

Selected ion flow tube studies of the gas-phase reactions of O^- , O_2^- and OH^- with a variety of brominated compounds

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Abstract

The reactions of fourteen bromine-containing molecules, CH_3Br , CH_2Br_2 , CHBrCl_2 , CHBr_2Cl , $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$, CF_3Br , CF_2Br_2 , CFBr_3 , CBrClF_2 , CFBr_2Cl , CCl_3Br and $\text{CF}_2\text{BrCF}_2\text{Br}$, with the anions O^- , O_2^- and OH^- in a 0.5 Torr helium buffer gas have been studied at 300 K using a selected ion flow tube. Reaction rate coefficients and branching ratios are presented. Several distinct reaction processes are observed among the large number of reactions studied, including nucleophilic attack, proton transfer, abstraction, and dissociative and non-dissociative electron transfer (within or out of a reaction complex). Of the forty-two bimolecular reactions, the rates of only two are significantly below the collisional rate and, for these two, competitive three-body processes are observed. Many of the reactions reported here have not previously been studied. This study, therefore, presents new data which provide additional insight into the reactions of anions with halogenated species.

Keywords: SIFT; Gas phase ion chemistry; Kinetics

1. Introduction

The study of the reactions of negative ions with molecules is of importance because of the role such reactions play in the chemical evolution of many gaseous environments, including planetary atmospheres, surface etchant plasmas, flames, and laser discharges [1–3]. Furthermore, chemical ionisation mass spectrometry uses negative ions as sensitive probes for the detection of halogenated compounds and other pollutants in the atmosphere [4,5].

The reactions of negative ions with halogenated compounds have been the subject of many studies over the years (see the compilation

by Ikezoe et al. [6] for rate data up to 1986). Fehsenfeld et al. [7] investigated the possible contribution of negative ion reactions to limiting the atmospheric concentrations of CFCl_3 and CF_2Cl_2 . Later, Dotan et al. [8] studied the reactions of anions with molecules containing chlorine. Other researchers, notably Streit [9] and Morris [3], continued this line of research, not only for the atmospheric interest but also because of their interest in understanding the fundamental ionic processes occurring in pollutant detectors which operate by using ions as probes of the environment. More recently Morris et al. [10,11] reported studies of atmospheric interest of negative ion reactions with a number of perfluorocarbons and hydrofluorocarbons. In an earlier paper we reported the results from a

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comprehensive study of the reactions of the atomic oxygen radical anion O^- and the dioxygen radical anion O_2^- with a variety of fluorinated and/or chlorinated methanes [12]. Indeed, to date much of the work appearing in the literature has concentrated on reactions involving O^- and O_2^- . The reason for this lies simply in the importance of these anions in mesospheric chemistry and their use as practical reagents in atmospheric pressure negative ion mass spectrometry [13], ion-mobility spectrometry [14], microcircuit fabrication [3], and enhancing response to certain halogenated compounds in electron capture detectors [15,16]. A recent review dealing with the reactions of O^- and the synthesis of organic reactive intermediates has been compiled by Lee and Grabowski [17].

Of the O^- and O_2^- reactions with halogenated compounds so far studied, little attention has been directed to those of brominated compounds. Futrell and Tiernan reported measurements of the reaction of O^- with CH_3Br and C_2H_5Br using a tandem mass spectrometer [18]. Except for this, and two recent investigations [3,10], other studies investigating the reactions of O^- and O_2^- with bromine compounds have been carried out using a flowing afterglow (FA) apparatus. Tanaka et al. [19] and McDonald and Chowdhury [20] measured the rate coefficients and ionic products for the O^-/CH_3Br and O_2^-/CH_3Br reactions, respectively. Reactions of O^- and O_2^- with HBr , IBr , CF_3Br , $CHBr_3$, $CBrClF_2$ and C_2F_5Br were investigated, also using a FA apparatus [9], but ionic products were not unambiguously identified because of the presence of more than one anion species in the flow tube. More recently Morris [3] and Morris et al. [10] used a selected ion flow tube (SIFT) and reported the reactions of O^- and O_2^- with CF_3Br and $CHBrF_2$, respectively.

