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A selected ion flow tube study of the reactions of OH^- with a number of fully and partially halogenated methanes

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It is a great pleasure to dedicate this paper to Professor Märk on the occasion of his 60th birthday.

Abstract

In this paper we report the reactions of OH^- with the halogenated methanes CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, CF_4, $CHCl_3$, $CHCl_2F$, $CHClF_2$, CHF_3, CH_2Cl_2, CH_2ClF, CH_2F_2, CH_3Cl, and CH_3F in a 0.5 Torr helium buffer gas at 300 K using a selected ion flow tube. Reaction rate coefficients were measured and branching ratios determined for the large number of reactions studied. The results are discussed in terms of the thermochemistry of the reactions and barriers that exist to different reaction pathways. It is demonstrated that there is no barrier to proton and Cl^+ abstraction, while significant barriers exist for nucleophilic substitution.

Keywords: Halogenated methanes; Nucleophilic substitution; Ion-molecule reactions

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1. Introduction

Hydroxide ion is both a powerful nucleophile and base. Its reactions in solution with halomethanes are dominated by nucleophilic displacement of halide ion and/or by reversible proton transfer to form a carbanion which can decompose to a halide ion and a carbene [1]. Compared to these exhaustive studies in solution, reactions of OH^- in the gas phase have been somewhat limited. Of the fluorinated and chlorinated halomethanes, published kinetic data are only available for the reactions of OH^- with CH_3Cl [2–5], CH_3F [3,5], CH_2Cl_2 [6], $CHCl_3$ [6], and CCl_4 [6]. The three fully halogenated chlorofluoromethanes have been studied in an FT-ICR but were reported not to react [7]. To obtain a self-consistent set of data, these compounds together with CH_2F_2, CHF_3, CF_4, CH_2ClF, $CHCl_2F$, and $CHClF_2$ have been studied in our selected ion flow tube (SIFT). Reaction rate coefficients and product branching ratios were determined. For each of the molecules we have examined the thermodynamics of many of the possible reaction pathways to determine which products are thermochemically accessible. A comparison of the thermochemistry against the observed products reveals that many exothermic pathways do not occur, and that competition between pathways is not solely governed by exothermicity.

These studies are part of our continuing research into the fundamental physical organic chemistry of gas phase ion–molecule processes [8].

2. Experimental details

The SIFT apparatus, experimental technique, and analysis of data have been extensively reviewed [9]. Only a brief description of points pertinent to the present study will be mentioned here. The OH^- anions were created in a high-pressure ion source using a 50/50 mixture of N_2O and CH_4 as the source gas. Dissociative attachment of electrons to N_2O produced O^-, which reacted rapidly with CH_4 by hydrogen abstraction to form OH^-: the OH^- anions were mass selected using a quadrupole mass filter, injected into a flow tube and convected towards the reaction region by a fast helium flow (~150 Torr l s^{-1}) at a pressure of 0.5–0.6 Torr. Commercially purchased neutral reagents, used without further

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purification were injected into the flow tube, to give a known, controlled reactant neutral number density, which could be varied from 0 to $\sim 10^{12}\,\mathrm{cm}^{-3}$. The main source for the neutral reagents was Aldrich. The purity of the chemicals in all cases was better than 99%, with the exception of CHF_3 (98%) and $CHCl_2F$ (98%). The CH_2ClF sample was purchased from Apollo Scientific Limited with a stated purity of 97% and CH_3F was purchased from Fluorochem with an unknown purity.

The precursor and product anions were mass analysed using a second quadrupole mass spectrometer downstream of the inlet, and detected by a channeltron electron multiplier. Possible contamination of the injected ions by O^- was checked using this mass spectrometer, and the ratio of O^- to OH^- was found to be less than 0.006. The decrease in the OH^- signal was monitored at different neutral flows to obtain rate coefficients. To ensure that the branching ratios for the primary product anions were not affected by secondary reactions, the product percentages were obtained by extrapolation to zero neutral reactant number density, taking into account the mass discrimination of the detection system. Values of reaction rate coefficients and product percentages are considered to be accurate to ±20%, although they are generally reproducible to better than this.

