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Dissociation dynamics and thermochemistry of chloroform and tetrachloroethane molecules studied by threshold photoelectron photoion coincidence

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Abstract

Threshold photoelectron photoion coincidence (TPEPICO) technique has been employed to determine accurate dissociative photoionization onsets for chloroform and 1,1,2,2-tetrachloroethane molecules. Our 0 K onsets for these reactions are $CHCl_3 + h\nu \rightarrow CHCl_2^+ + Cl$ (11.500 ± 0.007 eV); $C_2H_2Cl_4 + h\nu \rightarrow C_2H_2Cl_3^+ + Cl^\bullet$ (11.565 ± 0.010 eV) and $C_2H_2Cl_4 + h\nu \rightarrow CHCl_2^+ + CHCl_2^\bullet$ (11.669 ± 0.030 eV). The well established heat of formation of $CHCl_3$ was used as an anchor and the measured dissociation energies were used to determine the heats of formation, $\Delta_f H^o_{298K}$ in kJ/mol, of the following species: $CHCl_2^+$ (888.9 ± 1.3), $CHCl_2^\bullet$ (87.1 ± 1.6), $C_2H_2Cl_4$ (-152.7 ± 3.5), and $C_2H_2Cl_4^+$ (918.3 ± 5.9). Our results also made possible the determination of reliable 298 K bond enthalpies for: $CHCl_2{-}Cl$ (311.1 ± 2.0 kJ/mol), $CHCl_2{-}H$ (400.6 ± 2.0 kJ/mol), and $CHCl_2{-}CHCl_2$ (326.9 ± 4.1 kJ/mol).

Keywords: Photoionization; Heats of formation; Chloroform; Tetrachloroethane; Coincidence

1. Introduction

Halogen-containing molecules have been receiving increasing attention in recent years as a result of their importance in diverse branches of the chemical industry as well as their major role in atmospheric chemistry. Chloroform ($CHCl_3$) and 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$), for instance, are important compounds widely employed in the chemical industry as organic solvents and other applications, in which large amounts of waste are released to the environment. Photoionization and photolysis of these species give rise to halogen atoms, small halogenated free radicals and ions, which contribute catalytically to the depletion of the atmospheric ozone layer.

Despite its importance, the thermochemistry of many chlorinated molecules, alkyl free radicals and ions is not well established in the literature. Heats of formation for some chlorine-containing molecules, including $CHCl_3$ and $C_2H_2Cl_4$, have been experimentally determined and were recently reviewed in the literature [1]. However, only a few studies dedicated to the thermochemistry of chlorinated free radicals [2–6] and ions [7–9] have been published. As a result, accurate bond dissociation enthalpies are also lacking, and discrepancies as high as 20 kJ/mol are not uncommon. An example is the 1,1,2,2-tetrachloroethane, whose heat of formation has an uncertainty of 30 kJ/mol [10]. In addition, the currently employed theoretical methods for determining thermochemical properties of polyatomic halogenated molecules still present many limitations, resulting in average uncertainties in the order of 8 kJ/mol or larger [11].

We have recently initiated an investigation into the dissociation dynamics and thermochemistry of several halogen-containing molecules by TPEPICO spectroscopy. The first result of this series is an accurate set of heats of formation and bond enthalpies for all Cl, Br, and I containing dihalomethane molecules [12,13]. In addition, vinyl bromide and 1,1,2 tribromoethane have been investigated [14]. The present work is concerned with the study of the dissociative photoionization and thermochemistry of chloroform and 1,1,2,2-tetrachloroethane molecules. From our dissociative photoionization onsets we are able to determine reliable molecular and radical heats of for-

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mation and bond dissociation energies, which serve to correct the discrepancies of the literature values as well as to reduce its uncertainties.

