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Formation, stability and structure of radical anions of chloroform, tetrachloromethane and fluorotrichloromethane in the gas phase

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Abstract

The gas-phase reactions of the $CH_2S^{\cdot-}$ radical anion with chloroform, tetrachloromethane, and fluorotrichloromethane ($CXCl_3$; X = H, D, Cl and F) have been studied using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The primary reactions lead to minor amounts of the molecular radical anions of the halomethanes in addition to CH_2SCl^- and Cl^-, which are formed as the major product ions. The initial step is suggested to be electron transfer with formation of a $[CH_2S + CXCl_3^{\cdot-}]$ ion/molecule complex, which may dissociate to the radical anion of the halomethane or react further to yield a $[CH_2S + Cl^- + CXCl_2^{\cdot-}]$ complex prior to the generation of the Cl^- or CH_2SCl^- ions. The radical anions of $CHCl_3$ and CCl_4 react with the parent compounds to yield $CHCl_4^-$ and CCl_5^- ions, respectively, whereas $CFCl_3^{\cdot-}$ transfer a Cl^- ion only to the CH_3SH molecules also present in the FT-ICR cell. On the basis of the facile occurrence of Cl^- transfer, the $CXCl_3^{\cdot-}$ ions are proposed to exist in a structure which can be described as a chloride ion weakly bonded to a $CXCl_2^{\cdot}$ radical. The formation of the $CXCl_3^{\cdot-}$ ions in the reaction with the $CH_2S^{\cdot-}$ radical anion places a lower limit of 45 kJ mol^{-1} for the electron affinities of the $CXCl_3$ molecules. The occurrence of Cl^- transfer from the $CHCl_3^{\cdot-}$ ion to the parent compound leads to an indicated upper limit of 75 kJ mol^{-1} for the electron affinity of chloroform. Similarly, the occurrence of Cl^- transfer from the $CCl_4^{\cdot-}$ ion to the parent compound is used to derive an upper limit of 110 kJ mol^{-1} for the electron affinity of tetrachloromethane. These upper limits suggest that previously reported values overestimate the electron affinities of chloroform and tetrachloromethane.

Keywords: Electron affinities; Electron transfer; Fourier transform ion cyclotron resonance; Halomethanes; Radical anions

1. Introduction

Electron transfer reactions involving radical anions and anions have been studied extensively in condensed phase systems [1,2]. For gas-phase systems, the majority of the reported studies is concerned with the determination of electron affinities [3–9] and the kinetics of electron transfer reactions involving stable radical anions or anions [3,10,11]. Only a limited number of studies have been concerned with the possible occurrence of electron transfer to haloalkanes in the gas phase [12–18] notwithstanding that special attention has been paid to the interplay between dissociative electron transfer and S_N2 substitution in reactions with

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these compounds in the condensed phase [1,19]. Furthermore, the reactions of a potential electron donor such as the super oxide ion, $O_2^{\cdot -}$, with halomethanes containing more than a single halogen atom (e.g. freons) are known to play a role in the negative ion chemistry occurring in the upper atmosphere [20,21].

The reported studies of gas-phase reactions with halomethanes indicate that radical anions and anions react preferentially with these molecules by dissociative electron transfer (Eq. (1)) or nucleophilic processes, whereas resonance electron transfer with formation of a stable molecular radical anion (Eq. (2)) is an uncommon process:

$$A^{\cdot -} + RX \rightarrow [A + R^{\cdot} + X^{-}]^{*} \rightarrow A + R^{\cdot +}X^{-} \quad (1)$$

$$A^{\cdot -} + RX \rightarrow [A + RX^{\cdot -}]^{*} \rightarrow A + RX^{\cdot -} \quad (2)$$

In a few instances stable radical anions of halomethanes have been observed. For example, minor amounts of the radical anions of CF_2Cl_2 and $CFCl_3$ are reported to arise by electron transfer from the $O_2^{\cdot -}$ ion [12,17] and in a recent study, we observed that $CBr_4^{\cdot -}$ ions are formed by electron transfer from the radical anion of azobenzene to tetrabromomethane [14]. Low but measurable yields of the tetrachloromethane radical anion have been formed also in the collisions of CCl_4 molecules with neutral potassium atoms with a controlled kinetic energy [22]. Likewise, attachment of electrons to free halomethane molecules in the gas phase is referred to normally as an inherent dissociative process leading mostly to the predominant or exclusive formation of a halide ion [23,24]. Low yields of $CCl_4^{\cdot -}$ ions have been generated, however, by attachment of electrons with an energy close to zero electronvolts to carbon dioxide clusters containing small amounts of tetrachloromethane [25]. Furthermore, $CF_3Cl^{\cdot -}$ ions have been reported to be formed by electron ionization of chlorotrifluoromethane clusters [26] and also by electron impact induced decarbonylation of CF_3COCl [27].