When association occurs, the kinetic results are interpreted in terms of the following kinetic scheme:

$$A + OH^- \xrightarrow{k_r} \text{products} \tag{A}$$

$$A + OH^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (A \cdot OH^-)^* \tag{B}$$

$$(A \cdot OH^-)^* + He \xrightarrow{k_s} A \cdot OH^- + He \tag{C}$$

which allows for competition between bimolecular reaction (A) and association, (B) and (C). For this scheme, the effective bimolecular rate coefficient is pressure dependent:

$$k_2^{\mathrm{eff}} = k_r + \frac{k_s k_a [He]}{k_{-a} + k_s [He]}$$

For those reactions where an association product was identified, the pressure dependence of k_2^{eff} was examined by running the SIFT at helium pressures between 0.3 and 0.75 Torr. In all cases, it was found that the association reactions were in the “unsaturated” region, where k_2^{eff} increases linearly with helium pressure:

$$k_2^{\mathrm{eff}} = k_r + \frac{k_s\, k_a}{k_{-a}} [He]$$

By fitting the pressure dependence of k_2^{eff} to the above equation, both the bimolecular rate coefficient k_r, and a three body association rate coefficient $k_s(k_a/k_{-a})$ were extracted from the data.

3. Results and discussion

The results of our study are summarised in Table 1. For the purpose of discussion, the reactant molecules are divided into four convenient groups, and the results and a thermodynamic analysis will be presented in turn for each of these groups: group (A), the choloromethanes—CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl; group (B), the fluoromethanes—CF_4, CHF_3, CH_2F_2, and CH_3F; group (C), the chlorofluoromethanes—CCl_3F, CCl_2F_2, and $CClF_3$; and group (D), the chlorofluorohydromethanes—CH_2ClF, $CHCl_2F$, and $CHClF_2$. It should be noted that with the exception of the halogenated alcohols the heats of formation are taken from the latest entries in the JANAF database [10].

3.1. Group (A): CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl

3.1.1. CCl_4

Observed ionic products (other than the association product) are CCl_3^- (45%), Cl^- (35%), and OCl^- (20%). The branching ratios are in good agreement with the FT-ICR study [6] in which the association product was, unsurprisingly, not observed. Pathways to be considered are;

$$CCl_4 + OH^- \rightarrow CCl_3^- + HOCl, \quad +27\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$CCl_4 + OH^- \rightarrow Cl^- + HOCl + CCl_2, \quad +170\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$CCl_4 + OH^- \rightarrow Cl^- + (CCl_3OH), \quad -287\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

$$CCl_4 + OH^- \rightarrow HCl + COCl_2, \quad -306\,\mathrm{kJ\,mol^{-1}} \tag{4}$$

$$CCl_4 + OH^- \rightarrow OCl^- + CHCl_3, \quad +12\,\mathrm{kJ\,mol^{-1}} \tag{5}$$

$$CCl_4 + OH^- \rightarrow OCl^- + HCl + CCl_2, \quad +261\,\mathrm{kJ\,mol^{-1}} \tag{6}$$

CCl_3^- results by direct displacement following nucleophilic attack of OH^- upon a chlorine (1). Subsequent decomposition of CCl_3^- to give Cl^- and CCl_2 is endoergic (2) and thus is not the pathway for the formation of Cl^- (see also comments in the section on $CHCl_3$). Cl^- must therefore result from nucleophilic attack of OH^- on carbon to produce trichloromethanol (3) which may decompose to yield HCl and $COCl_2$ (4) but this is unlikely on the present time scale [11]. OCl^- must result from nucleophilic attack of OH^- upon a chlorine but with migration of the hydrogen

Table 1
Summary of data for OH^- reactions, including product percentages, suggested reaction schemes and reaction rate coefficients

Molecule	Products	Suggested neutral(s)	Product percentages	k_{exp}	k_c
CCl_4	Cl^-	$HCl + CCl_2O$	35 [40]	1.3 (−10)	2.0 (−9)
	OCl^-	$CHCl_3$	20 [20]	[2.2 (−11)]	
	CCl_3^-	OHCl	45 [40]		
	$CCl_4 \cdot OH^-$			$k_3 = 9.5$ (−27)	
$CHCl_3$	CCl_3^-	H_2O	100 [100]	1.5 (−9)	2.3 (−9)
				[2.6 (−9)]	
CH_2Cl_2	$CHCl_2^-$	H_2O	100 [100]	1.8 (−9)	2.6 (−9)
				[2.1 (−9)]	
CH_3Cl	Cl^-	$CH_2O + H_2$	100 [100][a]	1.7 (−9)	2.8 (−9)
		CH_3OH		[1.5–2.0 (−9)][a]	
CF_4	No reaction			<1.0 (−13)	1.2 (−9)
CHF_3	CF_3^-	H_2O	100	2.1 (−9)	2.5 (−9)
CH_2F_2	CHF_2^-	H_2O	86	2.5 (−12)	2.9 (−9)
	HF_2^-	CH_2O	3		
	F^-	$HF + CH_2O$	11		
	$CH_2F_2 \cdot OH^-$			$k_3 = 3.5$ (−28)	
CH_3F	F^-	CH_3OH	100 [100][b]	1.4 (−11)	2.9 (−9)
				[2.5 (−11)][b]	
CCl_3F	Cl^-	HCl + CClFO	55	5.0 (−11)	2.0 (−9)
	CCl_2F^-	OHCl	45		
	$CCl_3F \cdot OH^-$			$k_3 = 2.0$ (−27)	
CCl_2F_2	Cl^-	$HCl + CF_2O$	100	2.0 (−11)	1.9 (−9)
	$CCl_2F_2 \cdot OH^-$			$k_3 = 1.4$ (−27)	
$CClF_3$	No reaction			<1.0 (−13)	1.6 (−9)
CH_2ClF	Cl^-	$CH_2O + HF$	10	2.3 (−9)	2.8 (−9)[c]
		$CHFO + H_2$			
	$CHClF^-$	H_2O	90		
$CHCl_2F$	Cl^-	$CClF + H_2O$	4	2.1 (−9)	2.3 (−9)
		$CClFO + H_2$			
	CCl_2F^-	H_2O	96		
$CHClF_2$	Cl^-	$CF_2 + H_2O$	47	2.2 (−9)	2.4 (−9)
		$CF_2O + H_2$			
	$CClF_2^-$	H_2O	53		

