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Threshold photoelectron photoion coincidence spectroscopy of trichloroethene and tetrachloroethene : the effect of Cl substitution in the series $C_2H_xCl_{4-x}$

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Professor Richard Tuckett (University of Birmingham) / July 2011

Threshold photoelectron photoion coincidence spectroscopy of trichloroethene and tetrachloroethene

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Abstract

The threshold photoelectron, the threshold photoelectron photoion coincidence and ion breakdown spectra of trichloroethene and tetrachloroethene have been recorded from 9 – 22 eV. Comparisons with the equivalent data for the three dichloroethene molecules and theoretical calculations highlight the nature of the orbitals involved during photoionisation in this energy range. The ground electronic state of $C_2HCl_3^+$ ($C_2Cl_4^+$) is bound, with excited valence states dissociating to $C_2HCl_2^+$ ($C_2Cl_3^+$) and C_2HCl^+ ($C_2Cl_2^+$). Appearance energies suggest that C_2HCl^+ forms from $C_2HCl_3^+$ by loss of two chlorine atoms, whereas $C_2Cl_2^+$ forms from $C_2Cl_4^+$ by loss of a Cl_2 molecule. The translational kinetic energy release into $C_2HCl_2^+$ ($C_2Cl_3^+$) + Cl is determined as a function of energy. In both cases, the fraction of the available energy released into translational energy of the two products decreases as the photon energy increases.

1. Introduction

It is of key importance to understand how structure affects the properties of molecules. For example, how does substituting hydrogen atoms for chlorine atoms in a series of hydrochlorocarbons change the products formed from photoionisation? In order to understand such effects, our group has performed a series of experiments on the chloroethenes, $C_2H_xCl_{4-x}$. There are six different chloroethenes: monochloroethene, 1,1-dichloroethene, (*Z*)-1,2-dichloroethene, (*E*)-1,2-dichloroethene, trichloroethene and tetrachloroethene. We have studied their photoionisation dynamics using both threshold photoelectron photoion coincidence (TPEPICO) spectroscopy and a selected ion flow tube to measure the reactions of these molecules with small cations. Previously we have published results for photoionisation and the ion-molecule reactions of the three isomers of dichloroethene [1,2], where the principal aim was to look for examples of isomeric effects in the reactions. The photoionisation results for trichloroethene and tetrachloroethene are described in this paper, and the results for reactions of a series of cations with monochloroethene, trichloroethene and tetrachloroethene will be published elsewhere [3]. Currently, we have not performed a photoionisation study on monochloroethene.

Trichloroethene and tetrachloroethene are relatively well-studied species, and both He(I) and He(II) photoelectron spectra have been published [4,5]. Potts *et al.* have also recorded the photoelectron spectra at a range of different photon energies [6], allowing examination of how the photoionisation cross-section varies with photon energy. Non-coincident photoionisation studies using tunable vacuum-UV radiation have been performed on both tri- and tetrachloroethene by Watanabe *et al.* [7]. More recently, Woo *et al.* have studied trichloroethene in detail using much higher-resolution photoionisation studies [8,9], while resonance-enhanced multi-photon ionisation spectra for both molecules have been reported by Williams and Cool [10,11]. Multi-photon ionisation spectra for tetrachloroethene have been published by Heath and Robins and Duttont *et al.* [12,13]. The photoabsorption spectrum of trichloroethene has been studied by Walsh and Warsop [14], and the electron energy loss spectra of both molecules has been published by Koerting *et al.* [15]. Electron ionisation cross sections have also been reported for both tri- and tetrachloroethene from threshold to 200 eV [16]. To the best of our knowledge, however, no threshold photoelectron spectra have been recorded for these two molecules, nor have any measurements been reported of energy-selected ion yields obtained under coincidence conditions. This paper reports these data for the first time, and compares the trends in photoelectron spectra and fragment ion yields as the number of chlorine atoms in $C_2H_xCl_{4-x}$ changes.

2. Experimental

The apparatus used for the TPEPICO study has been described in detail previously [17]. It consists of a threshold electron detector and a time of flight (TOF) mass spectrometer aligned opposite each other across an interaction region into which the gas-phase sample is introduced. With suitable electronics it is possible to detect the electrons and ions, generated from a precursor neutral irradiated by vacuum-UV radiation, in coincidence. Such an experiment can determine the fragment ions produced from a defined electronic state of the parent cation and the kinetic energy (KE) release into that ion, from which the dynamics of the fragmentation may be inferred. All measurements were performed using tunable vacuum-UV radiation from the Daresbury synchrotron source and a 5 m focal length, normal-incidence McPherson monochromator, range 8–30 eV (station 3.2) [18].

