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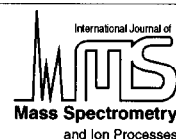
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The interplay between electron transfer and attack on halogen in gas-phase reactions of negative ions with fluoro-chloromethanes and fluoro-bromomethanes[☆]

P.O. Staneke, G. Groothuis, S. Ingemann, N.M.M. Nibbering*

Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

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Abstract

The gas-phase reactions of HO^- , CH_2S^- and $\text{CH}_2=\text{CH}-\text{CH}_2^-$ with the complete series of fluoro-chloromethanes and fluoro-bromomethanes have been studied with use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The HO^- ion is unreactive towards CF_3Cl , CF_2Cl_2 , CFCl_3 and CF_3Br but reacts with CCl_4 by attack on a chlorine atom and with CF_2Br_2 , CFBr_3 and CBr_4 by attack on a bromine atom. The CH_2S^- radical anion is also unreactive towards CF_3Cl , whereas an efficient electron transfer takes place with the other halomethanes. For most of the halomethanes, the electron transfer from CH_2S^- yields stable molecular radical anions together with X^- and CH_2SX^- ions ($\text{X} = \text{Cl}$ and Br). The allyl anion reacts with nearly all substrates by nucleophilic attack on a chlorine or bromine atom and/or electron transfer. Nucleophilic attack on a chlorine atom is the exclusive reaction of the allyl anion with CF_3Cl and the most important pathway in the reaction with CF_2Cl_2 and CFCl_3 . Electron transfer from the allyl anion leads to minor amounts of the radical anions of CF_2Cl_2 , CF_3Br and CF_2Br_2 , whereas only Cl^- or Br^- ions arise by electron transfer to most of the other halomethanes. The occurrence of electron transfer and/or halogen attack is discussed in terms of the trend in the electron affinities of the substrates and the thermodynamics of the different overall processes.

Keywords: Electron transfer; FT-ICR; Halogen attack; Halomethanes; Ion/molecule reactions

1. Introduction

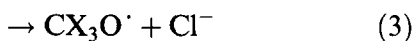
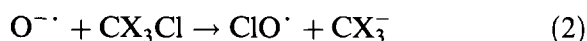
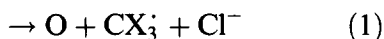
In recent years, a number of reports have been concerned with laboratory studies of gas-phase reactions of the O^- and O_2^- ions as well as other negative ions with freons and

also non-fluorine-containing halomethanes [1–9]. These studies have been performed in part with the purpose of probing the possible reactions occurring between the O^- or O_2^- ions with halomethanes which may be present in the upper atmosphere [10–12] and/or with the objective of gaining insight into the intrinsic molecular reactivity of halomethanes in gas-phase ion/molecule processes. The general outcome of the studies concerned with the reactions of these radical anions [1,2] is that

[☆] Dedicated to Professor David Smith FRS on the occasion of his 60th birthday with thanks for his contribution to gas-phase ion chemistry.

* Corresponding author.

they can react with a halomethane by a number of pathways, including overall dissociative electron transfer, nucleophilic attack on a halogen atom and attack on the carbon atom as illustrated in Eqs. (1)–(3), respectively, for the reaction of $O^{\cdot-}$ with CX_3Cl species ($X = F$ or Cl):



In order to examine the competition between these pathways, we selected three negative ions, OH^- , $CH_2S^{\cdot-}$ and $CH_2=CH-CH_2^-$, for a closer study and allowed these ions to react with the full series of fluoro-chloromethanes and fluoro-bromomethanes under the low pressure conditions characteristic of the Fourier transform ion cyclotron resonance (FT-ICR) method [13]. The HO^- anion was selected since it is a typical nucleophile and reacts efficiently, for example, with monohalogen-substituted methanes in the gas phase by an S_N2 substitution [14]. The corresponding HO^{\cdot} radical has a relatively high electron affinity ($EA(HO^{\cdot}) = 176 \text{ kJ mol}^{-1}$) [15] indicating that the HO^- ion is unlikely to react as an electron donor. The $CH_2S^{\cdot-}$ radical anion, however, is a weak nucleophile and is reported to react solely by electron transfer with a number of halomethanes [7,9] in agreement with the low electron affinity of thioformaldehyde ($EA = 45 \text{ kJ mol}^{-1}$) [16]. By contrast, the allyl anion is known to react as a nucleophile with some halomethanes [9,17] and is also expected to be able to react as an electron donor in view of the low electron affinity of the allyl radical ($EA = 39 \text{ kJ mol}^{-1}$) [15]. A study of the reactivity pattern of the three negative ions may shed light, therefore, on the molecular properties which determine the occurrence of electron transfer and/or nucleophilic

reactions with the selected fluoro-chloromethanes and fluoro-bromomethanes.