The capture rate coefficients, calculated using parametrized fits to results from trajectory calculations k_c [22], are presented to the right of the experimental values, k_{exp}. The measured rate coefficients and product percentages are considered to be accurate to ±20%. Values of rate coefficients and branching ratios represented in the square brackets next to or below our own values have been taken from reference [6] except for those indicated.

[a] From references [2–4].

[b] From Tanaka et al. [3].

[c] The polarisability for this molecule is unknown. In order to calculate the collisional rate coefficient the following value was adopted $\alpha(CH_2ClF) = 5 \times 10^{-24}\,cm^3$.

to the carbon centre to produce $CHCl_3$ as the neutral product (5). This is energetically allowed, but only just within the lower limit of exothermicity set mainly by the error on $\Delta H_f(OCl^-)$ of $\pm 18\,kJ\,mol^{-1}$. Migration of the hydrogen to the chlorine to produce HCl and CCl_2 (6) is mechanistically attractive, as it would proceed by a five-membered transition state, it is endoergic. It is likely that the transition state for pathways (1), (3) and (5) is common and is in the form of an ion–dipole (induced) complex and that the products merely reflect the similar proton affinities of OCl^- and CCl_3^-. Collisional stabilisation of this common intermediate leads to the association complex. It is uncertain whether the rates of pathways (1) and (5) are significantly below the collisional rate as a consequence of a small activation barrier or merely because of their endoergodicity, although there is the usual degree of uncertainty surrounding the actual values. That pathway (3) is slow is almost certainly due entirely to steric constraints (shielding by the chlorines) as the carbon is likely to be considerably more electrophilic than the carbon in CH_3Cl where nucleophilic displacement of Cl^- occurs at close to the collisional rate (see Table 1).

Charge transfer and the formation of CCl_4^- is energetically allowed ($\Delta H = -17\,kJ\,mol^{-1}$) but is not observed.

The subsequent decomposition of CCl_4^- into CCl_3 and Cl^- is endothermic ($\Delta H = +125\,kJ\,mol^{-1}$).

3.1.2. $CHCl_3$

The observed ionic product is CCl_3^-. Pathways and alternative ionic products to be considered are;

$$CHCl_3 + OH^- \rightarrow CCl_3^- + H_2O, \quad -140\,kJ\,mol^{-1} \tag{7}$$

$$CHCl_3 + OH^- \rightarrow Cl^- + CCl_2 + H_2O, \quad +9\,kJ\,mol^{-1} \tag{8}$$

$$CHCl_3 + OH^- \rightarrow Cl^- + CHCl_2OH, \quad -264\,kJ\,mol^{-1} \tag{9}$$

$$CHCl_3 + OH^- \rightarrow OCl^- + CH_2Cl_2, \quad +26\,kJ\,mol^{-1} \tag{10}$$

Although proton abstraction to form CCl_3^- and water (7) is exoergic, its occurrence as the only reaction is at first sight surprising as the reaction of chloroform with base in solution yields dichlorocarbene via a CCl_3^- intermediate (this will be discussed in detail later). Formation of Cl^- and CCl_2 and water is endoergic by $9\,kJ\,mol^{-1}$ (8), unimolecular decomposition of CCl_3^- to Cl^- and CCl_2 being endoergic by $149\,kJ\,mol^{-1}$.