2. Experimental approach

The threshold photoelectron photoion coincidence (TPEPICO) apparatus has been described in detail elsewhere [12,14,15]. Briefly, room temperature samples are introduced into the ionization region by means of a stainless steel capillary, and ionized with VUV photons generated from a hydrogen (H_2) discharge lamp dispersed by a 1 m normal incidence monochromator. The entrance and exit slits are set to 100 μm, which provide a photon resolution of 1 Å (8 meV at photon energy of 10 eV). The energy scale is calibrated by using the hydrogen Lyman-α resonance line. Ions and electrons are accelerated in opposite directions by a 20 V/cm extraction field. Electrons travel toward an electrode with a gridless 12.7 mm aperture located 6 mm from the center of the ionization region. A second gridless acceleration electrode, located 12 mm from the first one, accelerates the electrons to 75 eV after which they pass through a 13 cm field free flight tube and are detected by a pair of Spiraltron Electron Multipliers, one located on the main axis and another located off-axis in order obtain a relative measure of the "hot" electron contribution. The procedure for eliminating the "hot" electron contribution has been previously described [12,14,15]. The ions are accelerated over a 5 cm region before drifting 40 cm through the first field free region to a single stage 20 cm long reflectron, were they are decelerated, reflected and then drifted for another 40 cm second drift region before being detected on tandem Burle MCP's. Some of the data were also collected with a normal two-stage TOF spectrometer. The electron and ion signals are used as start and stop pulses for obtaining the ion TOF spectrum. Separate ion TOF distributions are collected in coincidence with the two electron detectors as a function of the photon energy. The sample pressure was kept in the range of 10^{-6} Torr during the experiments. The collection efficiencies have been recently improved to about 40% for threshold electrons and 12% for ions. The high purity samples of chloroform and 1,1,2,2-tetrachloroethane were purchased from Sigma–Aldrich. No further purification was used except for degassing the liquid samples by multiple freeze–pump–thaw cycles before admitting the vapor into the chamber.

3. Computational methods

Ab initio molecular orbital calculations [16] were carried out by using the Gaussian 03 system of programs [17]. The ground state geometries of the neutral and ionic species studied in this work were fully optimized using density functional theory (DFT), with the B3LYP and B3P86 functionals, together with the aug-cc-pVTZ and 6-311++G(3df,3pd) basis sets. The vibrational frequencies and rotational constants required for the thermal energy distribution calculations and RRKM analysis of the experimental breakdown diagrams were also obtained in these calculations and, in general, agree with the available literature data [18]. Gaussian G2 and G3 methods [19,20] have also been used to estimate ionization energies and heats of formation for some of the species.

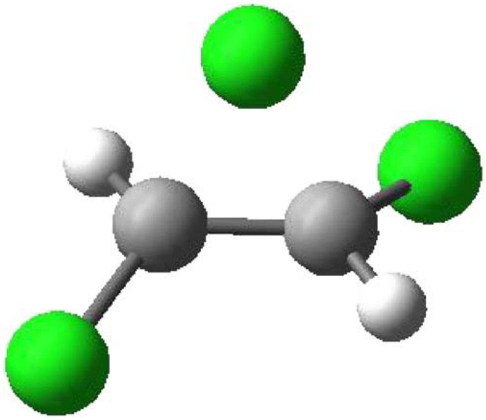

Fig. 1. Optimized geometry of $C_2H_2Cl_3^+$ at the B3LYP/aug-cc-pVTZ level of theory.

The geometry of $C_2H_2Cl_3^+$ cation has not been previously discussed in the literature. Our calculations performed at DFT levels suggest that the most stable geometry of this ion corresponds to a bridged structure, where one chlorine atom is bending out of the plane of the molecule between the central carbon atoms, as shown in Fig. 1.

4. Results and discussion

In this dissociative photoionization study, we have measured the dissociation onsets for the following reactions:

$$CHCl_3 + h\nu \rightarrow CHCl_2^+ + Cl \tag{1}$$

$$1,1,2,2\text{-}C_2H_2Cl_4 + h\nu \rightarrow 1,1,2\text{-}C_2H_2Cl_3^+ + Cl \tag{2a}$$

$$1,1,2,2\text{-}C_2H_2Cl_4 + h\nu \rightarrow Cl_2C{=}CClH^+ + HCl \tag{2b}$$

$$1,1,2,2\text{-}C_2H_2Cl_4 + h\nu \rightarrow CHCl_2^+ + CHCl_2 \tag{3}$$

If the energies of any two of the species are known, then the third can be determined from the measured dissociation onset, and by using Eq. (4):

$$\begin{aligned} &AB + h\nu \rightarrow A^+ + B + e^- \quad (E_0) \\ &E_0 = \Delta_f H_0[A^+] + \Delta_f H_0[B] - \Delta_f H_0[AB] \end{aligned} \tag{4}$$

In the present work we rely on the well established heat of formation of chloroform, $\Delta_f H^o_{298K} = -102.7 \pm 1.2 \text{kJ/mol}$ [10] (converted to −97.9 kJ/mol at 0 K) to anchor the energy scale, in order to derive the heat of formation for all other species.