Two different types of spectra can be recorded. Firstly, a TPEPICO spectrum can be recorded by collecting the coincidence signal of parent and fragment ions as a function of photon energy. The raw spectrum is a three-dimensional false-colour map of coincidence counts *vs.* TOF *vs.* photon energy. Cuts through the map at a fixed ion TOF produce the ion yields as a function of photon energy. The process of recording the TPEPICO spectrum also produces the threshold photoelectron (TPES) spectrum and total photoion yield as a function of photon energy. Secondly, if the photon energy is fixed, higher-resolution TOF spectra can be produced at the optimum time resolution of our apparatus, 8 ns, limited by the time-to-digital converter. Analysis of the peak shape of the TPEPICO-TOF spectrum can reveal the translational kinetic energy release into the ion, $\langle \text{KE} \rangle_t$, and hence by dividing by the available energy, E_{av} , the fraction of energy released into translational motion of the fragments, $\langle f \rangle_t$. Comparison of $\langle f \rangle_t$ to impulsive and statistical models can indicate whether the bond dissociation takes place impulsively or statistically, *i.e.* on a timescale faster than or slower than energy redistribution. The analysis and models have been discussed in detail in previous papers [19,20]. For a pure impulsive model, $\langle f \rangle_t$ is determined solely by kinematics, being given by μ_b / μ_f where μ_b is the reduced mass of the two atoms whose bond is broken and μ_f is the reduced mass of the two product fragments [21]. If the dissociation is statistical then it can be modelled in several ways. The simplest is to estimate a lower limit of $\langle f \rangle_t$ from $1/(x+1)$ where x is the number of vibrational degrees of freedom in the transition state which leads to dissociation [22]. Alternatively, Klots [23] derived the following analytical relationship between E_{av} and $\langle \text{KE} \rangle_t$:

$$E_{av} = k_B T^* + \frac{(R-1)}{2} k_B T^* + \sum_i \frac{h\nu_i}{\exp\left(\frac{h\nu_i}{k_B T^*}\right) - 1} \quad (1)$$

where T^* is a microcanonical temperature defined by $T^* = \langle KE \rangle_t / k_B$. R is the number of rotational degrees of freedom and ν_i are the vibrational frequencies of the fragment ion. This microcanonical distribution will have a different distribution to the true canonical distribution, but will have the same average energy [24]. This equation applies for loose transition states, characteristic of a single bond cleavage. For tight transition states the $R-1$ term is replaced by $R-2$ [23].

The trichloroethene and tetrachloroethene samples were purchased from Sigma-Aldrich with quoted purities of greater than 99 %. The two samples were further purified by successive freeze-pump thawing cycles before use.

3. *Ab initio* calculations

The structures and molecular orbitals of the six neutral chloroethene molecules listed in Section 1 were calculated in Gaussian 03 starting from experimental structures which were then optimised to give the final structure [25]. The final structures were calculated at the MP2 level with a 6-311 G + (d,p) basis set. The structures are very similar to those given by gas-phase electron diffraction and microwave measurements [26,27]. Ionisation energies of the orbitals were calculated using the outer valence Green's functions (OVGF) method included in Gaussian 03. To aid interpretation of the results, it is necessary to know the vibrational frequencies of some of the fragment ionic species generated following dissociative photoionisation. These frequencies are unknown for $C_2HCl_2^+$ and $C_2Cl_3^+$. Therefore, the values have been calculated using Gaussian 03 at the B3LYP 6-311 G + (d,p) level of theory.

4. Energetics

From the energy-selected ion yields it is possible to extract appearance energies of fragment ions at 298 K, AE_{298} . The AE_{298} values are measured from the first onset of signal above the background noise, however it is wrong simply to equate AE_{298} with the enthalpy of the corresponding reaction at 298 K, $\Delta_r H^{\circ}_{298}$, as this effectively neglects thermal effects. Therefore, some form of correction must be made to the value of AE_{298} . If the product ion is formed *via* only a single bond cleavage then the method of Traeger and McLoughlin can be used to convert AE_{298} to an upper limit to $\Delta_r H^{\circ}_{298}$ [28]; the upper limit arises due to the possibility of an exit channel barrier or kinetic shift moving the AE_{298} away from the thermochemical onset. A major caveat to the use of this procedure with TPEPICO data is that it was developed for use with photoionisation yield curves, whereas the energy-selected ion yields produced from the TPEPICO experiment are strictly the derivatives of the photoionisation curves. With the resolution and step size used in our experiments this is unlikely to cause much error, far less than applying no correction to AE_{298} at all. Therefore this correction

has been applied to the ionic fragments formed by loss of a chlorine atom. As stated earlier the vibrational frequencies of the fragment ions $C_2HCl_2^+$ and $C_2Cl_3^+$ have been calculated using Gaussian 03.

To determine predicted enthalpies of reaction, enthalpies of formation of products and reactants are taken from standard sources [29,30]. The exceptions are the values for neutral trichloroethene and tetrachloroethene which are taken from Manion [31], and the values for C_2HCl^+ and $C_2Cl_2^+$ which were calculated from the enthalpy of formation of the corresponding neutral molecule plus the respective ionisation energy (IE). No enthalpy of formation was available for the smallest fragment ion formed from tetrachloroethene, C_2Cl^+ . From the measured AE_{298} data, new thermochemical values have been derived for $C_2HCl_2^+$ and $C_2Cl_3^+$, and details are given in Section 5.3.