Nucleophilic attack on carbon would yield Cl^- with dichloromethanol as the neutral product (9). That it does not occur is almost certainly a consequence of the susceptibility of the proton to abstraction by base rather than to an energy barrier to nucleophilic attack on carbon. Proton abstraction reactions generally proceed via a barrierless potential energy surface.

Nucleophilic attack on chlorine to yield OCl^- [(10) analogous to (5)] is slightly endoergic but even if it did occur, it would be expected to proceed at a rate similar to that observed for CCl_4 and thus would not be observed, because it cannot compete with the fast proton transfer channel. Nucleophilic attack on chlorine to yield $CHCl_2^-$ is not energetically feasible ($+204\,kJ\,mol^{-1}$).

3.1.3. CH_2Cl_2

The observed ionic product is $CHCl_2^-$. Pathways and alternative ionic products to be considered are;

$$CH_2Cl_2 + OH^- \rightarrow CHCl_2^- + H_2O, \quad -63\,kJ\,mol^{-1} \tag{11}$$

$$CH_2Cl_2 + OH^- \rightarrow Cl^- + CH_2ClOH, \quad -240\,kJ\,mol^{-1} \tag{12}$$

$$CH_2Cl_2 + OH^- \rightarrow OCl^- + CH_3Cl, \quad +31\,kJ\,mol^{-1} \tag{13}$$

Nucleophilic attack on carbon to produce Cl^- and chloromethanol is a more exoergic pathway (12) than that observed but does not occur. This again can be attributed to the susceptibility of the proton to abstraction by base rather than to an energy barrier to nucleophilic attack on carbon. Reaction (13) would normally not be considered on mechanistic grounds but is included because of the corresponding reaction (5) in the case of CCl_4.

Reaction channel (11) was not observed in an earlier study, but only reaction (12) [6]. A reason for this is possibly because the earlier investigation did not take into account the reaction of $CHCl_2^-$ with CH_2Cl_2 which leads rapidly to Cl^- and $CHCl_2–CH_2Cl$ ($CHCl_2^- + CH_2Cl_2 \rightarrow Cl^- + CHCl_2–CH_2Cl$, $\Delta H = -221\,kJ\,mol^{-1}$).

3.1.4. CH_3Cl

The observed ionic product is Cl^-. Pathways and alternative ionic products to be considered are;

$$CH_3Cl + OH^- \rightarrow Cl^- + CH_3OH, \quad -208\,kJ\,mol^{-1} \tag{14}$$

$$CH_3Cl + OH^- \rightarrow CH_2Cl^- + H_2O, \quad +45\,kJ\,mol^{-1} \tag{15}$$

That the strongly exoergic nucleophilic attack on the carbon is now dominant is considered to reflect the lower acidity of the proton compared to those of CH_2Cl_2 and $CHCl_3$ rather than a markedly decreased barrier to nucleophilic attack.

3.2. Group (B): CF_4, CHF_3, CH_2F_2, and CH_3F

3.2.1. CF_4

It might be expected that CF_4 would be less likely to undergo attack on the halogen atom and more likely to undergo attack on the carbon atom compared to CCl_4 as a consequence of the greater electronegativity of fluorine versus chlorine. The greater bond strength of the C–F bond compared to the C–Cl bond (ca. $100\,kJ\,mol^{-1}$ [12]) ensures however that no reaction occurs:

$$CF_4 + OH^- \rightarrow F^- + CF_3OH, \quad +105\,kJ\,mol^{-1} \tag{16}$$

Decomposition of CF_3OH to COF_2 + HF is $11\,kJ\,mol^{-1}$ and even though it can be driven entropically, its high energy of activation would make it extremely slow [13,14].

3.2.2. CHF_3

The reaction of CHF_3 with OH^- follows the same pathway observed for $CHCl_3$, abstraction of the proton, so that only CF_3^- is observed as a product ion. Pathways and alternative ionic products to be considered are;

$$CHF_3 + OH^- \rightarrow CF_3^- + H_2O, \quad -54\,kJ\,mol^{-1} \qquad (17)$$

$$CHF_3 + OH^- \rightarrow F^- + CHF_2OH, \quad -96\,kJ\,mol^{-1} \qquad (18)$$

$$CHF_3 + OH^- \rightarrow OF^- + CH_2F_2, \quad +273\,kJ\,mol^{-1} \qquad (19)$$

$$CHF_3 + OH^- \rightarrow CHF_2^- + HOF, \quad +381\,kJ\,mol^{-1} \qquad (20)$$

Proton abstraction, reaction (17), is the only pathway observed although nucleophilic attack upon the carbon to produce difluoromethanol (18) is exoergic. Whilst the dominance of proton abstraction may superficially be considered to be a consequence of the acidity of the proton rather than a high intrinsic barrier to nucleophilic attack on carbon (see previous arguments on the chloromethanes) the slow rates observed when F^- is a product (vide infra) indicates that there is a considerable barrier to nucleophilic displacement. Pathways involving nucleophilic attack upon fluorine [(19) and (20)] are so endoergic that they will not be considered further.