2. Experimental

The experiments were performed with an FT-ICR [13] instrument designed and constructed at the University of Amsterdam [18–20]. 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 (approx. -1 V) to the trapping plates of the cubic inch FT-ICR cell. The $O^{\cdot-}$ ions were formed by dissociative electron capture of electrons with an energy of 1.2 eV by nitrous oxide [21]. The $O^{\cdot-}$ ions reacted subsequently with methanethiol by a $1,2-H_2^+$ abstraction to form the $CH_2S^{\cdot-}$ radical anion [22]. The allyl anions were generated by first forming HO^- by the reaction of the $O^{\cdot-}$ ion with propene [23] and allowing these HO^- ions to react with propene by proton abstraction. In the experiments concerned with the reactivity of the HO^- ion towards the selected halomethanes, these ions were generated from water by dissociative capture of electrons with a kinetic energy of 5 eV. This process leads initially to H^- ions which readily abstract a proton from the water molecules present in the FT-ICR cell. The ions of interest were isolated by ejecting all other ions from the cell with the notch ejection technique applied in such a way that the translational energy of the isolated ions was minimized [24–26]. The reactions of the selected ions with the halomethanes were studied as a function of time by varying the delay between the selection of this ion and the start of the excitation pulse [13]. Abundant Cl^- ions were generated by dissociative electron attachment to the chlorine-containing halomethanes, whereas Br^- ions were formed readily by electron capture of the fluoro-bromomethanes [27–29].

The occurrence of these processes during the period in which the selected negative ions were allowed to react with the halomethanes was avoided by ejecting the low energy electrons from the FT-ICR cell as described previously [30].

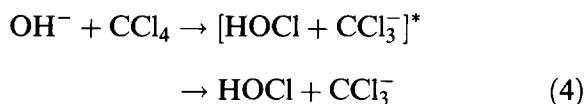
The total pressure in the experiments with the allyl anion and the $\text{CH}_2\text{S}^{\cdot-}$ radical anion was around 8×10^{-5} Pa with a background pressure lower than 3×10^{-7} Pa. The ratio between the partial pressures of N_2O , $\text{CH}_2=\text{CH}-\text{CH}_3$ or CH_3SH , and the halomethane was typically 1:1:1. In the experiments with the HO^- ion the total pressure was around 5×10^{-5} Pa, and the ratio between the partial pressures of H_2O and the halomethane was mostly 1:1. The pressures were measured with an uncalibrated ionization gauge manometer placed in the side arm of the main pumping line. The inlet lines and the main vacuum vessel were at room temperature, while the temperature of the trapping plate opposite the filament was between 330 and 340 K in a typical experiment. All the chemicals were commercially available and used without further purification.

3. Results

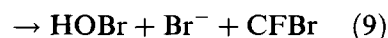
3.1. Reactions of HO^- with the halomethanes

The HO^- ion does not display any reactivity towards the CF_3Cl , CF_2Cl_2 , CFCl_3 and CF_3Br species as indicated in Table 1. With CCl_4 , the HO^- ion reacts very slowly to yield CCl_3^- , OCl^- and Cl^- ions [9]. The formation of the former two ions may involve initial attack on a chlorine atom with formation of a complex composed of HOCl and CCl_3^- . This complex may dissociate to the observed CCl_3^- ions (Eq. (4)) or react further by proton transfer from the HOCl molecule prior to dissociation with formation of the OCl^- ions

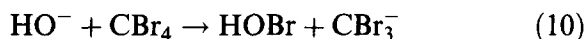
(Eq. (5)):



The reactions of the HO^- ion with the substrates containing more than a single bromine atom are relatively fast compared to the reaction with CCl_4 . With CF_2Br_2 , only HOBr_2^- ions are formed (Eq. (6)) [31], whereas the reaction with CFBr_3 leads to two additional product ions (Eqs. (7)–(9)):



The relative abundances of the product ions of these processes remain constant with time, indicating that no further reactions occur with the neutral species present in the FT-ICR cell. With CBr_4 , the HO^- anion reacts relatively fast to form only CBr_3^- ions by attack on a bromine atom as implied in Eq. (10):



3.2. Reactions of the $\text{CH}_2\text{S}^{\cdot-}$ radical anion with the halomethanes

The thioformaldehyde radical anion, $\text{CH}_2\text{S}^{\cdot-}$, does not react with CF_3Cl under the present experimental conditions, whereas Br^- ions arise in an efficient process if CFBr_3 or CBr_4 is the substrate. With the other halomethanes, the $\text{CH}_2\text{S}^{\cdot-}$ ion reacts to form a number of product ions, which react further with the neutral species present in the cell (Table 2).