The rare observations of stable molecular radical anions of simple halomethanes appear to be in conflict with the large and positive adiabatic electron affinities which have been suggested for species such as chloroform, tetrachloromethane and fluorotrichloromethane on the basis of results obtained by experiments [22,28] and high level calculations [29,30]. These apparently inconsistent findings raise questions as to the true adiabatic electron affinities of these molecules as well as to the intrinsic stability of the molecular radical anions with respect to dissociation into a halide ion and a halogen substituted methyl radical. In an attempt to answer these questions, we examined the gas phase reactions of various (radical) anions with selected halomethanes and observed that the thioformaldehyde radical anion reacts uniquely with $CHCl_3$, $CDCl_3$, CCl_4 and $CFCl_3$ to afford minor amounts of stable molecular radical anions. This allowed us to derive upper limits for the adiabatic electron affinities of these molecules and experimentally study the reactivity of the related radical anions.

2. Experimental

The experiments were performed with a Fourier transform ion cyclotron resonance (FT-ICR) [31] instrument designed and constructed at the University of Amsterdam [32–34]. In a typical experiment, the primary negative ions were formed by a pulsed electron beam (duration 150 ms) and trapped in a magnetic field of 1.23 T by applying a small negative voltage (≈ -1 V) to the trapping plates of

the cubic inch FT-ICR cell. The $CH_2S^{\cdot -}$ and *ortho*-benzyne ($C_6H_4^{\cdot -}$) radical anions were formed by reacting $O^{\cdot -}$ with methanethiol [35] and benzene [36,37] respectively. The $O^{-\cdot}$ ions were formed by dissociative capture of electrons with an energy of ≈ 1.2 eV by nitrous oxide [38]. The ions $CH_3NO_2^{\cdot -}$ and $C_6F_6^{\cdot -}$ were formed by electron transfer from NO^-, which was generated in a secondary reaction between $O^{\cdot -}$ and N_2O [39,40]. The reactant ions of interest were isolated by ejecting all other ions from the cell as described elsewhere [41,42]. The reactions of the various ions with the halogenated methanes were studied subsequently as a function of time by varying the delay between the selection of the ions of interest and the start of the excitation pulse [31]. The relative abundances of the isotopic chloride containing product ions were measured with an accuracy of $\leqslant 5\%$ by following procedures described elsewhere [33,41,43].

The total pressure was around 8×10^{-5} Pa with a background pressure better than 3×10^{-7} Pa. The ratio between the partial pressure of N_2O, the halomethane, and the neutral precursor of the reactant radical anion was typically 1 : 1 : 1. The pressures were measured with an uncalibrated ionization gauge placed in the side arm of the main pumping line. The inlet lines and the main vacuum vessel were at room temperature, whereas the temperature of the trapping plate opposite the filament was between 330 and 340 K in a typical experiment. All the chemicals used were commercially available.

3. Results

The $CH_2S^{\cdot -}$ ion reacts efficiently with $CXCl_3$ molecules (X = H, D, Cl and F) in the gas phase to form $CXCl_3^{\cdot -}$, CH_2SCl^- and Cl^- as primary product ions (Eqs. (3)–(5)) [44].