3.2.3. CH_2F_2

For this reaction, a bimolecular process is in competition with three-body association. Observed bimolecular product ions are CHF_2^- (86%), F^- (11%), and HF_2^- (3%). Pathways to be considered are;

$$CH_2F_2 + OH^- \rightarrow CHF_2^- + H_2O, \quad -9\,kJ\,mol^{-1} \qquad (21)$$

$$CH_2F_2 + OH^- \rightarrow F^- + CH_2FOH, \quad -94\,kJ\,mol^{-1} \qquad (22)$$

$$CH_2F_2 + OH^- \rightarrow HF_2^- + CH_2O, \quad -234\,kJ\,mol^{-1} \qquad (23)$$

Although essentially thermoneutral, proton abstraction is the dominant reaction (21), albeit at a rate very much slower than collisional. Nucleophilic attack on carbon to produce F^- (22) and HF_2^- (23) is exoergic. HF_2^- could be a precursor to F^- but even invoking the ‘rubber band’ hypothesis [15] it is unlikely that sufficient energy would be deposited via reaction (21) to overcome the endoergodicity of its decomposition (190 kJ mol^{-1}). We thus favour reaction (22) for the production of F^-. It is difficult to envisage a direct mechanism for the formation of the thermodynamically favoured HF_2^-. We suggest that either a proportion of the transient CH_2FOH decomposes before the F^- has separated from the complex and the resulting HF is captured by the F^- or that a concerted decomposition of all of the CH_2FOH occurs but only a proportion of the resulting HF is in the correct orientation for capture by F^- to occur. The ergodicities given above are taken from references [10,13]. High level ab initio calculations have given considerable insight to the processes involved in this system [16], with the energetics and potential energy surfaces for reactions (21) and (22) having been determined. For reaction (21) it is found from these calculations that a reactant like intermediate lies approximately 80 kJ mol^{-1} below the reactants. The reaction path rises smoothly to the separate products from this reactant like intermediate with no potential energy barrier between reactants and products, and an overall ergodicity of +36 kJ mol^{-1}. As there is no change in the number of species on reaction, a negligible entropy change is to be expected, and therefore with this degree of endoergodicity no reaction would be observed. Detailed calculations show, however, that there is a favourable entropy change making the overall reaction endoergonic by 24 kJ mol^{-1}. The calculations employed conventional transition state theory to determine a rate only five times slower than that observed (without the entropy considerations a reaction endoergonic by +36 kJ mol^{-1} would proceed approximately 4×10^{-3} slower than that observed). The finding of a reactant like intermediate in such a deep well suggests that this is the structure of the collisionally stabilised complex. The computed exoergodicity for reaction (22) is in good agreement with that given above (the calculated ΔH_f for CH_2FOH is almost identical with that used here [13]). Again the calculation found a reactant-like intermediate followed by an S_N2-like transition state but, despite a thorough search, no product like intermediates were found. The relative energies of the stationary points for reaction (22) are inadequate to explain the observed slow rate. Entropy considerations increased the barrier to product formation sufficiently to make the transition state endoergonic relative to the reactants, although the calculated reaction rate was much lower than that observed.

3.2.4. CH_3F

The reaction of fluoromethane with OH^- is similar to that with chloromethane although the rate is much slower. OH^- reacts with CH_3F with a rate coefficient of $1.2 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$, compared to a collisional rate coefficient of $2.4\times10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$. The only product ion observed is F^-. Pathways and an alternative ionic product to be considered are;

$$CH_3F + OH^- \rightarrow F^- + CH_3OH, \quad -80\,kJ\,mol^{-1} \qquad (24)$$

$$CH_3F + OH^- \rightarrow CH_2F^- + H_2O, \quad +76\,kJ\,mol^{-1} \qquad (25)$$

Nucleophilic attack on carbon with the displacement of F^- (24) is the only reaction observed although despite its exoergodicity it is slow indicating a transition state barrier. Proton abstraction is endoergic. The F^- product ion is seen to react further with CH_3F in an efficient association reaction producing $CH_3F{\cdot}F^-$.