The initial relative yields of the product ions for the reactions with the different substrates

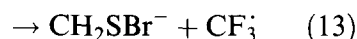
Table 1

Normalized abundances (%) of the product ions formed in the reactions of HO⁻ with the fluoro-chloromethanes and fluoro-bromomethanes (see also text)

Product ion	CF ₃ Cl	CF ₂ Cl ₂	CFCl ₃	CCl ₄
	Cl ⁻	No reaction	No reaction	No reaction
OCl ⁻				40
CCl ₃ ⁻				20
	CF ₃ Br	CF ₂ Br ₂	CFBr ₃	CBr ₄
Br ⁻	No reaction		10	
CBr ₃ ⁻				100
HOBr ₂ ⁻		100	30	
CFBr ₂ ⁻			60	

are given in Table 2 together with the yields of the various ions present after a reaction time of about 0.7 s. The abundances of the initial product ions are determined by following the reactions as a function of time and subsequently extrapolating to zero time. As shown in Fig. 1, the reaction of the CH₂S^{-•} ion with CF₃Br yields mainly the radical anion of this halomethane (Eq. (11)), Br⁻ ions (Eq. (12)) and minor amounts of a CH₂SBr⁻ ion

(Eq. (13)):



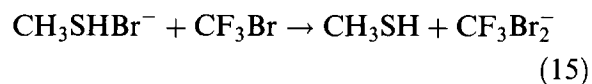
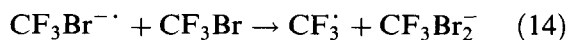
The molecular radical anion of CF₃Br reacts further by transfer of a bromide ion to the parent compound (Eq. (14)) and also to

Table 2

Normalized abundances (%) of the initial product ions formed in the reactions of the CH₂S^{-•} ion with the fluoro-chloromethanes and fluoro-bromomethanes (M) and the abundances of the product ions present in the FT-ICR cell after a reaction time of 0.7 s (see also text)

Product ions	CF ₃ Cl	CF ₂ Cl ₂	CFCl ₃	CCl ₄
	$t \rightarrow 0$ $t = 0.7$ s	$t \rightarrow 0$ $t = 0.7$ s	$t \rightarrow 0$ $t = 0.7$ s	$t \rightarrow 0$ $t = 0.7$ s
Cl ⁻	No reaction	30 30	60 60	85 85
CH ₂ SCI ⁻		40 0	15 4	10 2
CH ₃ SHCl ⁻		0 60	15 33	0 10
M ^{-•}		30 0	10 3	5 0
[M + Cl] ⁻		0 10		0 3
	CF ₃ Br	CF ₂ Br ₂	CFBr ₃	CBr ₄
	$t \rightarrow 0$ $t = 0.7$ s	$t \rightarrow 0$ $t = 0.7$ s	$t \rightarrow 0$ $t = 0.7$ s	$t \rightarrow 0$ $t = 0.7$ s
Br ⁻	30 30	60 60	100 100	100 100
CH ₂ SBr ⁻	15 3	5 0		
CH ₃ SHBr ⁻	0 17	0 3		
M ^{-•}	55 5	35 12		
[M + Br] ⁻	0 45	0 25		

CH₃SH. The CH₂SBr⁻ ion reacts also by Br⁻ ion transfer to the neutral species present in the FT-ICR cell. In addition, transfer of Br⁻ from the CH₃SHBr⁻ ion to the parent halo-methane, CF₃Br, becomes visible at prolonged reaction times (Eq. (15), see also Fig. 1):



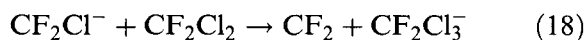
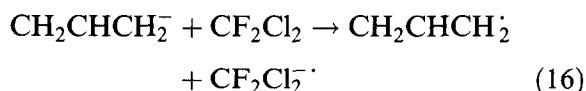
Similarly, the CF₂Br₂⁻ species react with transfer of a Br⁻ ion to the parent halo-methane, whereas the radical anions of CF₂Cl₂, CFCl₃ and CCl₄ readily transfer a Cl⁻ ion to their corresponding precursors (see Table 2).

3.3. Reactions of CH₂=CH-CH₂⁻ with the halomethanes

The relative yields of the initial product ions formed in the reactions of the allyl anion are listed in Table 3 together with the abundances of the ions present after a reaction time of 0.7 s. The allyl anion reacts with CF₃Cl to afford

only CF₃⁻, whereas CFCl₂⁻ and CCl₃⁻ ions are also formed in the reactions with CFCl₃ and CCl₄, respectively.

A distinct reactivity pattern is observed for the CF₂Cl₂ halo-methane. The allyl anion reacts with this substrate to form minor amounts of a radical anion (Eq. (16)), which reacts further by Cl⁻ ion transfer to the parent neutral species (Eq. (17)); in addition, the CF₂Cl⁻ ion transfers a Cl⁻ ion to CF₂Cl₂ as indicated in Eq. (18):



Stable radical anions are also generated in the reactions of the allyl anion with CF₃Br and CF₂Br₂ (Table 3). In the experiments with CF₂Br₂, the initially formed CF₂Br⁻ is observed to react with the parent compound by Br⁻ ion transfer. With CFBr₃ and CBr₄, the formation of Br⁻ ions is the