5. Results

5.1 Threshold photoelectron spectra

Figure 1 (a) – (f) presents the threshold photoelectron spectrum (TPES) and energies of the molecular orbitals calculated by the OVGf method from 9–23 eV for monochloroethene, 1,1-dichloroethene, (*Z*)-1,2-dichloroethene, (*E*)-1,2-dichloroethene, trichloroethene and tetrachloroethene, respectively. Except for monochloroethene, they were all recorded on beamline 3.2 at the Daresbury SRS with an optical resolution of 0.3 nm. The TPES of monochloroethene was taken from the work of Locht *et al* [32]. The dichloroethene results have been previously published but are shown here for ease of comparison [1]. The adiabatic ionisation energies of trichloroethene and tetrachloroethene measured at Daresbury are 9.46 and 9.30 eV, with an estimated error in each value of ± 0.05 eV. These two values are in good agreement with the accepted literature values [30]. Recently, working under supersonic beam conditions Woo *et al.* reported the adiabatic ionisation energy for trichloroethene to be 9.478 eV [9]. This value is slightly higher than our 298 K value, to be expected as the beam work is quoted at 0 K.

The Gaussian 03 calculations give the orbital energies and symmetries of the molecular orbitals (MO), and their IE values were obtained by the OVGf technique. Table 1 list the electronic state and its symmetry, experimental and calculated vertical IE values for trichloroethene and tetrachloroethene; note that the $\tilde{B} - \tilde{F}$ states of $C_2Cl_4^+$ are not resolved under our experimental conditions. Overall, the experimental and calculated values are in good agreement, although the agreement is worse at lower photon energies, especially for the ground electronic state, a result also seen for the dichloroethenes [1]. The experimental values are in good agreement with the vertical IE values from von Niessen *et al.* and Lake and Thompson [4,5]. In C_s symmetry, from the MP2 calculations the outer valence MOs for trichloroethene can be labelled:

.... (18a')², (19a')², (20a')² (21a')² (4a'')² (22a')², (5a'')², (23a')², (6a'')², (24a')², (25a')², (7a'')².

Similarly in D_{2h} symmetry the outer valence MOs for tetrachloroethene are labelled:

.... (8a_g)², (5b_{2u})², (2b_{3u})², (6b_{3g})², (2b_{2g})², (9a_g)², (8b_{1u})², (2b_{1g})², (6b_{2u})², (2a_u)², (7b_{3g})², (3b_{3u})².

where the numbering includes core orbitals. The relative ordering of the MOs is in excellent agreement with those obtained by previous OVGf calculations of von Niessen *et al.* [4].

At this stage, it is useful to compare the TPES of all six chloroethenes to gain insight into how substitution of chlorine atoms affects the results of photoionisation. The first point to note is that as the number of chlorine atoms increases, the IE decreases. This is due to conjugation between the C=C π-orbitals and the out-of-plane chlorine lone pairs, and it has the effect of increasing the energy of the C=C orbital (hence lowering its IE) but decreasing the energy of the MO consisting of the out-of-plane chlorine lone pair. This effect, often seen before in related molecules, has been noted by Lake and Thompson [5].

All six molecules show a similar progression of states. The ground electronic state is largely C=C π-bonding with some conjugation from out-of-plane chlorine lone pairs. The next set of related states spans 11.0–13.5 eV. For monochloroethene there is only one state, for the three dichloroethenes there are three states, for trichloroethene five states, and for tetrachloroethene seven states, although not all are resolved at our spectral resolution. This increase in number of states by two for the addition of one extra chlorine atom strongly suggests that they arise from lone pairs on the chlorine atoms, and the Gaussian 03 calculations show this to be correct. It should be noted that the count of ionic electronic states in this region due to chlorine lone pairs is one less than it should be. This arises due to the conjugation of the out-of-plane chlorine lone pairs with the C=C bond, which moves one of the chlorine lone pair states to a higher IE. After this cluster of chlorine lone pair states there is a peak which consists of two states. Gaussian 03 calculations show that one of these is due to this conjugated chlorine lone pair, the other to a mixture of C–Cl and C–H bonding. The ordering of these two states depends on the molecule. For monochloroethene, (*Z*)-1,2-dichloroethene and (*E*)-1,2-dichloroethene the state with lower IE is derived from the conjugated chlorine lone pair; for 1,1-dichloroethene, trichloroethene and tetrachloroethene the state of lower IE is made up of C–Cl and C–H σ-bonds. It is not clear why the ordering reverses between these two sets of molecules.

The next peak at ~16–17 eV consists of two states and is resolved for monochloroethene, (*Z*)-1,2-dichloroethene and trichloroethene, but not for 1,1-dichloroethene, (*E*)-1,2-dichloroethene and tetrachloroethene. Both states are combinations of C–Cl, C=C and in some cases C–H bonding. In general, the bonding in the state of lower IE is σ -bonding along the C–Cl and C–H bond axis, whereas in the higher IE state the C–Cl and C–H bonds are π -bonds in the plane of the molecule. It should be noted that, with states so close in energy, the ordering could easily change in *ab initio* calculations depending on the method and basis set used. Whether the peaks are resolved depends on the symmetry of the two states. For molecules where the two states are resolved, they both have the same symmetry which causes an enhanced separation of the states (*e.g.* in (*Z*)-1,2-dichloroethene [1]).