3.3. Group (C): CCl_3F, CCl_2F_2, and $CClF_3$

3.3.1. CCl_3F

Three products are observed in this reaction, including the association product, $CCl_3F{\cdot}OH^-$. The bimolecular product ions are Cl^- (55%) and CCl_2F^- (45%). From a pressure-dependent study, the bimolecular rate coefficient has been ascertained to be $(5.0 \pm 1.0) \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$, and the three body rate coefficient to form $CCl_3F{\cdot}OH^-$ to be $2.0 \times 10^{-27}\,cm^6\,molecule^{-2}\,s^{-1}$. Pathways and an alternative ionic product for the bimolecular reaction to be considered are;

$$CCl_3F + OH^- \rightarrow Cl^- + CCl_2FOH, \quad -?\,kJ\,mol^{-1} \tag{26}$$

$$CCl_3F + OH^- \rightarrow CCl_2F^- + HOCl, \quad +44\,kJ\,mol^{-1} \tag{27}$$

$$CCl_3F + OH^- \rightarrow OCl^- + CHCl_2F, \quad +25\,kJ\,mol^{-1} \tag{28}$$

Although ΔH_f for CCl_2FOH is not known it can be estimated as $\sim$520 kJ mol^{-1} as this is the combined heats of formations for HCl and COFCl and decomposition of both CF_3OH and CCl_3OH into the corresponding hydrogen halide and carbonyl halide are approximately thermoneutral (+9 and −19 kJ mol^{-1}, respectively) [13]. Thus, (26) will be approximately 341 kJ mol^{-1} exoergic. That reaction (27) is observed (albeit at a rate considerably below collisional) suggests that some doubt must be placed upon the most recently published value of ΔH_f for CCl_2F^-, although as was noted for the reactions of CH_2F_2 entropy can make a surprising contribution. It should be noted that the reported thermochemistry for the halocarbenes and halocarbanions has varied very widely over the years, cf. Paulino and Squires [17] and Lias et al. [18]. Indeed, combining ΔH_f for CFCl from reference [18] with ΔH for the dissociation of CCl_2F^- into CClF and Cl^- from reference [14] gives a ΔH of +17 kJ mol^{-1} for (27), a value which is quite consistent with the measured rate. Although reaction (28) is close to thermoneutral (given the likely errors) it is not observed. As was suggested earlier for reaction (5), reaction (27) requires a four-centre transition state involving migration of the hydrogen to the carbon centre to form the haloform. However, by replacing a chlorine with a fluorine, it will make the carbon centre much more positively charged (whilst not directly analogous see Table 5 in reference [13]) thus making the necessary transition state unfavourable even though the overall reaction is still approximately thermoneutral.

3.3.2. CCl_2F_2

The only observed ionic product (with the exception of a trace of the association complex) is Cl^-. A pathway and alternative ionic products to be considered are;

$$CCl_2F_2 + OH^- \rightarrow Cl^- + CClF_2OH, \quad -?\,kJ\,mol^{-1} \tag{29}$$

$$CCl_2F_2 + OH^- \rightarrow CClF_2{}^- + HOCl, \quad +124\,kJ\,mol^{-1} \tag{30}$$

$$CCl_2F_2 + OH^- \rightarrow OCl^- + CHClF_2, \quad +29\,kJ\,mol^{-1} \tag{31}$$

As for CCl_2FOH, although $\Delta H_f(CClF_2OH)$ is unknown, it can be estimated to be $\sim$715 kJ mol^{-1}, thus making reaction (29) 328 kJ mol^{-1} exoergic. Nucleophilic attack on chlorine is not observed as both reactions (30) and (31) are endoergic although in the case of reaction (31), not by much.

3.3.3. $CClF_3$

No ionic products are observed. Pathways of potential ionic products to be considered are;

$$CClF_3 + OH^- \rightarrow Cl^- + CF_3OH, \quad -303\,kJ\,mol^{-1} \tag{32}$$

$$CClF_3 + OH^- \rightarrow CF_3{}^- + HOCl, \quad +127\,kJ\,mol^{-1} \tag{33}$$

$$CClF_3 + OH^- \rightarrow OCl^- + CHF_3, \quad +32\,kJ\,mol^{-1} \tag{34}$$

Although thermodynamically favourable, nucleophilic attack on carbon does not occur. This is perhaps not too surprising given the low rates of reaction for the other two members of this series of compounds and the tendency for the rates to decrease as the number of fluorines increases.