Table 3

Normalized abundances (%) of the initial product ions formed in the reactions of the CH₂=CH-CH₂⁻ ion with the fluoro-chloro-methanes and fluoro-bromomethanes (M) as well as the abundances of the ions present in the FT-ICR cell after a reaction time of 0.7 s (see also text)

Product ion	CF ₃ Cl		CF ₂ Cl ₂		CFCl ₃		CCl ₄	
	t → 0	t = 0.7 s	t → 0	t = 0.7 s	t → 0	t = 0.7 s	t → 0	t = 0.7 s
Cl ⁻			23	23	30	30	80	80
M ⁻			7	2				
[M + Cl] ⁻			0	20				
[M - Cl] ⁻	100	100	70	55	70	70	20	20
Product ion	CF ₃ Br		CF ₂ Br ₂		CFBr ₃		CBr ₄	
	t → 0	t = 0.7 s	t → 0	t = 0.7 s	t → 0	t = 0.7 s	t → 0	t = 0.7 s
Br ⁻	12	12	70	70	95	95	100	100
M ⁻	13	7	10	7				
[M + Br] ⁻	0	6	0	13				
[M - Br] ⁻	75	75	20	10	5	5		
[M + Br] ⁻	0	45	0	25				

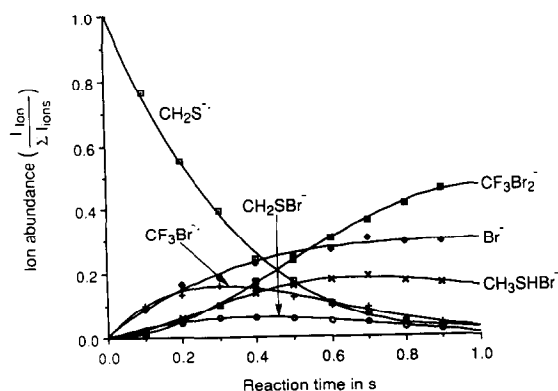


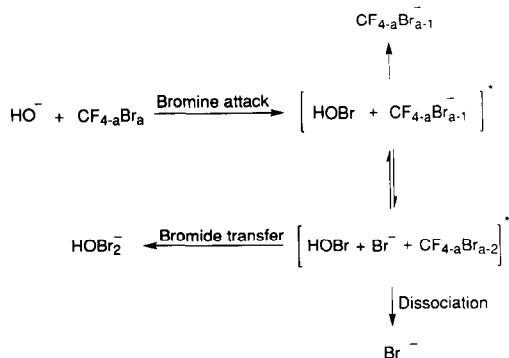
Fig. 1. Normalized abundances of the different product ions formed in the $\text{CH}_2\text{S}^-/\text{CH}_3\text{SH}/\text{CF}_3\text{Br}$ system as a function of reaction time (see also text).

predominant or exclusive reaction as indicated in Table 3.

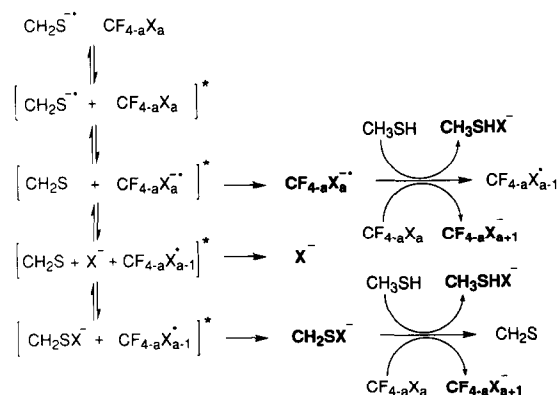
4. Discussion

4.1. Reaction pathways

The combined results for the HO^- ion can be interpreted in terms of an initial attack on a chlorine or bromine atom. The occurrence of nucleophilic attack on a halogen atom is indicated by the formation of, for example, ClO^- in the reaction with CCl_4 and the generation of HOBr_2^- ions with CF_2Br_2 as the substrate [31]. The proposed pathway leading to the latter ion

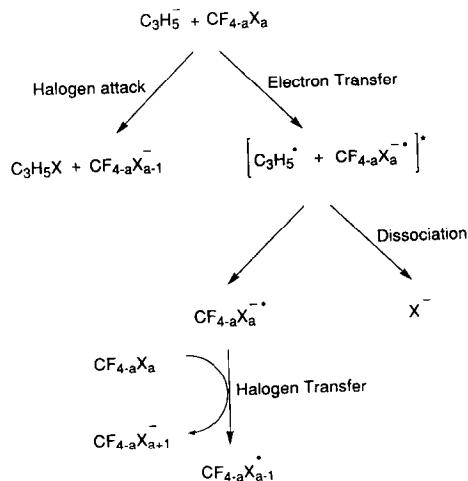


Scheme 1. Proposed mechanisms for the reactions of the HO^- ion with the fluoro-bromomethanes ($\text{CF}_{4-a}\text{Br}_a$, $a = 2-4$).