The values for the 0 K enthalpies of formation can be converted to the corresponding 298 K and vice versa by means of the conventional thermochemical cycle, given by Eq. (5):

$$\Delta_f H^o_{0K} = \Delta_f H^o_{298K} - [H^o_{298K} - H^o_{0K}]\left(\frac{\text{molecule}}{\text{ion}}\right) + [H^o_{298K} - H^o_{0K}](\text{elements}) \tag{5}$$

We have used the $H^o_{298K} - H^o_{0K}$ values from the literature [21] for the atomic elements, and the calculated $H^o_{298K} - H^o_{0K}$

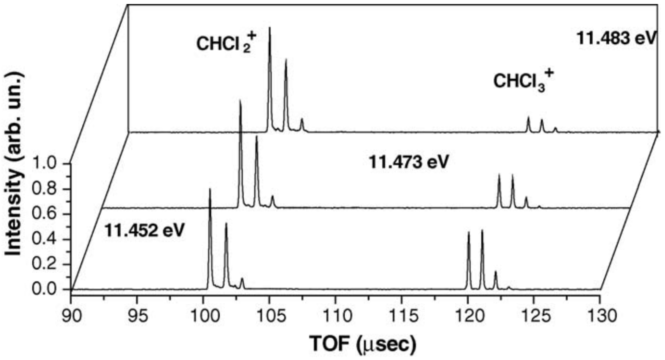

Fig. 2. Time of flight distributions using the reflectron at selected photon energies showing the parent ion and the $CHCl_2^+$ fragment ion from chloroform.

values for the molecules and fragment ions, from the vibrational frequencies obtained at B3LYP/aug-cc-pVTZ and B3P86/6-311++G(3df,3pd) levels of theory, which are in good agreement with the experimental values that could be found in the literature [18,22]. For the $H^{\mathrm{o}}_{298\mathrm{K}} - H^{\mathrm{o}}_{0\mathrm{K}}$ calculations, the heat capacity of the electron was chosen as 0.0 kJ/mol at all temperatures, according to the ion Convention [23].

4.1. Ion TOF distributions and breakdown diagrams

Time of flight mass spectra have been obtained for $CHCl_3$ and $C_2H_2Cl_4$ in the range from 11 eV to 12 eV. In this energy range the first chlorine loss from both $CHCl_3$ and $C_2H_2Cl_4$ is observed as well as the C–C bond rupture from $C_2H_2Cl_4$. Typical TOF distributions at selected photon energies are shown in Figs. 2 and 3. The dissociation reaction of chloroform is fast ($k > 10^7\ \mathrm{s}^{-1}$) [24], which can be confirmed by the narrow and symmetric peak shapes in the TOF distributions at different photon energies, as shown in Fig. 2. In the case of 1,1,2,2-tetrachloroethane molecule the dissociation channels are parallel. As a consequence, the dissociation rate constants for these pathways should be of about same order of magnitude so that they compete with each other. The TOF distributions for the 1,1,2,2-$C_2H_2Cl_4$ were collected with both the RETOF and linear TOF arrangements. The advantage of the TOF, shown in Fig. 3, is that the metastable character of the Cl/HCl loss channel is more obvious. The disadvantage is that the Cl and HCl loss fragments are not easily distinguished, so that we simply combine the two channels. From the RETOF data it is evident that the HCl loss channel is slow, while the Cl loss channel proceeds by a fast reaction. However, at energies close to the dissociation limit, the HCl loss channel dominates, and the Cl loss channel is never large. HX loss from halocarbon ions is well known, and the slow reactions have been quantitatively analyzed by a mechanism that involves tunneling through an H atom transfer barrier [25,26]. If in the case of the 1,1,2,2-$C_2H_2Cl_4$, the HCl loss barrier lies below the Cl or the C–C bond break barrier, then this channel will be slow and show up as a metastable dissociation, which exhibits the asymmetric TOF distribution shown in Fig. 3. Once the ion energy exceeds the rapid Cl loss or C–C bond breaking energy, the tunneling reaction is no longer competitive.

