorine atoms yield π* bonding character overall weakening all C—Cl bonds. These calculations suggest that no parent anions will be observed in the experiment, because within the detection time of a few microseconds the parent anion would have dissociated. Table 1 and Table 2 provide the computational calculations of the threshold energies for formation of the experimentally observed product anions via single bond cleavages for the anaesthetics and chloroethanes, respectively. Results were obtained at G4(MP2) and CBS-4M level of theory.

In agreement with the theoretical predictions and despite the high sensitivity of the instrument, we were not able to detect any parent anion, instead DEA dominates. This indicates that autodetachment or fragmentation occurs in a time window shorter than the detection time, resulting in the absence of an observable parent negative ion. The *m*/*z* values of the most significant anion