Scheme 2. Proposed mechanisms for the formation of the product ions of the reactions between the CH_2S^- ion and the halomethanes, $\text{CF}_{4-a}\text{X}_a$, $a = 1-4$; $\text{X} = \text{Cl}$ and Br . The product ions of the subsequent reactions of the initially generated ions are also given in the scheme.

is indicated in Scheme 1. In this scheme, initial attack on a bromine atom is shown to lead to a complex of HOBr and a $\text{CF}_{4-a}\text{Br}_{a-1}^-$ ($a = 2-4$) ion. This complex may dissociate into a free $\text{CF}_{4-a}\text{Br}_{a-1}^-$ ion or react further to form a complex composed of a Br^- ion, an HOBr molecule and a dihalogen-substituted carbene (see also Table 1). Subsequently, this latter



Scheme 3. Proposed mechanisms for the generation of the product ions of the reactions between the $\text{CH}_2=\text{CH}-\text{CH}_2^-$ ion and the halomethanes, $\text{CF}_{4-a}\text{X}_a$, $a = 1-4$; $\text{X} = \text{Cl}$ and Br . The subsequent reaction of the radical anions of the halomethanes with the parent compound is also shown in the scheme.

complex may dissociate into free Br^- ions or expel the carbene species with formation of an HOBr_2^- ion [31].

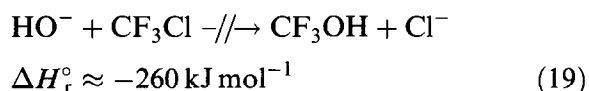
For the $\text{CH}_2\text{S}^{\cdot-}$ ion, the formation of radical anions of the halomethanes and CH_2SX^- ($\text{X} = \text{Cl}, \text{Br}$) ions suggests that electron transfer is the dominant or exclusive process occurring. In Scheme 2, this reaction is shown as involving initial formation of a complex of $\text{CH}_2\text{S}^{\cdot-}$ and a halomethane molecule. If electron transfer is energetically feasible, a complex of the radical anion of the halomethane and CH_2S can be formed. This complex can react further to form the observed molecular radical anion of the halomethane or a tertiary complex composed of CH_2S , a halide ion and a $\text{CF}_{4-a}\text{X}_{a-1}^{\cdot-}$ radical ($\text{X} = \text{Cl}$ and Br) can arise. Subsequently, dissociation into X^- or CH_2SX^- ions may occur (Scheme 2).

In contrast to the HO^- and $\text{CH}_2\text{S}^{\cdot-}$ ions, the allyl anion displays a more complex reactivity pattern with the halomethanes involving competing electron transfer and halogen atom attack as indicated in Scheme 3. The occurrence of electron transfer from the allyl anion is evidenced by the formation of radical anions of a number of the halomethanes, whereas the attack on a chlorine or bromine atom is indicated by the formation of, for example, the CF_3^- ion in the reactions with the CF_3Cl and CF_3Br molecules (Table 3).

The formation of Cl^- becomes increasingly important as the number of chlorine atoms increases in the substrate and a similar situation is encountered for the bromine-containing substrates, that is, Br^- is the dominant or exclusive product ion formed in the reactions of the allyl anion with CFBr_3 and CBr_4 (Table 3). This trend in the tendency to generate Cl^- or Br^- ions suggests that these ions are not formed as a result of a direct nucleophilic attack on the carbon atom by the $\text{S}_{\text{N}}2$ pathway since this process is known to become less favourable as the number of chlorine atoms attached to the carbon atom is increased [32].

The formation of the Cl^- or Br^- ions is ascribed, therefore, to the occurrence of an overall dissociative electron transfer from the allyl anion and/or a dissociation of the halogen-substituted methyl anion generated by the initial attack on a halogen atom (see Sections 4.2 and 4.3).

The absence of nucleophilic substitutions by the $\text{S}_{\text{N}}2$ pathway in the reactions of the HO^- ion or the allyl anion with CF_3Cl and CF_3Br is somewhat surprising since this process is strongly exothermic. For example, the $\text{S}_{\text{N}}2$ substitution is estimated to be about 300 kJ mol^{-1} exothermic for the HO^- ion as well as for the allyl anion if CF_3Br is the substrate and about 260 kJ mol^{-1} exothermic with CF_3Cl as the substrate (Eq. (19)):

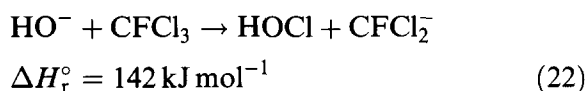
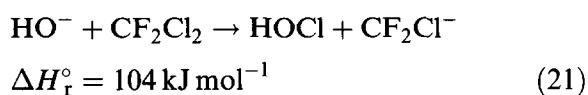
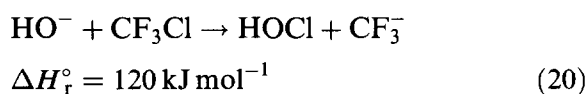