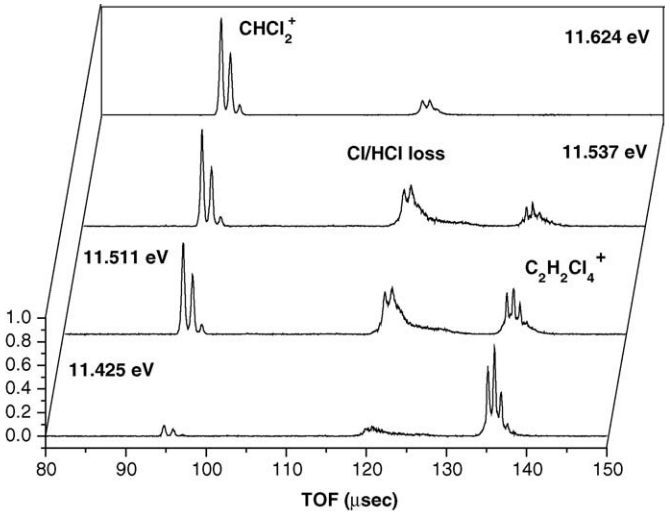

Fig. 3. Time of flight distributions using the linear TOF instrument at selected photon energies showing the parent and fragment ions from 1,1,2,2-tetrachloroethane. The broad asymmetric peaks are a result of a slow dissociation from metastable parent ions.

A breakdown diagram, B(*I*), which represents a plot of the parent ion and fragment abundances as a function of the parent ion internal energy, is obtained from the integrated peak areas corrected for the presence of hot electrons by using Eq. (6) [12]:

$$\mathrm{B}(I) = \frac{(I_\mathrm{c}) - f(I_\mathrm{r})}{(T_\mathrm{c}) - f(T_\mathrm{r})} \tag{6}$$

The terms I_c and T_c represent the integrated peak areas of an ion and the total area of ions associated with the central detector, respectively. I_r and T_r are the corresponding quantities for the ring or off-axis detector data. The experimental subtraction factor, *f*, is basically constant, and independent of the photon energy and of the molecule studied, as explained in previous publications [12,15,24]. In practice, we record a number of TOF distributions at different photon energies from which we obtained the fractional abundances of parent and ionic fragments from Eq. (6). The corresponding breakdown diagrams for $CHCl_3$ and 1,1,2,2-$C_2H_2Cl_4$ are presented in Figs. 4 and 5. The points rep-

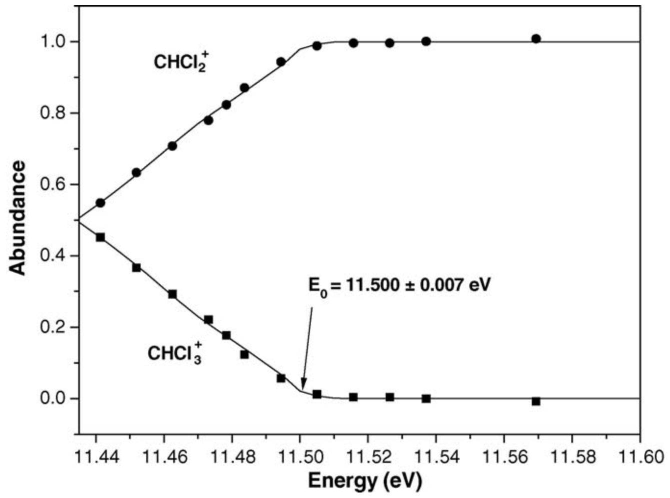

Fig. 4. Breakdown diagram for $CHCl_3$ in the 11.4–11.6 eV energy range.