5.2 Scanning-energy TPEPICO ion yields

Figure 2(a) shows the TPES, figure 2(b) the energy-selected ion yields, and figure 2(c) the breakdown diagram for trichloroethene over the range 9–24 eV. Figure 3(a) shows the TPES, figures 3(b) and 3(c) the energy-selected ion yields for tetrachloroethene. Although the experimental conditions were similar for the tri- and tetrachloroethene studies, it is clear that the signal-to-noise ratio of the ion yields is significantly inferior for the tetrachloroethene spectra. The poor results may possibly be due to a higher photoionisation cross-section for tetrachloroethene; this would lead to an increase in false coincidences which would cause an increase in the background signal. Due to this poor signal-to-noise ratio the breakdown diagram was found to be of unusable quality, and it is not reproduced here. The spectra for both molecules were recorded from the onset of ionisation to *ca.* 24 eV with an optical resolution of 0.3 nm and a TOF resolution of 64 ns. This TOF resolution is degraded from the optimum achievable with the time-to-digital converter (TDC) card of 8 ns, but it was then possible to record all ionic fragments from a chloroethene molecule on one 3D coincidence map. Use of such a degraded resolution, however, means that any loss of hydrogen atoms from $C_2HCl_3^+$ cannot be resolved on the 3D map as it would shift the fragment TOF by only one acquisition channel of the TDC. Measurement at a selection of fixed energies of the TOF distribution at higher time resolution for all detected products did not indicate the presence of any H-loss channels. Therefore, it is assumed that H-atom loss from any of the product channels is insignificant; to be accurate, however, the branching ratios of all ionic products (*e.g.* $C_2HCl_2^+$) should be considered as incorporating fragments formed by H-atom loss (*i.e.* $C_2HCl_2^+$ and $C_2Cl_2^+$). For fragmentation of $C_2Cl_4^+$, there is obviously no such issue.

The two molecules show similar types of photoionisation products. At low energies, only the parent ion is detected. At higher energies a chlorine atom is lost, and as the energy is raised more a second chlorine atom is lost. At high enough energies (15.92 eV) a third chlorine atom is lost from tetrachloroethene. Table 2 lists

the product ions and their respective AE_{298} values. The Table also lists the experimental $\Delta_r H^{\circ}_{298}$ values from applying the method of Traeger and McLoughlin to the values of AE_{298} , as well as the calculated values of $\Delta_r H^{\circ}_{298}$ and data for $\Delta_r H^{\circ}_{298}$ of the chemical species involved in the unimolecular dissociations. All values are given in eV, except $\Delta_r H^{\circ}_{298}$ values which are in kJ mol^{-1} . It should be noted that there is no value for $\Delta_r H^{\circ}_{298}(\text{C}_2\text{Cl}^+)$ available, so no calculation has been made for this channel produced from C_2Cl_4 .

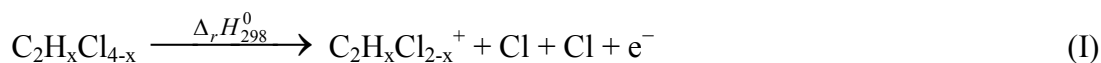
For trichloroethene three product ions were detected. The parent ion is the only product formed from onset of ionisation for the ground and first three excited electronic states of C_2HCl_3^+ . The first fragment ion detected is C_2HCl_2^+ with an AE_{298} value of 12.35 ± 0.05 eV. Above this energy the signal for the parent ion drops essentially to zero. From 13–16 eV C_2HCl_2^+ is the only fragment ion detected. At 15.5 ± 0.05 eV the third fragment C_2HCl^+ is formed, and once again the signal of the previous fragment decreases essentially to zero leaving C_2HCl^+ as the dominant ion.

Four product ions were observed for ionisation of tetrachloroethene. They are the parent ion (C_2Cl_4^+) and fragments due to loss of one (C_2Cl_3^+), two (C_2Cl_2^+) and three (C_2Cl^+) chlorine atoms. The AE_{298} values are 9.30 eV, 9.48, 12.52 eV and 15.92 eV, respectively. Due to the poor signal-to-noise ratio, errors are put conservatively at ± 0.1 eV, except for the formation of the first fragment C_2Cl_3^+ where the error is a lot greater. This fragment appears to have a surprisingly low AE_{298} value, considering that a C–Cl bond is broken; data for the other chloroethenes suggest an energy of about 2 eV excess above the IE is required. It is likely that the presence of the long, low-intensity slow rise in signal from 9.48–11.40 eV in the C_2Cl_3^+ cross-section is an artefact due to the low signal-to-noise ratio of these measurements and the background subtraction method used to obtain the cross-section. If this is correct, then the true AE_{298} value is *ca.* 11.40 eV. In Table 2 both possible values for $AE_{298}(\text{C}_2\text{Cl}_3^+)$ have been included and the Traeger and McLoughlin correction has been applied in both cases, numbers in square brackets in the Table representing the results when $AE_{298} = 9.48$ eV. Assuming that the AE_{298} of C_2Cl_3^+ is indeed 11.40 eV, then from onset to 12.50 eV the parent ion dominates. Its intensity drops above this energy, falling to zero above *ca.* 14 eV. From 12.5 eV C_2Cl_3^+ is the major ion for an interval of *ca.* 1 eV before C_2Cl_2^+ is formed. The production of C_2Cl_2^+ begins at 12.52 eV, and from 13.5 eV it has roughly equal intensity with C_2Cl_3^+ . From 16 eV C_2Cl_2^+ is the main ion fragment. At this energy there is also a decline in the signal of C_2Cl_3^+ , and the onset of formation of C_2Cl^+ is reached. C_2Cl^+ has only very weak intensity for all higher photon energies.