The failure of the HO^- and allyl anions to react by $\text{S}_{\text{N}}2$ substitution with the CF_3Cl and CF_3Br species is unlikely to be a result of steric hindrance by the three fluorine atoms since the van der Waals radius for a fluorine atom is only slightly larger than for a hydrogen atom. A possible explanation for the absence of $\text{S}_{\text{N}}2$ substitution may be sought however, in the charge distribution within the CF_3Cl and CF_3Br molecules. In these molecules, the electronegative fluorine atoms can withdraw electron density from the chlorine or bromine atom which then becomes an electron-deficient functionality. Partial negative charge will be localized on the fluorine atoms, thus shielding the carbon atom from nucleophilic attack and as a result, the chlorine or bromine atom becomes a poor leaving group. Accordingly, no reaction occurs between the HO^- ion and CF_3Cl or CF_3Br , whereas the allyl anion reacts with CF_3Cl only by chlorine atom attack and with CF_3Br by competing bromine atom attack and electron transfer (see below).

4.2. Attack on a halogen atom

Direct nucleophilic attack on a halogen atom in organic molecules has been described for reactions occurring in the condensed phase [33,34]. This process has been suggested to become more facile as the electronegativity of the halogen atom decreases and as the electronegativity of the carbon atom carrying the halogen atom is increased, for example, by a change in hybridization or by bonding to electronegative atoms or functional groups [33]. For the gas-phase reactions with the present halomethanes, this implies that (i) halogen attack is less facile for the fluoro-chloromethanes than for the fluoro-bromomethanes and (ii) halogen attack is expected to decrease in importance as the number of fluorine atoms is decreased.

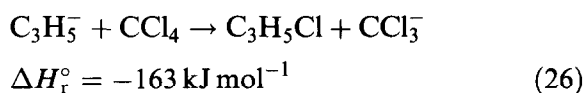
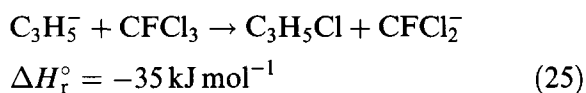
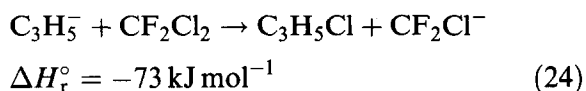
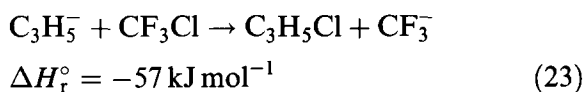
For the reactions of the HO^- ion with the CF_3Cl , CF_2Cl_2 and CFCl_3 species, halogen attack is estimated to be strongly endothermic (Eqs. (20)–(22)) and accordingly not observed [35]:



For CCl_4 , this reaction is endothermic by only about 14 kJ mol^{-1} if CCl_3^- ions are formed and by about 22 kJ mol^{-1} if ClO^- ions are generated (see Eqs. (4) and (5)). Both of these product ions are formed in an exceedingly slow reaction in agreement with the fact that slightly endothermic processes may occur under the low pressure conditions in an FT-ICR instrument.

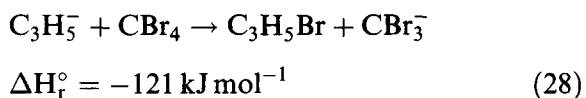
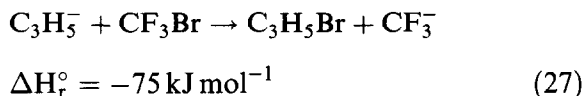
For the allyl anion, the attack on a chlorine

atom to form 1-chloro-2-propene becomes energetically favourable as shown in Eqs. (23)–(26) [35]:



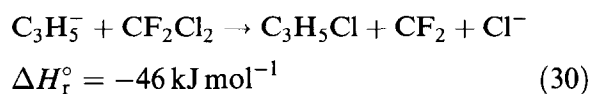
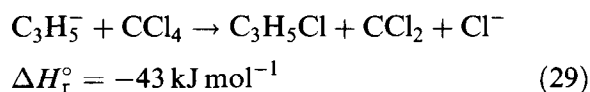
For the bromine-containing substrates, the thermodynamic data are limited and the available data are associated with relatively large uncertainties. Nevertheless, attack of HO^- on the bromine atom in CF_3Br with formation of HOBr and CF_3^- is estimated to be endothermic by about 58 kJ mol^{-1} in agreement with the observation that no reaction occurs in this system (Table 1). For CBr_4 as the substrate, attack on the bromine atom to afford HOBr and CBr_3^- is endothermic by about 12 kJ mol^{-1} [35]. The facile occurrence of the reaction between the HO^- and CBr_4 to give only CBr_3^- ions (Eq. (10)) suggests, however, that this value may represent an overestimation of the reaction enthalpy.