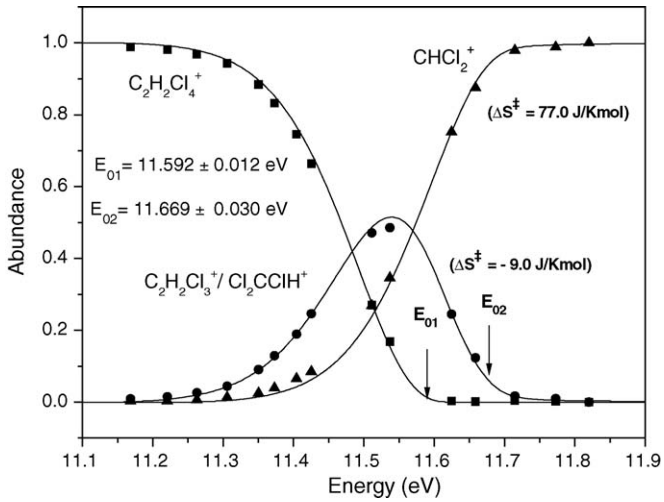

Fig. 5. Breakdown diagram for 1,1,2,2-$C_2H_2Cl_4$ in the 11.0–12.0 eV energy range.

resent the experimental data and the solid lines correspond to the calculated breakdown diagram taking into account the thermal energy. In the case of room temperature samples, the ion energy is given by $h\nu + E_{th}$, where E_{th} is the thermal energy which is given by a distribution, $P(E) \propto \rho(E) \exp[-E/RT]$, where $\rho(E)$ is the ro-vibrational density of states. The thermal energy distribution can be obtained from the calculated or experimental vibrational frequencies of the parent molecule. In this approach it is assumed that all ions with internal energies in excess of the dissociation limit will fragment. Sample temperatures of 298 K were assumed for both the $CHCl_3$ and 1,1,2,2-$C_2H_2Cl_4$ analyses.

The 0 K dissociation onsets, determined from the analysis of the experimental breakdown diagrams are also shown in Figs. 4 and 5. In the case of fast reactions, such as for chloroform, the 0 K onset is very close to the energy at which the parent ion signal goes to zero. The only adjustable parameter in this modeled breakdown diagram of Fig. 4 is the 0 K dissociation onset, E_0, which is adjusted to achieve a best fit for the experimental breakdown diagram. The onset for the reaction (1), $CHCl_3 + h\nu \rightarrow CHCl_2^+ + Cl$, was determined to be 11.500 ± 0.007 eV. This value is much more accurate than the previous literature values [27], including the 11.49 ± 0.02 eV obtained from photoionization experiments by Werner et al. [29] and 11.52 ± 0.07 eV from electron impact by Lossing [8], which agree with our result, and the much higher value of 11.70 ± 0.1 reported by Harrison and Shannon [7].

The breakdown diagram for $C_2H_2Cl_4$ involves parallel channels so that fitting the breakdown diagram requires taking into account the relative rate constants of the two reaction paths. We do this by the use of the statistical RRKM theory [28]. The rate constants as a function of the ion energy can be calculated with a knowledge of the vibrational frequencies of the molecular ion and the transition state (TS). The molecular ion frequencies are obtained from ab initio calculations, while the TS frequencies were adjusted until a best fit to the data was obtained. Fitting of the second dissociation channel thus involves two adjustable parameters: the dissociation energy and the TS frequencies. This analysis shown as a fit to the data in Fig. 5, is consistent with the proposed mechanism that involves a low energy tunneling of the H atom leading to HCl loss. The HCl and the small Cl loss yields go to zero at high energies and the dominant product is the $CHCl_2^+$ ion coming from the C–C bond break. In the analysis of this reaction, we were forced to assume a tight TS for the HCl/Cl loss reactions and fitted the breakdown diagram by allowing the transition state frequencies associated with the C–C bond break to vary until an optimum fit was obtained. The entropies of activation shown in Fig. 5 reflect the tight HCl/Cl losses and the loose C–C bond breaking steps. The determined dissociation onsets for the 1,1,2,2-$C_2H_2Cl_4$ molecule are 11.592 ± 0.012 eV (reactions (2a) and (2b)) and 11.669 ± 0.030 eV (reaction (3), corresponding to a Cl/HCl loss and C–C bond breaking, respectively. The only dissociation onset found in the literature for this molecule corresponds to the C–C breaking channel, obtained from electron impact experiments by Harrison and Shannon [7]. Their derived onset of 11.55 ± 0.10 eV agrees with our present result within the uncertainties of the experiments, but our value is considerably more accurate. No information on the Cl/HCl loss channels has been found in the literature. This is not surprising because it is a very minor process that is important over a very small energy range (11.4–11.6 eV) and thus not readily observable by ionization methods other than by threshold photoionization. Our onset value of 11.592 ± 0.012 eV is the first reported onset for the reactions (2a) and (2b).