3.4. Group (D): CH_2ClF, $CHCl_2F$, and $CHClF_2$

3.4.1. CH_2ClF

Observed product ions are Cl^- (10%) and $CHClF^-$ (90%). Pathways and a potential ionic product to be considered are;

$$CH_2ClF + OH^- \rightarrow Cl^- + CH_2FOH, \quad -261\,kJ\,mol^{-1} \tag{35}$$

$$CH_2ClF + OH^- \rightarrow CHClF^- + H_2O, \quad -18\,kJ\,mol^{-1} \tag{36}$$

$$CH_2ClF + OH^- \rightarrow OCl^- + CH_3F, \quad +47\,kJ\,mol^{-1} \tag{37}$$

It should be noted that $CHClF^-$ reacts further with CH_2ClF to form Cl^- ($CHClF^- + CH_2ClF \rightarrow Cl^- + CHClFCH_2F$) with a determined rate coefficient of $1.1 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$.

3.4.2. $CHCl_2F$

Observed product ions are Cl^- (4%) and CCl_2F^- (96%). Pathways and a potential ionic product to be considered are;

$$CHCl_2F + OH^- \rightarrow Cl^- + CHClFOH, \quad -?\,kJ\,mol^{-1} \tag{38}$$

$$CHCl_2F + OH^- \rightarrow CCl_2F^- + H_2O, \quad -130\,kJ\,mol^{-1} \tag{39}$$

$$CHCl_2F + OH^- \rightarrow OCl^- + CH_2ClF, \quad +40\,kJ\,mol^{-1} \tag{40}$$

ΔH_f for CHClFOH is unknown but, by using the arguments presented above, can be estimated to be $\sim$465 kJ mol^{-1}, thus making (38) exoergic by 274 kJ mol^{-1}.

3.4.3. $CHClF_2$

Observed product ions are Cl^- (47%) and $CClF_2^-$ (53%). Pathways and a potential ionic product to be considered are;

$$CHClF_2 + OH^- \rightarrow Cl^- + CHF_2OH, \quad -289\,kJ\,mol^{-1} \tag{41}$$

$$CHClF_2 + OH^- \rightarrow CClF_2^- + H_2O, \quad -54\,kJ\,mol^{-1} \tag{42}$$

$$CHClF_2 + OH^- \rightarrow CCl^- + CH_2F_2, \quad -50\,kJ\,mol^{-1} \tag{43}$$

Both products are observed to react further with $CHClF_2$; $CClF_2^-$ bimolecularly reacts to produce Cl^-; and Cl^- associates to form $CHClF_2{\cdot}Cl^-$.

4. Comments

4.1. Proton abstraction

With the exception of CH_3F (and CH_3Cl) for which it is strongly endoergic, proton abstraction is the dominant, and sometimes only, reaction pathway occurring with the partially halogenated methanes, and usually occurring at, or near, the collisional rate. The occurrence of proton abstraction, albeit in small amount, with CH_3Cl suggests that ΔH_f $CHCl_2^-$ should be somewhat less endothermic (probably by at least 25 kJ mol^{-1}) than the most recent JANAF value +66 kJ mol^{-1} [19] which would make it in close agreement with an earlier value of 45 ± 13 kJ mol^{-1} [20].

The slow proton abstraction from CH_2F_2 suggests that reaction (21) should be endoergic by $\sim$17 kJ mol^{-1} (assuming no activation barrier to proton abstraction) unless, as suggested by published ab initio calculations [16], entropic considerations are taken into account.

4.2. Nucleophilic attack on carbon

This occurs with all but five of the halomethanes viz. $CHCl_3$, CH_2Cl_2, CF_4, CHF_3 and $CClF_3$. The occurrence or non-occurrence of nucleophilic attack is not determined by the overall ergodicity of the reactions, as all are exoergic. Nor does the degree of exoergodicity correlate with the measured rates. Let us consider each of the four groupings in turn.

In the case of the chloromethanes increasing the degree of chlorination increases the exoergodicity of nucleophilic substitution on carbon. So why does S_N2 attack on carbon only occur in the least exoergodic case? Increasing the degree of chlorination increases the exoergodicity of proton abstraction, and it can be concluded that nucleophilic attack on carbon is only seen with CH_3Cl and not with CH_2Cl_2 and $CHCl_3$, because of the greater ease of proton abstraction in the latter two compounds. This is substantiated by the observation of only a slow S_N2 attack on carbon in CCl_4, where proton abstraction cannot of course occur and the competing reactions are slow (see Table 1). Trajectory considerations may also be important; the OH^- ion has to approach the hydrogens in the chloromethanes on route to the carbon. In the case of CH_3Cl it does this without difficulty as the hydrogens are insufficiently acidic. In the cases of CH_2Cl_2 and $CHCl_3$, the hydrogens are sufficiently more acidic than those in CH_3Cl (by 88 and 160 kJ mol^{-1}, respectively) to make them attractive to the OH^- and thus abstraction occurs even though the carbon is also attractive. In addition to this, if the OH^- ion approached a Cl then repulsion/steric hindrance would occur slowing the S_N2 reaction—even though it was exoergodic. This explains the slow S_N2 reaction with CCl_4.