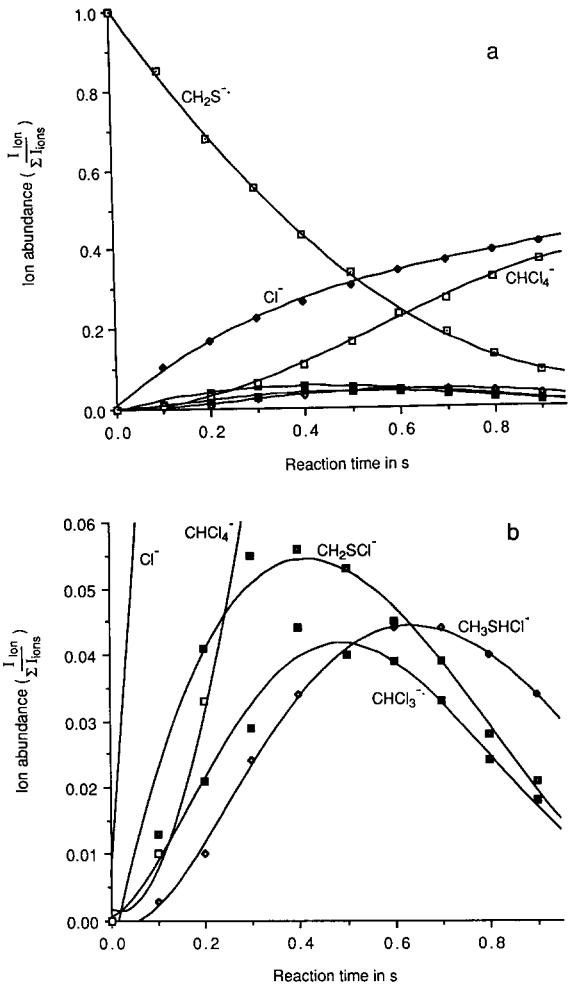


Fig. 1. Relative intensities of the ions formed in the reaction of $CH_2S^{\cdot -}$ with chloroform as a function of reaction time: a, an overall plot of the abundances of all ions present in the cell; b, magnification of the region corresponding to ion abundances lower than 0.06.

$$\rightarrow CXCl_3^{\cdot -} + CH_2S \quad (3)$$

$$CH_2S^{\cdot -} + CXCl_3 \rightarrow Cl^- + CH_2S + CXCl_2^{\cdot} \quad (4)$$

$$\rightarrow CH_2SCl^- + CXCl_2^{\cdot} \quad (5)$$

The identification of these ions as primary products is based on experiments in which the ion abundances are followed as a function of time as illustrated in Fig. 1 for the reaction with $CHCl_3$. Subsequent extrapolation to

Table 1
Normalized abundances (%) of the product ions formed in the reaction between $CH_2S^{\cdot -}$ and the $CXCl_3$ (X = H, D, F and Cl) compounds at short reaction times and after 0.7 s (see also text)

	$CHCl_3$		$CDCl_3$		$CFCl_3$		CCl_4	
	$t \to 0$	$t = 0.7$ s	$t \to 0$	$t = 0.7$ s	$t \to 0$	$t = 0.7$ s	$t \to 0$	$t = 0.7$ s
Cl^-	50	50	70	60	60	60	85	85
CH_2SCl^-	35	5	20	5	15	4	10	2
CH_3SHCl^-	0	5	0	5	15	33	0	10
$CXCl_3^{\cdot -}$	15	5	10	5	10	3	5	0
$CXCl_4^-$	0	35	0	25	0	0	0	3

zero reaction time of the normalized product ion abundances leads to the relative yields of the different product ions unperturbed by secondary processes. The relative yields of the various ions are given in Table 1 for the different $CXCl_3$ compounds together with the abundances of all product ions present in the cell after a reaction time of 0.7 s.

The time dependence of the relative abundances of the CH_2SCl^- and $CHCl_3^{\cdot -}$ ions (Fig. 1b) indicates clearly that these ions react further with the neutral species in the cell. This is also revealed by the results of experiments in which the $CH^{35}Cl_3^{\cdot -}$ or $CH_2S^{35}Cl^-$ ions are isolated and subsequently allowed to react for 0.2 s. After selection of the $CH^{35}Cl_3^{\cdot -}$ ions, $CHCl_3\,^{35}Cl^-$ and $^{35}Cl^-$ are formed in the abundance ratio of roughly 1:1. The formation of the $CHCl_3\,^{35}Cl^-$ species reveals the occurrence of a chloride ion transfer to chloroform (Eq. (6)). The generation of $^{35}Cl^-$ ions may be a result of low kinetic energy collision-induced dissociation (CID) caused by off-resonance excitation [45] of the translational motion of the $CH^{35}Cl_3^{\cdot -}$ ions by the r.f. pulses applied in order to isolate these species (see also Section 2):

$$CH^{35}Cl_3^{\cdot -} + CHCl_3 \rightarrow CH^{35}Cl_2^{\cdot} + CHCl_3\,^{35}Cl^- \quad (6)$$

After isolation of the $CH_2S\,^{35}Cl^-$ ions, $^{35}Cl^-$, $CH_3SH^{35}Cl^-$ and $CHCl_3\,^{35}Cl^-$ ions are generated in the abundance ratio of 1:2:4. The formation of the $^{35}Cl^-$ ion is also here likely to be a result of low kinetic energy CID, whereas the latter two ions arise by competing chloride ion transfer from $CH_2S\,^{35}Cl^-$ to CH_3SH (Eq. (7)) and $CHCl_3$ (Eq. (8)) respectively:

$$CH_2S^{35}Cl^- + CH_3SH \rightarrow CH_2S + CH_3SH^{35}Cl^- \quad (7)$$

$$CH_2S^{35}Cl^- + CHCl_3 \rightarrow CH_2S + CHCl_3\,^{35}Cl^- \quad (8)$$

Additionally, the $CH_3SH^{37}Cl^-$ ion was selected and allowed to react for 0.2 s with the molecules present in the cell. This leads only to the formation of $CHCl_3\,^{37}Cl^-$ ions, indicating the occurrence of chloride ion transfer from $CH_3SH^{37}Cl^-$ to chloroform (Eq. (9)):