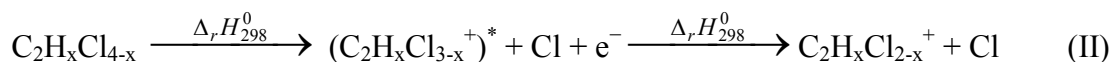
It is interesting to examine some of the trends observed in the photoionisation properties of the six chloroethenes studied. As the number of Cl atoms increases from two to three, the difference in energy

between the onset of ionisation and formation of the first fragment increases from *ca.* 2 to *ca.* 3 eV. For four chlorine atoms, *i.e.* $C_2Cl_4^+$, the difference reverts back to *ca.* 2 eV, assuming the upper value for $AE_{298}(C_2Cl_3^+)$ is indeed the correct value. In a photoionisation study of monochloroethene the energy difference between onset of ionisation and appearance of the first fragment, $C_2H_3^+$, was *ca.* 2.5 eV [33]. For formation of the next fragment formed by loss of a second Cl atom, for the three dichloroethenes the energy difference is *ca.* 4 eV, for trichloroethene it is *ca.* 3 eV and for tetrachloroethene it is *ca.* 1 eV. It is likely that these differences arise from the relative stability of the daughter cations formed, which in itself will depend on the interplay between conjugation and induction effects due to the chlorine atoms on the C=C double bond.

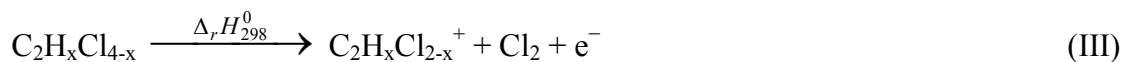
Another interesting trend can be observed in the formation of the fragment ion due to the loss of two chlorine atoms. There are three possible unimolecular reaction channels for formation of this ion :



or



or



where x is 0, 1 or 2. Reactions (I) and (II) are essentially the same process, and the distinction between them depends largely on the timescale of the dissociation. Reaction (III) has a lower calculated enthalpy of reaction because of the energy recouped by formation of a Cl–Cl bond. For the three dichloroethenes and trichloroethene, the AE_{298} of this ionic fragment is very close in energy to the calculated enthalpy of reaction (I). This onset lies *ca.* 2.5 eV above the enthalpy of reaction for reaction (III), formation of a Cl_2 molecule. This second channel will probably involve an exit-channel barrier whose value could coincidentally be around 2.5 eV, so energetics cannot rule out this possibility. For 1,1-dichloroethene, (*Z*)-1,2-dichloroethene and trichloroethene, where two chlorine atoms are adjacent to each other, it is easy to see that following dissociation it would be simple to eliminate Cl_2 . For (*E*)-1,2-dichloroethene where the chlorine atoms are on opposite sides of the molecule, it harder to see this happening as the transition state will be highly constrained, unless upon ionisation the C=C bond becomes weak enough for pseudo-rotation to occur. For the three dichloroethenes [1] and trichloroethene, the consistency of the onset for this channel suggests that the same process must be occurring. However, for tetrachloroethene this product is formed at 12.52 eV,

around 2 eV lower than the channel involving formation of two chlorine atoms but above the limit for the channel involving formation of Cl₂. The data therefore suggest that three isomers of C₂H₂Cl₂⁺ and C₂HCl₃⁺ dissociate by loss of two Cl atoms (reactions I or II), whilst C₂Cl₄⁺ dissociates by loss of molecular Cl₂ (reaction III). The alternative explanation, that all five chloroethene cations dissociate by loss of Cl₂, seems unlikely because in four of the five cases an exit-channel barrier would coincidentally have to take the same value as the strength of a Cl–Cl bond, *ca.* 2.5 eV.