For the allyl anion, attack on a bromine atom with formation of 1-bromo-2-propene as the neutral product is estimated to be exothermic by 75 kJ mol^{-1} with CF_3Br as the substrate (Eq. (27)) and by 121 kJ mol^{-1} if CBr_4 is the substrate (Eq. (28)) [35]:



From a thermodynamic point of view, attack on the chlorine atom in CF_3Cl by the allyl anion (Eq. (23)) is thus seen to be about 18 kJ mol^{-1} less favourable than attack on the bromine atom in CF_3Br (Eq. (27)). This situation reverses as the fluorine atoms are replaced by chlorine atoms or the less electronegative bromine atoms. For example, chlorine attack on CCl_4 by the allyl anion is about 40 kJ mol^{-1} more exothermic than bromine atom attack on CBr_4 (see Eqs. (26) and (28)).

In the experiments, the allyl anion reacts with CCl_4 to give 20% CCl_3^- ions and 80% Cl^- (Table 3). The formation of CCl_3^- is inclined to be a result of chlorine atom attack, whereas the pathway leading to the formation of Cl^- is uncertain. A possible route to the latter ion can involve initial attack on the chlorine atom with formation of CCl_3^- ions, which then dissociate into Cl^- and dichlorocarbene, CCl_2 . Overall, this process is exothermic by -43 kJ mol^{-1} (Eq. (29)) and a similar value is obtained for CF_2Cl_2 as the substrate (Eq. (30)):



With the bromine-containing species, CFBr_3 and CBr_4 , the allyl anion reacts to afford only Br^- ions (Table 3). The estimation of the enthalpy changes for the formation of Br^- by initial bromine atom attack and subsequent dissociation of, for example, the CFBr_2^- or CBr_3^- ions into a Br^- and a halogen-substituted carbene is hampered, however, owing to the limited thermodynamic data available. Therefore, it is not possible to reach a firm conclusion as to whether the Br^- ions formed in the reaction of the allyl anion with CF_2Br_2 , CFBr_3 and CBr_4 (Table 3) arise as a consequence of initial attack on a

bromine atom or whether processes such as an overall dissociative electron transfer is an important pathway leading to the formation of these product ions (see below).

4.3. Electron transfer to the halomethanes

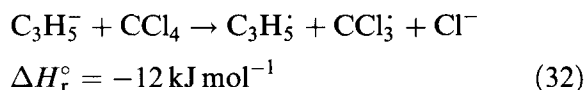
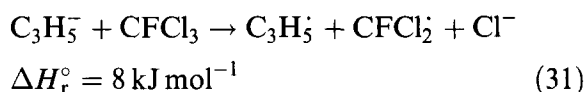
In a recent study, we reported that electron transfer from the CH_2S^- ion to the halomethanes, CXCl_3 ($\text{X} = \text{H, D, F}$ and Cl), yields stable radical anions of these species as well as Cl^- ions [7]. Limits for the electron affinities of these halomethanes were derived on the basis of the formation of stable radical anions in combination with the facile occurrence of Cl^- ion transfer from the CXCl_3^- ions either to the parent compound or methanethiol. For chloroform, the electron affinity was placed between the value for CH_2S (45 kJ mol^{-1}) [16] and 75 kJ mol^{-1} , whereas the upper limit to the value for CCl_4 was placed at 110 kJ mol^{-1} and for CFCl_3 , the value was suggested to be $\leq 98 \text{ kJ mol}^{-1}$. With respect to the present halomethanes, the electron affinity of CF_3Cl is likely to be only slightly positive [36], in keeping with the fact that a radical anion of this substrate is not formed in the reactions with CH_2S^- or the allyl anion (Tables 2 and 3). For CF_2Cl_2 , the electron affinity is given in the literature as approx 40 kJ mol^{-1} and for the CF_3Br species, a value of approx 95 kJ mol^{-1} is reported [15]. Both of these values are in agreement with the occurrence of electron transfer from the CH_2S^- ion and the allyl anion ($\text{EA}(\text{CH}_2=\text{CH}-\text{CH}_2) = 39 \text{ kJ mol}^{-1}$) [15] with formation of stable radical anions. For the CF_2Br_2 species, the formation of CF_2Br_2^- radical anions in the reactions with the CH_2S^- ion places the lower limit to the electron affinity of this halomethane at 45 kJ mol^{-1} .