$$CH_3SH^{37}Cl^- + CHCl_3 \rightarrow CH_3SH + CHCl_3\,^{37}Cl^- \quad (9)$$

In the experiments with CCl_4, minor amounts of CCl_5^- ions are generated in secondary processes (Table 1) together with CH_3SHCl^- ions. Isolation of $CH_2S^{35}Cl^-$ reveals that in the subsequent reactions of this ion, only $CH_3SH^{35}Cl^-$ is formed. The absence of formation of $CCl_4\,^{35}Cl^-$ in this particular experiment indicates that the former CCl_5^- ions arise by Cl^- transfer from $CCl_4^{\cdot -}$ to the parent compound (Eq. 10)):

$$CCl_4^{\cdot -} + CCl_4 \rightarrow CCl_5^- + CCl_3^{\cdot} \quad (10)$$

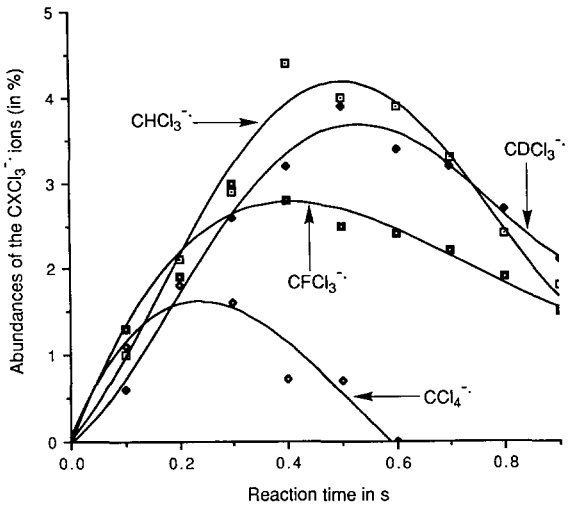


Fig. 2. Normalized abundances of the $CXCl_3^{\cdot -}$ (X = H, D, F and Cl) ions as a function of reaction time (see also text).

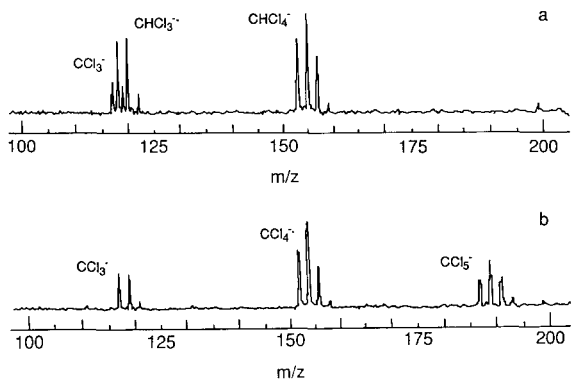


Fig. 3. Partial mass spectra of product ions present in the cell after the $CH_2S^{\cdot -}$ ion has reacted with $CHCl_3$ (a) and CCl_4 (b) for 200 ms (see also text).

The occurrence of the reaction in Eq. (10) is also supported by experiments in which the $CCl_4^{\cdot -}$ ions are ejected from the cell during the entire reaction period. Under these conditions, no CCl_5^- ions are generated and, in addition, less CH_3SHCl^- ions are formed than if the $CCl_4^{\cdot -}$ ions are not ejected from the cell. These results indicate that $CCl_4^{\cdot -}$ also transfers a Cl^- ion to CH_3SH.

In the $CH_2S^{\cdot -}/CFCl_3$ system, no $CFCl_4^-$ ions are observed even after prolonged reaction times. With the exception of Cl^-, the CH_3SHCl^- species is the dominant ion after a reaction time of 0.7 s (Table 1). This indicates that the $CFCl_3^{\cdot -}$ radical anion transfers a Cl^- ion only to CH_3SH (Eq. (11)) and not to the parent compound:

$$CFCl_3^{\cdot -} + CH_3SH \rightarrow CH_3SHCl^- + CFCl_2^{\cdot} \quad (11)$$

The finding that the molecular radical anions of the $CXCl_3$ species react readily in secondary processes is revealed also by the change in the normalized abundances of these ions as a function of reaction time as shown in Fig. 2. From the time dependence of these relative abundances, it can be concluded that the $CCl_4^{\cdot -}$ ion reacts faster with the neutral species in the cell than the other $CXCl_3^{\cdot -}$ ions.