Another anion of atmospheric interest, which has received little attention in terms of reaction with brominated compounds, is the hydroxyl anion OH^- . To our knowledge, there are only a few reports in the literature. Three of these relate to an investigation of nucleophilic substitution

(S_N2) reactions with CH_3Br , two using a FA [19,21] and the other using a pulsed ion cyclotron resonance (ICR) spectrometer [22]. Another study deals with the reaction of OH^- (and other nucleophiles) with six bromine-containing molecules, including two investigated in this study— CH_3Br and C_2H_5Br [23]. More recently the reactions of OH^- with CF_3Br , CF_2Br_2 and $CFBr_3$ [24] have been reported.

A systematic investigation of the reactions of brominated molecules with O^- , O_2^- and OH^- is useful for the following reasons: (i) to make a comparison with the negative ion chemistry of fluorinated and/or chlorinated compounds, (ii) to determine the role they play (if any) in the fate of bromine-containing molecules released into the atmosphere, (iii) to characterise the response in negative chemical ionisation mass spectrometers used to detect these pollutants in the environment, (iv) to improve our general understanding and knowledge of atmospheric negative ion chemistry, and finally (v) because the ion chemistry of the brominated compounds is essentially unexplored.

In our continuing studies of the reactions of negative ions with halogenated compounds, we report here a detailed SIFT study of the reactions of O^- , O_2^- and OH^- with fourteen brominated compounds, CH_3Br , CH_2Br_2 , $CHBrCl_2$, $CHBr_2Cl$, C_2H_5Br , CH_2BrCH_2Br , CH_2BrCH_2Cl , CF_3Br , CF_2Br_2 , $CFBr_3$, $CBrClF_2$, $CFBr_2Cl$, CCl_3Br and CF_2BrCF_2Br , many being reported here for the first time (particularly the OH^- reactions), significantly contributing to the body of data already reported. Where this present study overlaps other investigations there is generally good agreement, although for some of the reactions discrepancies with the reaction rate coefficients and branching ratios have been found.

2. Experimental

The SIFT, its operation and its application to the investigation of gas-phase ion–molecule

reactions are reported in a detailed review by Adams and Smith [25]. Therefore, only those aspects pertinent to the present study will be mentioned here. O^- , O_2^- or OH^- anions were generated in a high pressure electron impact chamber by using N_2O , N_2/O_2 or CH_4/N_2O as respective source gases. The anions were then mass selected and injected into a fast flowing helium carrier gas (≈ 150 Torr 1 s^{-1}) maintained at a pressure of ≈ 0.5 Torr in which they were thermalised (to 300 K) and transported along the flow tube. Neutral reactant gases, obtained

commercially and used without further purification, were added in controlled amounts to the carrier gas/ion stream. 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. The rate coefficients and ion product distributions were then determined in the usual way (Adams and Smith [25,26]). However, it is worth mentioning that the determination of product distribution may be affected by the varying diffusional losses of the various anion products in

Table 1

Compilation of the measured rate coefficients k_{exp} and product anion distributions for the reactions of O^- with the series of halogenated compounds in Group I investigated using the SIFT apparatus at 300 K. The calculated collisional rate coefficients k_{calc} are also presented. The rate coefficients (experimental and calculated) are in units of $10^{-9}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The experimental results are considered accurate to $\pm 20\%$