5.3 New thermochemistry

Some new thermochemical values have been calculated from this study. The enthalpies of formation of the parent ions have been calculated from the enthalpy of formation of the neutral plus the onset of ionisation measured in this study. For C₂HCl₂⁺ formed from trichloroethene and C₂Cl₃⁺ from tetrachloroethene, values for the enthalpy of formation for the neutral radicals C₂HCl₂· and C₂Cl₃· were not available. Therefore the calculation to determine the enthalpy of formation of these fragment ions was not as trivial as for the parent ions. For the reactions :



and



it was assumed that the fragment ion turns on at its thermochemical threshold, and therefore $\Delta_f H_{298}^0(\text{calc.})$ is equivalent to the experimental AE₂₉₈ of the fragment ion plus the appropriate correction factor which allows for thermal effects (Section 4) [30]. This method effectively assumes that there is no exit-channel barrier or kinetic shift. As both reactions are simple cleavages of a single C–Cl bond, the lack of a barrier seems a reasonable assumption to make. In this way we determine $\Delta_f H_{298}^0(\text{C}_2\text{HCl}_2^+) \leq 1066 \text{ kJ mol}^{-1}$. As there is some uncertainty in which value of AE₂₉₈ (C₂Cl₃⁺) from C₂Cl₄ is correct, two values of its enthalpy of formation have been calculated. If the AE₂₉₈ is 9.48 eV, then $\Delta_f H_{298}^0(\text{C}_2\text{Cl}_3^+) \leq 798 \text{ kJ mol}^{-1}$, if the AE₂₉₈ is 11.40 eV then $\Delta_f H_{298}^0(\text{C}_2\text{Cl}_3^+) \leq 984 \text{ kJ mol}^{-1}$.

5.4 Fixed-energy TPEPICO spectra

TPEPICO-TOF scans were performed with a TOF resolution of 8 ns at the energies of the peaks in the TPES of C₂HCl₃ and C₂Cl₄. The parent ion TOF spectra show the expected convolution of several Gaussian distributions for molecules with three or four Cl atoms, respectively, each Cl atom showing a ³⁵Cl:³⁷Cl 3:1 weighting factor. The TOF spectra for the fragment ions formed by the loss of a single chlorine atom,

$C_2HCl_2^+$ and $C_2Cl_3^+$, have been analysed to produce the kinetic energy distribution (KERD) and hence average total kinetic energy release, $\langle KE \rangle_t$, see Table 3 [34]. Briefly, for each spectrum a small basis set of peaks, each with a discrete energy release ε_i is computed, and assigned a probability [35]. The discrete energies are given by $\varepsilon_i(n) = (2n-1)^2\Delta E$, where $n = 1,2,3,4 \dots$. ΔE depends on the statistical quality of the data; the higher the signal-to-noise ratio, the lower ΔE and the higher n can be set. Each computed peak in the kinetic energy release distribution spans the range $4(n-1)^2\Delta E$ to $4n^2\Delta E$, centred at $\varepsilon_i(n) + \Delta E$. The reduced probability of each discrete energy, $P(\varepsilon_i)$, is varied by linear regression to minimise the least-squared errors between the simulated and experimental TOF peak. From the basis set of ε_i and $P(\varepsilon_i)$, $\langle KE \rangle_t$ is easily determined. Allowance is made in the fitting for the presence of two or three chlorine isotopomers in the daughter ions $C_2HCl_2^+$ and $C_2Cl_3^+$, respectively [37]. By comparing the $\langle KE \rangle_t$ values with the available energy, the fractional release into translational energy for the loss of a chlorine atom, $\langle f \rangle_t$ (expt), can be determined. These values for $\langle f \rangle_t$ can be compared with the predictions of statistical and pure-impulsive models [21-23]. For the statistical theories, values have been calculated using the formula of Klots [23], and an estimate of the lower limit from Franklin [22]. The pure-impulsive model of Holdy *et al.* has been used to determine $\langle f \rangle_{t \text{ imp}}$ [21]. For formation of $C_2Cl_3^+$ from C_2Cl_4 , two values of AE_{298} are possible, as described above. Hence the results have been calculated twice, the more-unlikely values for $AE_{298} = 9.48$ eV being given in square brackets.

The KERDs for tetrachloroethene confirm the belief that a value for $AE_{298}(C_2Cl_3^+)$ of 9.48 eV is probably too low. Using this energy the \tilde{D} state of $C_2Cl_4^+$ has a $\langle f \rangle_t$ value of only 0.08, and this value then increases with increasing photon energy. If, however, the 11.40 eV value is used then the results for $\langle f \rangle_t$ are more reasonable; the fragmentation begins as approximately impulsive, becoming more statistical in nature as the photon energy increases. For loss of one Cl atom from both parent ions, the value of $\langle f \rangle_t$ now decreases with increasing photon energy above threshold. This result is predicted by statistical theories such as RRKM, and is shown here numerically by the values calculated using the formula of Klots. At higher energies, for both molecules $\langle f \rangle_t$ approaches 0.08, the value calculated as the lower statistical limit for fractional kinetic energy release. Such behaviour was also seen in previous studies by us on the dichloroethenes and similar-sized molecules [1,19]. The fact that $\langle f \rangle_t$ decreases with increasing energy is easily reconciled with the theories of intramolecular energy redistribution. As the photon energy increases, successively more electronic and vibrational energy levels of the parent ion can be accessed. The available energy is shared between states, and hence is less likely to be localised in a vibrational mode that would lead to mode-specific dissociation of the $C_2H_xCl_{4-x}^+$ ion. The same pattern was observed in our study of the three dichloroethenes [1]. This seems

to confirm that the fragmentation of the chloroethene cations is statistical in nature at higher energies, but becomes more non-statistical as energies approach their threshold values.