In order to ascertain the indicated formation of $CHCl_3^{\cdot -}$ and $CCl_4^{\cdot -}$, the $CH_2S^{\cdot -}$ ions were allowed to react with $CHCl_3$ and CCl_4 respectively for 200 ms. Just prior to the excitation pulse, an r.f. pulse was applied in order to eject the most abundant product ions present in the cell. This resulted in an improved detection of the less abundant product ions. In Fig. 3 are shown the spectra of the product ions with an m/z ratio between 100 and 200 formed in the reaction of $CH_2S^{\cdot -}$ with $CHCl_3$ (Fig. 3a) and CCl_4 (Fig. 3b). In Fig. 3a the peaks corresponding to $CHCl_3^{\cdot -}$ (m/z = 118, 120 and 122), CCl_3^- (m/z = 117, 119 and 121) and $CHCl_4^-$ (m/z = 153, 155, 157 and 159) are clearly present. In Fig. 3b, peaks corresponding to $CCl_4^{\cdot -}$ (m/z = 152, 154, 156 and 158), CCl_3^- (m/z = 117, 119 and 121), and CCl_5^- (m/z = 187, 189, 191 and 193) are apparent. The expected relative intensities of the isotope peaks of the different ions are compared with the experimental values in Table 2. These values are almost identical and in agreement with the elemental composition assigned to the different ionic species.

In addition to the $CH_2S^{\cdot -}$ ion, a number of other potential electron donors were allowed to react with chloroform. The selected electron donors included $CH_3NO_2^{\cdot -}$, $C_6F_6^{\cdot -}$

Table 2
Experimental and theoretical relative abundances of the isotopic product ions corresponding to the peaks in Figs. 3a and 3b.[a]

		Fig. 3a		Fig. 3b	
	m/z	Experimental	Theoretical	Experimental	Theoretical
CCl_3^-	117	0.44	0.42	0.44	0.42
	119	0.42	0.42	0.43	0.42
	121	0.14	0.14	0.13	0.14
$CHCl_3^{\cdot -}$	118	0.42	0.42		
	120	0.44	0.44		
	122	0.14	0.14		
$CCl_4^{\cdot -}$	152			0.30	0.32
	154			0.44	0.42
	156			0.22	0.21
	158			0.04	0.05
$CHCl_4^-$	153	0.33	0.32		
	155	0.43	0.42		
	157	0.19	0.21		
	159	0.05	0.05		
CCl_5^-	187			0.24	0.25
	189			0.41	0.41
	191			0.27	0.28
	193			0.09	0.05

[a] The experimental abundances are calculated by dividing the intensity of the peak of interest by the sum of the intensities of all peaks contributing to the product ion. The ratio between the natural abundances of the ^{35}Cl and ^{37}Cl isotopes used for calculating the theoretical isotope abundances peaks of the product ions is taken to be 3 : 1; see also Section 2.

and the *ortho*-benzyne radical anion, $C_6H_4^{\cdot -}$. The neutral species corresponding to these radical anions all have an electron affinity ($EA(CH_3NO_2) = 46\,kJ\,mol^{-1}$, $EA(C_6F_6) = 52\,kJ\,mol^{-1}$ and $EA(C_6H_4) = 54\,kJ\,mol^{-1}$) [3,28] close to the value for CH_2S ($EA = 45\,kJ\,mol^{-1}$) [46]. Nevertheless, $CHCl_3^{\cdot -}$ ions are not formed in the reactions with the $CH_3NO_2^{\cdot -}$, $C_6F_6^{\cdot -}$ and $C_6H_4^{\cdot -}$ radical anions. The main product ion for all three species is Cl^-. In addition to this product ion, the $CH_3NO_2^{\cdot -}$ and $C_6H_4^{\cdot -}$ ions react to form $CH_3NO_2Cl^-$ (Eq. (12)) and $C_6H_4Cl^-$ ions respectively:

$$CH_3NO_2^{\cdot -} + CHCl_3 \rightarrow CH_3NO_2Cl^- + CHCl_2^{\cdot} \quad (12)$$