4.2. *Thermochemistry*

We have measured the 0 K dissociation onsets for the reactions (1)–(3). By using the onset for reaction (1) together with the well established enthalpies of formation of chloroform, $\Delta_f H^o_{298K}(CHCl_3) = -102.7 \pm 1.2 kJ/mol$ [10], (converted to −97.9 kJ/mol at 0 K), and chlorine atom, $\Delta_f H^o_{298K}(Cl) = 121.3 kJ/mol^{21}$ (119.6 kJ/mol at 0 K), we can derive the heat of formation of the dichloromethyl ion ($CHCl_2^+$) from Eq. (4). Because this ion is also a product of reaction (3), it can be used to obtain the heat of formation of $C_2H_2Cl_4$. The thermochemical results are summarized in Table 1.

From electron impact experiments, Harrison and Shannon [7] determined an average value of 899.6 ± 12.5 kJ/mol for 298 K heat of formation of $CHCl_2^+$. Later, Lossing [8] and Holmes et al. [9] reported a value of 887.0 ± 8.4 kJ/mol, also from electron impact experiments. Werner et al. [29], from photoionization studies, derived a much lower value of 883.7 kJ/mol. However, a reevaluation of this quantity using their results and the auxiliary thermochemical data yields a $CHCl_2^+$ heat of formation of 887.4 ± 2.4 kJ/mol, which seems more reasonable. Our accurate experimental 0K heat of formation for the dichloromethyl ion, $\Delta_f H^o_{0K}(CHCl_2^+) = 892.1 \pm 1.3 kJ/mol$ (converted to 888.9 ± 1.3 kJ/mol at 298 K), serve to correct the discrepancies of the literature values and substantially reduce the uncertainty for the heat of formation of this important ion (Table 2).

The adiabatic ionization energy (IE_{ad}) for the dichloromethyl radical ($CHCl_2$) has been accurately determined by Andrews et al. [30] from He I photoelectron spectroscopy experiments. Their measured IE_{ad} value of 8.32 ± 0.01 eV can be combined

Table 1
Summary of the thermochemical results (in kJ/mol)

Species	$\Delta_f H^o_{0K}$ [a]	$\Delta_f H^o_{298K}$ [a]	$H^o_{298K} - H^o_{0K}$	$\Delta_f H^o_{298K}$ [b]
$CHCl_3$	−97.9	−102.7 ± 1.2[c]	14.2	−102.7 ± 1.2[c] −102.9 ± 2.5[d]
$CHCl_2{}^+$	892.1	888.9 ± 1.3	11.3	887.0 ± 8.4[e]
$CHCl_2{}^\bullet$	89.4	87.1 ± 1.6	12.2	89.0 ± 3.0[f]
$C_2H_2Cl_4$	−144.4	−152.7 ± 3.5	20.6	−149.3 ± 8.4[c] −156.7 ± 3.5[d]
$C_2H_2Cl_4{}^+$	926.6	919.3 ± 5.9	21.6	–
$C_2H_2Cl_3{}^+$	854.2[g]	847.6[g]	17.9	–
$C_2HCl_3{}^+$	899.1[g]	896.0[g]	16.7	897 ± 3.0[h]

[a] Present work unless otherwise noted.
[b] Literature values.
[c] Pedley [10].
[d] Manion [1].
[e] Holmes et al. [9].
[f] Seetula [6].
[g] Calculated at G3 level of theory.
[h] Obtained by combining a neutral heat of formation from Manion [1] with an IE reported by Woo et al. [34].

with our 0 K heat of formation of $CHCl_2{}^+$ in order to derive the 0 K heat of formation for the dichloromethyl radical, which yields a value of $\Delta_f H^o_{0K}(CHCl_2{}^\bullet) = 89.4 \pm 1.6$ kJ/mol (converted to 87.1 ± 1.6 kJ/mol at 298 K). This is in good agreement with the currently recommended 298 K value of 89.0 ± 3.0 kJ/mol determined from kinetics experiments by Seetula [6], but again its uncertainty is considerably reduced. We have also performed calculations on this radical at the G2 and G3 levels of theory, which predict 298 K heats of formation of 85.0 and 86.9 kJ/mol, respectively, and agree quite well with our present results.