The radical anions of the halomethanes, CF_2Cl_2 , CF_3Br and CF_2Br_2 , react relatively easily by transfer of a Cl^- or Br^- ion to the parent compound and methanethiol as

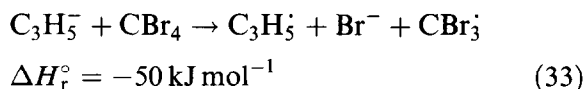
observed previously for the $CXCl_3^-$ ($X = H, D, F$ and Cl) ions. The latter species were proposed to have a structure resembling a Cl^- ion bonded relatively weakly to a $CXCl_2$ radical [7]. For the radical anion of CF_2Cl_2 a similar structure can be proposed, whereas the radical anions of CF_3Br and CF_2Br_2 may be described as a Br^- ion bonded to a CF_3 and a CF_2Br radical, respectively. Such structures of the radical anions of the halomethanes are in line with the low endothermicity for their dissociation into free Cl^- or Br^- ions. For example, the dissociation of $CF_2Cl_2^-$ radical anion into a CF_2Cl radical and a Cl^- ion is estimated to be only 16 kJ mol^{-1} endothermic on the basis of an electron affinity of about 40 kJ mol^{-1} for the parent halomethane. For the dissociation of the $CFCl_3^-$ ion into $CFCl_2$ and Cl^- , a value of $\leq 65 \text{ kJ mol}^{-1}$ is obtained [7], while the reported electron affinity of about 95 kJ mol^{-1} leads to an enthalpy change of about 75 kJ mol^{-1} for the dissociation of the CF_3Br^- radical anion into Br^- and a CF_3 radical.

A relatively facile dissociation of the halomethane radical anions into free halide ions may also play a role in the more pronounced tendency to form the latter species in the reactions of the CH_2S^- and allyl ions as the number of chlorine or bromine atoms is increased in the substrate (see Tables 2 and 3). This trend in the product ion distributions may be considered to be a result of the variation in the enthalpy changes of the overall processes with the increase in the number of chlorine or bromine atoms. For example, formation of Cl^- by electron transfer and dissociation of an intermediate molecular radical anion are endothermic by 62 kJ mol^{-1} for the reaction of the allyl anion with CF_3Cl and accordingly not observed (Table 3). For $CFCl_3$, dissociative electron transfer is endothermic by only about 8 kJ mol^{-1} (Eq. (31)) and for CCl_4 this process becomes slightly

exothermic (Eq. (32)) [35]:



For the bromine-containing halomethanes, overall dissociative electron transfer with formation of Br^- is associated with lower reaction enthalpies than the related reactions with the chlorine-substituted substrates. For example, electron transfer from the allyl anion yielding Br^- is endothermic by about 16 kJ mol^{-1} for CF_3Br and exothermic by about 50 kJ mol^{-1} for the CBr_4 species (Eq. (33)) [35]:



Based on the electron affinities of CH_2S and the allyl radical (see above), the enthalpy changes for the formation of Cl^- or Br^- ions by an overall dissociative electron transfer are not more than about 6 kJ mol^{-1} lower for the CH_2S^- ion than for the allyl anion. However, the CH_2S^- ion reacts with the CF_2Cl_2 to afford 30% of the molecular radical anion, whereas in the reaction with the allyl anion only 7% of the total product ions corresponds to $CF_2Cl_2^-$ (see Tables 2 and 3). Moreover, the allyl anion reacts with $CFCl_3$ to form only Cl^- and $CFCl_2$ ions in contrast to the formation of $CFCl_3^-$ radical anions in the reaction with the CH_2S^- ion.

The minor differences in the thermodynamics of the overall reactions may suggest a subtle balance between the formation of stable radical anions of the halomethanes and the possible ensuing dissociation of these species into a halide ion. However, the details of the reactions of the CH_2S^- and the allyl anion with the halomethanes are still unknown and, in addition, the uncertainties in the

electron affinities of the halomethanes and also the heats of formation of the halogen-substituted radicals are relatively large. Furthermore, the $\text{CH}_2\text{S}^{\cdot-}$ radical anion reacts only by electron transfer, whereas the allyl anion shows a strong tendency to attack a chlorine or bromine atom. The indicated possible formation of Cl^- or Br^- following attack on a chlorine or bromine atom (see Section 4.3) thus prevents a determination of the extent to which electron transfer from the allyl anion leads to these ions in the reactions with the present halomethanes.

5. Conclusions

Nucleophilic attack on a chlorine or bromine atom appears to be a relatively facile process in the gas-phase reactions of negative ions with fluoro-chloromethanes and fluoro-bromomethanes if the overall process is thermodynamically allowed. The attack on a chlorine atom by the HO^- ion is only observed for tetrachloromethane, whereas attack on a bromine atom occurs readily in the reactions with the fluoro-bromomethanes. In addition

mine atom, the allyl anion reacts by electron transfer to form either stable molecular anions of the halomethane and/or free Cl^- or Br^- ions. Electron transfer is the only reaction with $\text{CH}_2\text{S}^{\cdot-}$ and yields for most of the studied halomethanes a stable radical anion together with free Cl^- or Br^- ions. The observation of halomethane radical anions reveals that electron transfer to a halomethane in the gas phase is not an inherently dissociative process. For the present systems, electron transfer is best described as formation of radical anions of the halomethanes followed by dissociation of part of these species into Cl^- or Br^- provided the overall process is exothermic or close to thermoneutral.

Acknowledgement

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