6. Conclusions

The photoionisation dynamics of trichloroethene and tetrachloroethene have been studied using synchrotron radiation in the energy range 9–22 eV by threshold photoelectron photoion coincidence spectroscopy. The measured energies of the electronic states of the parent ion compare well with energies calculated using an outer valence Greens' functions method. From energy-selected ion yields appearance energies and branching ratios have been determined for the fragments formed from photoionisation of tri- and tetrachloroethene. In order of increasing AE_{298} , the fragments in all cases are found to be the parent ion, a fragment formed from loss of a chlorine atom and a fragment formed from loss of two chlorine atoms. For tetrachloroethene, a fourth product is seen in which three chlorine atoms are lost. This is in agreement with our photoionisation results for the dichloroethenes [1]. Examination of thermochemistry and branching ratios from this and the dichloroethene study suggest that when two chlorine atoms are lost following photoionisation, they are lost as two Cl atoms for the three isomers of dichloroethene and trichloroethene, but as molecular Cl_2 from C_2Cl_4 .

Upper limits on the enthalpies of formation at 298 K of the parent ions, $C_2HCl_3^+$ and $C_2Cl_4^+$, have been determined. Assuming there is no kinetic shift or exit-channel barrier, upper limits at 298 K on the enthalpies of formation for $C_2HCl_2^+$ and $C_2Cl_3^+$ have also been determined. For $C_2Cl_3^+$ two values for the enthalpy of formation have been determined, depending on which value is used for the appearance energy of this fragment. The translational energy released when the parent ion fragments by loss of one Cl atom has been shown to be impulsive at low photon energies, but becomes more statistical in nature as the energy increases.

Trends due to the increasing number of chlorine atoms for all six chloroethenes are also noted. Firstly, we note the increase in ionic states present in the threshold photoelectron spectra due to the increasing number of chlorine lone pairs. This leads to a reduction in ionisation energy because of the increased conjugation of the $C=C$ π -orbitals and the chlorine lone pairs. Secondly, we note the variation in energy difference between the onset of ionisation and the appearance of the first fragment ion. Future work will include a study of the photoionisation dynamics of monochloroethene to complete the chloroethene series. It will also be of interest to expand this study to examine other haloethenes such as the fluoro-, bromo- and iodo-ethenes. An ultimate conclusion of this work would be to examine the dynamics of mixed haloethenes.

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Table 1 : Experimental and theoretical vertical ionisation energies (eV) for trichloroethene and tetrachloroethene.

Trichloroethene			Tetrachloroethene		
State ^a	VIE / eV ^b	OVGF / eV ^c	State ^a	VIE / eV ^b	OVGF / eV ^c
\tilde{X} (² A'')	10.15	9.28 (0.91)	\tilde{X} (² B _{3u})	9.65	9.08 (0.98)
\tilde{A} (² A')	11.73	11.50 (0.91)	\tilde{A} (² B _{3g})	11.5	11.17 (0.91)
\tilde{B} (² A')	12.15	11.95 (0.91)	\tilde{B} (² A _u)	11.96 ^d	11.98 (0.91)
\tilde{C} (² A'')	12.31	12.11 (0.91)	\tilde{C} (² B _{2u})	-	12.18 (0.90)
\tilde{D} (² A')	12.68	12.45 (0.91)	\tilde{D} (² B _{1g})	-	12.34 (0.90)
\tilde{E} (² A'')	12.94	12.73 (0.9)	\tilde{E} (² B _{1u})	-	12.48 (0.90)
\tilde{F} (² A')	14.38	14.31 (0.9)	\tilde{F} (² A _g)	-	12.62 (0.91)
\tilde{G} (² A'')	14.66	14.57 (0.89)	\tilde{G} (² B _{2g})	13.53	13.27 (0.90)
\tilde{H} (² A')	16.24	16.20 (0.89)	\tilde{H} (² B _{3g})	14.66	14.53 (0.90)
\tilde{I} (² A')	16.74	16.81 (0.88)	\tilde{I} (² B _{3u})	15.03	15.08 (0.88)
\tilde{J} (² A')	18.56	-	\tilde{J} / \tilde{K}	16.68	16.62 (0.88)
			(² B _{2u}) / (² B _{1u})		16.73 (0.89)
			\tilde{L} (² A _g)	18.23	18.51 (0.86)

^a Electronic state of the parent cation to which ionisation occurs.

^b Experimentally measured vertical ionisation energy.

^c Vertical ionisation energy calculated using the outer valence Greens' function method in Gaussian 03 [25]. The pole strength, *i.e.* the calculated relative photoionisation intensity, is shown in brackets.

^d The series of electronic states calculated to occur in the range 11.98–12.62 eV in C₂Cl₄⁺ cannot be resolved in the experimental spectrum.

Table 2 : Energetics of the dissociative ionisation pathways of trichloroethene and tetrachloroethene at 298 K. Values in square brackets are if the AE_{298} of $C_2Cl_3^+$ is assumed to be 9.48 eV.