4. Discussion

4.1. Electron affinities of the $CXCl_3$ molecules and structure of the $CXCl_3^{\cdot -}$ ions

Under our experimental conditions only exothermic to thermoneutral reactions are observed normally. Thus the first condition for electron transfer is that the electron affinity of $CXCl_3$ is larger than the value for thioformaldehyde; this is $45\,kJ\,mol^{-1}$ [46]. For the observation of stable $CXCl_3^{\cdot -}$ ions in the reaction with $CH_2S^{\cdot -}$ another requirement is needed since the former species may dissociate to Cl^- and $CXCl_2^{\cdot}$ as shown in Eq. (13) [47]:

$$CXCl_3^{\cdot -} \rightarrow Cl^- + CXCl_2^{\cdot} \quad (13)$$

The amount of energy necessary for the dissociation of the $CXCl_3^{\cdot -}$ ions to Cl^- and a $CXCl_2^{\cdot}$ radical is given by Eq. (14), whereas the heat of formation for $CXCl_3^{\cdot -}$ can be approximated by the relationship in Eq. (15):

$$BDE(CXCl_3^{\cdot -}) = \Delta H_f^\circ(CXCl_2^{\cdot}) + \Delta H_f^\circ(Cl^-) - \Delta H_f^\circ(CXCl_3^{\cdot -}) \quad (14)$$

$$\Delta H_f^\circ(CXCl_3^{\cdot -}) \approx \Delta H_f^\circ(CXCl_3) - EA(CXCl_3) \quad (15)$$

The electron affinity of chloroform has been reported to be $\approx 170\,kJ\,mol^{-1}$, whereas the value for tetrachloromethane has been given as $\approx 190\,kJ\,mol^{-1}$ [22,28]. Based on an electron affinity of chloroform of $170\,kJ\,mol^{-1}$ in combination with known heats of formation of the other species involved in the reaction in Eq. (13), the bond dissociation energy of the $CHCl_3^{\cdot -}$ ion is estimated to be $\approx 155\,kJ\,mol^{-1}$, whereas a value of $140\,kJ\,mol^{-}$ is obtained for $CCl_4^{\cdot -}$ if the electron affinity of tetrachloromethane is assumed to be $\approx 190\,kJ\,mol^{-1}$. These dissociation energies should be contrasted with the energy necessary to dissociate the $CXCl_4^-$ ions formed readily in the reaction of the molecular radical anions with the parent compounds. Based on the available heats of formation data, the energy necessary to dissociate the $CXCl_4^-$ ions into a $CXCl_3$ molecule and a Cl^- ion is estimated to be $\approx 65\,kJ\,mol^{-1}$ for $CHCl_4^-$ and $\approx 60\,kJ\,mol^{-1}$ for CCl_5^- [28]. These values lead to the prediction that the Cl^- ion transfer reactions to the parent molecules should be endothermic with $\approx 95\,kJ\,mol^{-1}$ for chloroform and $\approx 80\,kJ\,mol^{-1}$ for tetrachloromethane in contrast to the occurrence of these processes under our experimental conditions.

The reaction enthalpy for chloride ion transfer from the molecular negative ion to the parent compound can be expressed as in Eq. (16):

$$\begin{aligned}\Delta H_r^\circ =& \mathrm{BDE}(CXCl_2^{\cdot} - Cl^-) \\ &- \mathrm{BDE}(CXCl_3 - Cl^-) \\ =& \Delta H_f^\circ(CXCl_2^{\cdot}) + \Delta H_f^\circ(CXCl_4^-) \\ &- \Delta H_f^\circ(CXCl_3^{\cdot -}) - \Delta H_f^\circ(CXCl_3) \\ \approx& \Delta H_f^\circ(CXCl_2^{\cdot}) + \Delta H_f^\circ(CXCl_4^-) \\ &- 2 \times \Delta H_f^\circ(CXCl_3) + \mathrm{EA}(CXCl_3)\end{aligned} \tag{16}$$

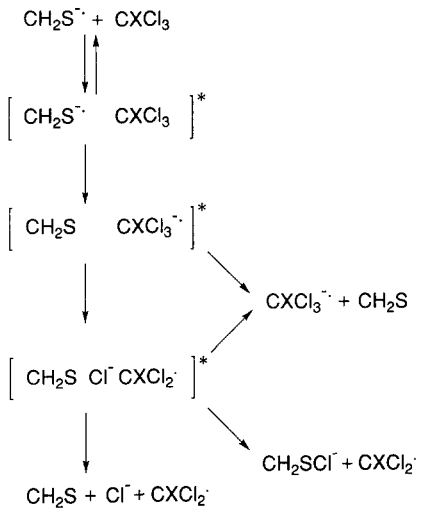
The heats of formation of the molecules and radicals can be considered to be accurate within $\pm 8\,kJ\,mol^{-1}$, implying that the electron affinities of the halomethanes are the least reliable parameters in the expression for ΔH_r° of chloride ion transfer. If Cl^- ion transfer to chloroform is assumed to be thermoneutral, we obtain an electron affinity of $75\,kJ\,mol^{-1}$ for chloroform. Similar considerations lead to an electron affinity of $110\,kJ\,mol^{-1}$ for tetrachloromethane. If the Cl^- ion transfer reactions from the molecular radical anions to the parent molecules are exothermic, this leads to even lower values for the electron affinities of chloroform and tetrachloromethane indicating that the given numbers represent upper limits for the true values. In conclusion, these considerations indicate that the adiabatic electron affinities of chloroform and tetrachloromethane are significantly lower than previously reported experimental [22,28] and also calculated values [29,30]. The previously reported experimental value [22] for the EA of tetrachloromethane was based upon a determination of the threshold energy for formation of $CCl_4^{\cdot -}$ ions in collisions between potassium atoms with a controlled kinetic energy and CCl_4 molecules. The yield of the $CCl_4^{\cdot -}$ ions was extremely low and in addition, the relative cross-section displayed a non-gradual increase at low values of the relative kinetic energy. The threshold for generation of the $CCl_4^{\cdot -}$ ions was obtained by linear extrapolation of the non-steep part of the curve, indicating that significant errors may have been introduced in the estimation of the EA of tetrachloromethane.