The C–Cl bond dissociation enthalpy (BDE) of chloroform can be calculated by using the heats of formation of chloroform, $\Delta_f H^o_{298K}(CHCl_3) = -102.7 \pm 1.2$ kJ/mol [10], and chlorine atom $\Delta_f H^o_{298K}(Cl) = 121.3$ kJ/mol [21] together with our derived heat of formation $\Delta_f H^o_{298K}(CHCl_2) = 87.1 \pm 1.6$ kJ/mol, and Eq. (6):

$$\mathrm{BDE}(A - B) = \Delta_f H^o(A) + \Delta_f H^o(B) - \Delta_f H^o(AB) \qquad (6)$$

This yields a BDE ($CHCl_2$–Cl) = 311.1 ± 2 kJ/mol, which matches almost exactly with the value 311.2 kJ/mol calculated by Lazarou et al. [11] at the empirically corrected B3P86/6–311++G(2df,p) level of theory. Our value also agrees reasonably well with the bond enthalpy of 308.0 ± 8 kJ/mol obtained by Chen et al. [4] from electron capture experiments. The present result reduces the uncertainties of previous studies and suggests that the currently recommended literature value of 320.5 ± 6.3 kJ/mol [31] should be adjusted. In addition, we can determine the BDE ($CHCl_2$–H) by combining the well known literature values for the heats of formation of CH_2Cl_2 (−95.5 kJ/mol) [12] and H (218.0 kJ/mol) [21] with our $CHCl_2$ (87.1 kJ/mol). The resulting BDE ($CHCl_2$–H) = 400.6 ± 2 kJ/mol agrees very well with the experimental value of 402.5 ± 3.2 kJ/mol derived by Seetula [6], but we reduce its uncertainty, and also correct the currently recommended literature value of 407.1 ± 4.2 kJ/mol [31].

Table 2
Bond dissociation enthalpies (in kJ/mol)

Species	BDE	
	This work	Literature[a]
$CHCl_2$–Cl	311.1 ± 2.0	320.5 ± 6.3
$CHCl_2$–H	400.6 ± 2.0	407.1 ± 4.2
$CHCl_2$–$CHCl_2$	326.9 ± 4.1	336.0 ± 8.4

[a] Recommended literature values taken from Luo [31].

The heat of formation of 1,1,2,2-$C_2H_2Cl_4$ was carefully reviewed in 2002 by Manion [1], who recommended a gas phase heat of formation of −156.7 ± 3.5 kJ/mol. This value is based primarily on three experimental measurements, which are the heat of chlorination of *Z*-1,2-$C_2H_2Cl_2$ reported by Kirkbride [32] in 1956, an unpublished dehydrochlorination study of Paker and Dickinson, as reported only by Kirdbridge [32], and the heat of isomerization between 1,1,2,2-$C_2H_2Cl_4$ and 1,1,1,2-$C_2H_2Cl_4$ reported by Kolesov and Papina [33] in 1983. These three measurements, in conjunction with the latest ancillary values for the heats of formation and vaporization agree very well, and are significantly lower than the value of −149.3 ± 8.4 kJ/mol listed by Pedley [10]. The Pedley value is based in part on the same original experimental measurements but differs because of the ancillary values used for the heat of formation of *Z*-1,2-$C_2H_2Cl_2$. The additional measurement included by Pedley and earlier complilations include a 1938 heat of combustion by Eftring reported in a Lund University thesis, which yields a gas phase heat of formation of −148.8 kJ/mol [1], Manion [1] suspects this value because of problems in “early combustion data on chlorinated compounds” and because this value is significantly higher than the value obtained by other methods.