	AE_{298} / eV <i>a</i>	$\Delta_r H^0_{298, \text{exp}} / \text{eV}$ ^{<i>b</i>}	$\Delta_r H^0_{298, \text{calc}} / \text{eV}$ ^{<i>c</i>}
Major^{<i>d</i>} products of C_2HCl_3 (-19)			
$C_2HCl_3^+ (894) + e^-$	9.46	-	-
$C_2HCl_2^+ (1066) + Cl (121) + e^-$	12.35	12.5	-
Minor^{<i>e</i>} products of C_2HCl_3			
$C_2HCl^+ (1237) + Cl (121) + Cl (121) + e^-$	15.50	-	15.53
$C_2HCl^+ (1237) + Cl_2 (0) + e^-$		-	13.01
Major products of C_2Cl_4 (-12)			
$C_2Cl_4^+ (887) + e^-$	9.30	-	-
$C_2Cl_3^+ (984) + Cl (121) + e^-$	11.40	11.58	-
	[9.48]	[9.66]	
Minor products of C_2Cl_4			
$C_2Cl_2^+ (1165) + Cl (121) + Cl (121) + e^-$	12.52	-	14.72
$C_2Cl_2^+ (1165) + Cl_2 (0) + e^-$		-	12.20
$C_2Cl^+ + Cl (121) + Cl (121) + Cl (121) + e^-$	15.92	-	-
$C_2Cl^+ + Cl_2 (0) + Cl (121) + e^-$		-	

^{*a*} Experimentally measured appearance energy of ionic product. For the parent ion this is equivalent to the ionisation energy.

^{*b*} Experimental enthalpy of reaction derived from the appropriate AE_{298} using the method of Traeger and McLoughlin [28].

^{*c*} Theoretically calculated enthalpy of reactions using standard thermochemistry.

^{*d*} Major products are defined as those products formed with either no or a single bond being broken.

^{*e*} Minor products are defined as those products which are formed by the breaking of more than one bond, and possibly also the formation of a new bond.

Table 3 : Total mean kinetic energy releases, $\langle \text{KE} \rangle_t$, for the two-body fragmentation of valence states of C_2HCl_3^+ and C_2Cl_4^+ . Values in square brackets apply in the unlikely scenario that the AE_{298} of C_2Cl_3^+ is 9.48 eV, and not 11.40 eV.

Parent Ion	State ^a	Daughter Ion	$h\nu /$ eV ^b	$E_{\text{avail}} /$ eV ^c	$\langle \text{KE} \rangle_t$ / eV ^d	$\langle f \rangle_t$ Exp ^e	$\langle f \rangle_t$ Klot ^f	$\langle f \rangle_t$ stat ^g	$\langle f \rangle_t$ Imp ^h
C_2HCl_3^+	\tilde{D}	C_2HCl_2^+	12.68	0.44	0.14	0.32	0.16	0.08	0.35
	\tilde{E}		12.90	0.66	0.19	0.29	0.14	0.08	0.35
	\tilde{F}		14.28	2.04	0.40	0.19	0.11	0.08	0.35
	\tilde{G}		14.66	2.42	0.43	0.18	0.11	0.08	0.35
C_2Cl_4^+	\tilde{D}	C_2Cl_3^+	12.34	1.09 ⁱ [3.01]	0.25	0.23 [0.08]	0.11 [0.10]	0.08	0.32
	\tilde{F}		12.84	1.59 [3.51]	0.34	0.22 [0.10]	0.11 [0.10]	0.08	0.32
	\tilde{G}		13.53	2.28 [4.20]	0.38	0.17 [0.09]	0.10 [0.10]	0.08	0.32
	\tilde{H}		14.72	3.47 [5.39]	0.47	0.14 [0.09]	0.10 [0.10]	0.08	0.32

^a Electronic state of the parent ion from which dissociation occurs.

^b Incident photon energy.

^c Energy available for the dissociation, defined as $h\nu - \text{AE}_{298} +$ (thermal energy of neutral molecule at 298 K). The final term has values of 0.11 and 0.15 eV for C_2HCl_3 and C_2Cl_4 , respectively.

^d Experimental average kinetic energy release.

^e Fraction of available energy released into translational kinetic energy of fragments.

^f Calculated fraction of energy released into translation from Klots [23].

^g Calculated fraction of energy released into translation from Franklin [24].

^h Calculated fraction of energy released into translation using an impulsive model [23].

ⁱ Values without brackets are calculated assuming $\text{AE}_{298}(\text{C}_2\text{Cl}_3^+) = 11.40$ eV, values in square brackets are for the unlikely scenario that $\text{AE}_{298}(\text{C}_2\text{Cl}_3^+) = 9.48$ eV.

Figure Captions

Figure 1. Threshold photoelectron spectrum for the six chloroethenes with an optical resolution of 0.3 nm. The data for monochloroethene, spectrum (a), is taken from reference [32]. The red drop lines represent the calculated OVGf ionisation energies.

Figure 2. (a) Threshold photoelectron spectrum and calculated OVGf spectrum, (b) ion yields, (c) breakdown diagram for trichloroethene over the energy range 9–22 eV. The photon resolution is 0.3 nm.

Figure 3. (a) Threshold photoelectron spectrum and calculated OVGf spectrum, (b) & (c) ion yields for tetrachloroethene over the energy range 9–22 eV. The photon resolution is 0.3 nm.