For the $CFCl_3$ compound, an electron affinity of $106\,kJ\,mol^{-1}$ has been reported [22]. Based on the occurrence of Cl^- ion transfer from the $CFCl_3^{\cdot -}$ radical anion to CH_3SH, it can be concluded that this process is exothermic or thermoneutral. The energy necessary for dissociating the CH_3SHCl^- ion into

CH_3SH and Cl^- has not been determined. However, we observe a slow Cl^- ion transfer from the CH_3SHCl^- ion to $CHCl_3$ (see Eq. (9)) indicating that the Cl^- ion affinity of methanethiol should be close to the value for chloroform (65 kJ mol^{-1}) [28]. This suggests that the dissociation of the $CFCl_3^{\cdot -}$ ion to Cl^- and $CFCl_2^{\cdot}$ is associated with an enthalpy change of $\leqslant$65 kJ mol^{-1}. Such a bond dissociation energy of the $CFCl_3^{\cdot -}$ ion leads to an electron affinity of $\leqslant$98 kJ mol^{-1} for the fluorotrichloromethane molecule. This upper limit is not in serious disagreement with the published value of 106 ± 30 kJ mol^{-1} although it may be suggested that this value represents an overestimate of the electron affinity of $CFCl_3$.

The present results indicate that the $CXCl_3^{\cdot -}$ ions formed in the experiments react as expected for a species, which can be described as a Cl^- ion loosely bonded to a $CXCl_2^{\cdot}$ radical. It is not possible, however, to conclude whether the Cl^- ion is bonded to the $CXCl_2^{\cdot}$ radical with an elongated C–Cl bond or the Cl^- ion is attached to one of the substituents. For $CCl_4^{\cdot -}$, the latter possibility implies the existence of species such a Cl^- ion attached to a Cl atom of a $CCl_3^{\cdot}$ radical or — in the extreme — a $Cl_2^{\cdot -}$ radical anion coordinated to a CCl_2 carbene. For the radical anion of chloroform it may be thought that the chloride ion is coordinated to the hydrogen atom by a weak hydrogen bond even though the proton affinity of Cl^- [28] is about 120 kJ mol^{-1} lower than that of the $CCl_2^{\cdot -}$ radical anion [48].

The suggested $[CXCl_2^{\cdot}Cl^-]$ structure for the molecular radical anions is in line with recent density functional calculations, which suggest that electron attachment to CCl_4 and $CFCl_3$ results in a significant elongation of one of the C–Cl bonds [29]. Moreover, the ESR spectra of $CCl_4^{\cdot -}$ generated by γ radiation in a tetramethylsilane matrix at 4 K have been concluded to be consistent with a $[CCl_3^{\cdot}Cl^-]$ structure [49]. Interestingly, a similar discussion applies to the radical cation of tetrachloromethane. This radical cation is formed only in a very low yield by direct electron ionization of tetrachloromethane but can be generated relatively easily by decarbonylation of the molecular radical cation of CCl_3COCl [50]. The $CCl_4^{\cdot +}$ radical cation formed in the latter process was suggested to have a structure of a $Cl^{\cdot}$ atom attached to one of the chlorine atoms of a CCl_3^+ ion on the basis of ab initio calculations. It can also be mentioned that the $SF_6^{\cdot -}$ radical anion has been proposed to exist as an ion/neutral complex, that is a $[SF_5^{\cdot}F^-]$ species may be generated upon electron attachment to SF_6 in the gas phase [51].



Scheme 1. Proposed reaction mechanism for the formation of the Cl^-, CH_2SCl^- and $CXCl_3^{\cdot -}$ ions in the reaction of the $CH_2S^{\cdot -}$ with the $CXCl_3$ (X = H, D, F and Cl) molecules.