In the case of the fluoromethanes a similar, although more extreme pattern is observed with S_N2 attack on carbon occurring, when it does, at substantially below the collisional rate. This is more likely to reflect a high activation barrier rather than the relatively low exoergodicity of S_N2 displacement of fluorine compared with chlorine.

With the chlorofluoromethanes there are, with the exception of (27), no competing channels to S_N2 attack on carbon. Even though S_N2 displacements of chlorine are the most exoergodic reactions observed in this study, they still occur at considerably below the collisional rate. Steric problems are likely to be severe in all three compounds and such difficulties, coupled with electron repulsion from the fluorine atoms in the developing transition state is most likely to account for the low rate coefficients.

Chlorofluorohydromethanes are unusual in that proton abstraction and S_N2 attack on carbon appear equally facile, occurring near the collisional rate for all three compounds. That the S_N2 pathway for chlorofluorohydromethanes appears more facile than for the chlorofluoromethanes supports the suggestion that steric problems are severe in the later group of compounds, the presence of the hydrogen(s) providing a relatively unhindered route. This raises the question, why in that case does not proton abstraction dominate to the exclusion of the S_N2 route, as occurs with $CHCl_3$ and CH_2Cl_2? A potential explanation is that Cl^- is not produced as a result of S_N2 attack on carbon but that it results from unimolecular decomposition of the anion resulting from proton abstraction before collisional thermalisation. Assuming that ΔH_f for CClF essentially thermoneutral, then the energetics of the necessary reactions are:

$$CHClF^- \rightarrow CHF + Cl^-, \quad +74\,kJ\,mol^{-1} \tag{44}$$

$$CCl_2F^- \rightarrow CClF + Cl^-, \quad +81\,kJ\,mol^{-1} \tag{45}$$

$$CClF_2{}^- \rightarrow CF_2 + Cl^-, \quad +22\,kJ\,mol^{-1} \tag{46}$$

Whilst the latter two reactions are energetically feasible given the energetics of the formation of the trihalocarbanions [reactions (39) and (42), respectively] reaction (44) is not as reaction (36) is only exoergic by 18 kJ mol^{-1}. We thus conclude that the formation of Cl^- results from nucleophilic attack on carbon to produce the haloalcohols, rather than by dissociation of the anion resulting from proton abstraction.

4.3. Nucleophilic attack on chlorine

Nucleophilic attack on chlorine to produce HOCl is, except in the cases of CCl_4 and CCl_3F, strongly endoergic and its non-occurrence is not therefore surprising. That it occurs with CCl_4 and CCl_3F is a consequence of the relatively low endoergodicity in these cases and the low reaction rates of competing channels. Nucleophilic attack on chlorine followed by hydrogen migration to yield OCl^- and a halogenated methane is much less endoergic and its non-observation, even when competing channels are slow, can be attributed to a high activation energy associated with an unfavourable 4-centre transition state (see the comments in Section 3.1.1).

4.4. Carbene formation and the relationship with solution chemistry

Whilst carbene formation from the trihalocarbanion occurs in solution [1] it is not observed in the gas phase—at least with thermalised ions. This is not surprising given the available thermochemistry. That it occurs in solution can be attributed to the greater degree of solvation of the halide ion than the trihalocarbanion. It is interesting to note that carbanion formation from CHF_3 cannot be detected in basic solution whereas it occurs with both $CHCl_3$ and $CHCl_2F$ and with $CHClF_2$ undergoing a different mechanism of concerted dehydrohalogenation with the observation that in the gas phase it occurs with all four compounds at virtually the collisional rate. It will be of interest to extend this study to include both the full range of trihalomethanes studied by Hine et al. [1] and the hydrated hydroxide ion [21]. High level ab initio calculations of the 4-centre transition state involved in the concerted nucleophilic attack of OH^- on chlorine with hydrogen transfer to carbon will also repay study.

5. Final comment

We stated at the beginning of this paper that the studies reported here are motivated from our continuing research into the fundamental physical organic chemistry of gas phase ion–molecule processes. However, OH^- has been highlighted as an obvious precursor ion for the analysis of trace gases in the atmosphere [23]. Thus, these results may be relevant to chemical ionisation mass spectrometry using OH^- as the reagent ion.

Acknowledgements

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