We have determined the 0 K heat of formation of 1,1,2,2-$C_2H_2Cl_4$ by combining our onset energy for reaction (3) (11.669 ± 0.030 eV) and the 0 K heats of formation of $CHCl_2{}^\bullet$ and $CHCl_2{}^+$, also determined in this work. It results in $\Delta_f H^o_{0K}(C_2H_2Cl_4) = -144.4 \pm 3.5$ kJ/mol, which can be converted to −152.7 ± 3.5 kJ/mol at 298 K. This value is based not only on our new experimental result, but also depends on different ancillary data, namely the $CHCl_2{}^\bullet$ radical and the $CHCl_2{}^+$ ion heats of formation. It is thus entirely independent of previous measurements. The difference of 4 kJ/mol relative to the Manion review, which is just outside the error limits of each measurement, is perhaps larger than we would like, but can nevertheless be viewed as satisfactory.

By using our determined heats of formation for $CHCl_2$ and $C_2H_2Cl_4$ and Eq. (6) we were also able to derive a reliable C–C bond enthalpy for the 1,1,2,2-tetrachloroethane. It yields a value of BDE($CHCl_2$–$CHCl_2$) = 326.9 ± 4.1 kJ/mol, which is about 9 kJ/mol lower than the value of −336.0 ± 8.4 recommended by Luo [31], based on old auxiliary heats of formation. In addition, combining the ionization energy of tetrachloroethane, IE($C_2H_2Cl_4$) = 11.10 ± 0.05 eV, determined from electron impact experiments by Harrison and Shannon [7], with our neutral heat of formation we can derive the heat of formation of the $C_2H_2Cl_4{}^+$ ion, $\Delta_f H^o_{298K}(C_2H_2Cl_4{}^+) = 919.3 \pm 5.9$ kJ/mol (926.6 ± 5.9 kJ/mol at 0 K).

The HCl/Cl loss onset is measured to be 11.52 eV. Because the HCl loss reaction proceeds by tunneling through a barrier, its onset energy is simply the energy at which the reaction rate becomes significant. We can calculate the thermochemical onset energy for the reaction: 1,1,2,2-$C_2H_2Cl_4 \rightarrow HClC{=}CCl_2^{+\bullet} + HCl$. The tri-chloroethylene ion heat of formation can be obtained from the recently measured IE of 9.4776 ± .0002 eV by Woo et al. [34] and the neutral heat of formation of −17.6 ± 3.0 kJ/mol as recommended by Manion [1], which yields a value of 897 ± 3 kJ/mol. (The trichloroethene heat of formation measurement was carried out by Papina and Kolesov [35] using a rotating bomb calorimeter.) When we combine this with the heats of formation of the tetrachloroethane and HCl, we obtain a thermochemical onset energy (298 K) of 10.0 eV for the HCl loss reaction. This is well below the observed onset of 11.56 eV, which means that this reaction indeed has a reverse barrier of about 1.6 eV.

We have estimated the heats of formation for the Cl loss and HCl loss ions by performing calculations at G3 level of theory. The computed 298 K heats of formation for $C_2H_2Cl_3^+$ and $C_2HCl_3^{+\bullet}$ are 847.6 kJ/mol and 896.0 kJ/mol, respectively. The latter is in agreement with both previously mentioned values of 905 ± 8.8 kJ/mol and 895.4 ± 3 kJ/mol. Finally, the expected 0 K onset for the 1,1,2,2-$C_2H_2Cl_4 \rightarrow C_2H_2Cl_3^+ + Cl^\bullet$ reaction is approximately 11.589 eV, which is very close to the experimentally observed onset of 11.592 ± 0.012 eV.

5. Summary

The dissociative photoionization of chloroform and 1,1,2,2-tetrachloroethane molecules has been investigated by using the threshold photoelectron photoion coincidence technique. Accurate ionization energies, breakdown diagrams, and dissociation onsets have been determined for those molecules and their ionic fragments. By using the well established heat of formation of $CHCl_3$ as an anchor, together with our experimental dissociation onsets, it has been possible to determine accurate 0 and 298 K heats of formation for the following species: $CHCl_2^+$, $CHCl_2$, $C_2H_2Cl_4$, $C_2H_2Cl_4^+$. Heats of formation for $C_2H_2Cl_3^+$ and $C_2HCl_3^+$ ions have been determined from calculations at G3 level of theory and found to be consistent with the experimental results. From our results we were also able to determine a reliable set of 298 K neutral and ion bond enthalpies for: $CHCl_2{-}Cl$, $CHCl_2{-}H$ and $CHCl_2{-}CHCl_2$.

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