4.2. Mechanistic aspects of the reactions with the $CXCl_3$ molecules

The suggestion that the $CXCl_3^{\cdot -}$ species may be characterized as a Cl^- ion weakly bonded to a $CXCl_2^{\cdot}$ radical renders it possible to propose a reaction scheme which accounts for the generation of the primary product ions in the reactions of the different radical anions with

halomethanes. This proposal is shown in Scheme 1 for the reactions of the $CH_2S^{\cdot -}$ ion.

The first step in the proposed mechanism is formation of an ion/molecule complex of the $CH_2S^{\cdot -}$ ion and a $CXCl_3$ molecule. Electron transfer may then occur with formation of a second complex composed of CH_2S and $CXCl_3^{\cdot -}$. This complex may dissociate to yield the observed radical anions of the $CXCl_3$ compounds or react to give a complex of CH_2S, $CXCl_2^{\cdot}$ and Cl^-, which then reacts to give either Cl^- or CH_2SCl^- as indicated in Scheme 1. In addition, this latter complex may expel a CH_2S molecule with formation of the $CXCl_3^{\cdot -}$ radical anions. Some support for the involvement of the latter complex can be found in the results of the reactions of the $CH_3NO_2^{\cdot -}$ (Eq. (12)) and $C_6H_4^{\cdot -}$ ions with $CHCl_3$. In the reaction of the former ion, $CH_3NO_2Cl^-$ arises and for the latter radical anion, minor amounts of $C_6H_4Cl^-$ ions are formed. The absence of the formation of $CHCl_3^{\cdot -}$ ions in the reactions with these ions may then indicate that the Cl^- affinity of the $CHCl_2^{\cdot}$ radical is lower than of the CH_3NO_2($\approx$ 70 kJ mol^{-1}) [28] and C_6H_4 molecules. The importance of the Cl^- ion affinity of the neutral species related to the reactant (radical) anion is also reflected in the results of the high pressure mass spectrometry (HPMS) study of Knighton and Grimsrud [16]. These authors examined the reactions between a number of halomethanes — including the present $CXCl_3$ compounds — and the radical anions of several nitrobenzenes as well as azulene. Stable radical anions of the halomethanes were not observed and the authors concluded that their results were consistent with a cluster-assisted dissociative electron transfer mechanism. In this mechanism, initial dissociative electron transfer to, for example, tetrachloromethane yields an ion/molecule complex composed of a Cl^- ion, the neutral species corresponding to the reactant radical anion, A, and a $CCl_3^{\cdot}$ radical. This complex was suggested to dissociate predominantly to a ACl^- cluster ion, which is in a fast equilibrium with free Cl^- and A molecules present in the HPMS ion source.

Based on our results in combination with observations of Knighton and Grimsrud [16], it may be concluded that stable $CXCl_3^{\cdot -}$ ions are formed only if the Cl^- affinity of the neutral species related to the reactant radical anion or anion is comparable with or lower than the binding energy of a Cl^- ion to a $CXCl_2^{\cdot}$ radical. Based on the occurrence of Cl^- ion transfer from CH_2SCl^- to chloroform but not to tetrachloromethane, the Cl^- ion affinity of CH_2S is expected to be in between the values for these compounds, that is, between 60 and 65 kJ mol^{-1} (vide supra) [47]. A comparable Cl^- ion affinity of CH_2S and of the $CXCl_2^{\cdot}$ radicals may then explain the formation of CH_2SCl^- as well as $CXCl_3^{\cdot -}$ as primary product ions (see Table 1).

5. Conclusions

The $CH_2S^{\cdot -}$ ion reacts uniquely with $CXCl_3$ (X = H, D, Cl and F) molecules to afford observable $CXCl_3^{\cdot -}$ ions, indicating that the adiabatic electron affinity of the $CXCl_3$ molecules is larger than the value for CH_2S (45 kJ mol^{-1}). The $CXCl_3^{\cdot -}$ radical anions can be described as a Cl^- ion relatively weakly bonded to a $CXCl_2^{\cdot}$ radical as indicated by the facile occurrence of Cl^- ion transfer in the reactions with the parent compounds and/or methanethiol. The occurrence of Cl^- transfer from the $CHCl_3^{\cdot -}$ and $CCl_4^{\cdot -}$ ions to the corresponding parent compounds leads to upper limits of the adiabatic electron affinities of chloroform ($\leqslant$ 75 kJ mol^{-1}) and tetrachloromethane ($\leqslant$ 110 kJ mol^{-1}). Similarly, the observation of Cl^- ion transfer from $CFCl_3^{\cdot -}$ to CH_3SH indicates an upper limit of 98 kJ mol^{-1} for the adiabatic electron affinity of fluorotrichloromethane.

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