Molecule	Products	Suggested neutrals	Product percentages	Reaction enthalpy $\Delta H/\text{kJ mol}^{-1}$	k_{exp}	k_{calc}
CH_3Br	Br^-	$+\text{CH}_3\text{O}^\cdot$	57	-267	2.2	2.4
	CHBr^- ^a	$+\text{H}_2\text{O}$	40	-97		
	OH^-	$+\text{CH}_2\text{Br}^\cdot$	3	-33		
CH_2Br_2	Br^-	$+\text{Br}^\cdot + \text{CH}_2\text{O}$	52	-318	1.3	2.4
	CHBr_2^- ^b	$+\text{OH}^\cdot$	38	-29		
	OBr^- ^c	$+\text{CH}_2\text{Br}^\cdot$	10	-35		
CHBrCl_2	CBrCl_2^- ^d	$+\text{OH}^\cdot$	88	< -122	2.5	
	Br^-	$+\text{Cl}^\cdot + \text{CHClO}^\cdot$	5	(-315)		
	BrCl^- ^e	$+\text{CHClO}^\cdot$	3	(< -351)		
	Cl^-	$+\text{Br}^\cdot + \text{CHClO}^\cdot$	3	(-338)		
	Cl_2^-	$+\text{CHBrO}^\cdot$ ^g	≈ 1	(-402)		
CHBr_2Cl	CBr_2Cl^-	$+\text{OH}^\cdot$	47	$\Delta H_f(\text{CBr}_2\text{Cl}^-) < 78$	2.1	
	OBr^- ^c	$+\text{CHBrCl}^\cdot$ ^h	20	(-68 ± 11)		
	Br^-	$+\text{Cl}^\cdot + \text{CHBrO}^\cdot$ ^g	20	(-320)		
	Cl^-	$+\text{Br}^\cdot + \text{CHBrO}^\cdot$ ^g	10	(-343)		
	OCl^- ⁱ	$+\text{CHBr}_2^\cdot$	3	-8 ± 9		
$\text{C}_2\text{H}_5\text{Br}$	Br^-	$+\text{CH}_3\text{CH}_2\text{O}^\cdot$ ^j	90	-235	2.0	2.7
	$\text{C}_2\text{H}_4\text{Br}^-$	$+\text{HO}^\cdot$	10	$\Delta H_f(\text{C}_2\text{H}_4\text{Br}^-) < 7$		
$\text{CH}_2\text{BrCH}_2\text{Br}$	Br^-	$+\text{Br}^\cdot + \text{CH}_2\text{OCH}_2$	100	-223	2.2	2.0^k
$\text{CH}_2\text{BrCH}_2\text{Cl}$	Br^-	$+\text{Cl}^\cdot + \text{CH}_2\text{OCH}_2$	68	-166	1.9	1.9^k
	Cl^-	$+\text{Br}^\cdot + \text{CH}_2\text{OCH}_2$	32	-189		

^a $H_f(\text{CHBr}^-) = 223\text{ kJ mol}^{-1}$ determined from $H_f(\text{CHBr}) = 373 \pm 18\text{ kJ mol}^{-1}$ [30] and $\text{EA}(\text{CHBr}) = 1.556\text{ eV}$ [31].

^b $H_f(\text{CHBr}_2^-) = 40\text{ kJ mol}^{-1}$ determined from $H_f(\text{CHBr}_2) = 227\text{ kJ mol}^{-1}$ and $\text{EA}(\text{CHBr}_2) = 1.94\text{ eV}$ [32].

^c $H_f(\text{OBr}^-) = -101\text{ kJ mol}^{-1}$ determined from $H_f(\text{OBr}) = 126\text{ kJ mol}^{-1}$ and $\text{EA}(\text{OBr}) = 2.35\text{ eV}$ [33].

^d $H_f(\text{CBrCl}_2^-) \leq -102\text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CBrCl}_3$.

^e $H_f(\text{CHClO}) = -164 \pm 1\text{ kJ mol}^{-1}$ estimated from H/Cl exchange in $\text{CH}_2\text{O}/\text{CCl}_2\text{O}$.

^f $H_f(\text{BrCl}^-) \leq -107 \pm 21\text{ kJ mol}^{-1}$, an upper limit estimated from the reaction $\text{OH}^- + \text{CFBr}_2\text{Cl}$.

^g $H_f(\text{CHBrO}) = -111 \pm 1\text{ kJ mol}^{-1}$ estimated from H/Br exchange in $\text{CH}_2\text{O}/\text{CBr}_2\text{O}$.

^h $H_f(\text{CHBrCl}) = 175 \pm 8\text{ kJ mol}^{-1}$ estimated from the average Br/Cl exchange in $\text{CHBr}_2/\text{CHCl}_2$ and $\text{CH}_2\text{Br}/\text{CH}_2\text{Cl}$.

ⁱ $H_f(\text{OCl}^-) = -118\text{ kJ mol}^{-1}$ determined from $H_f(\text{OCl}) = 101\text{ kJ mol}^{-1}$ and $\text{EA}(\text{OCl}) = 2.27\text{ eV}$ [33].

^j $H_f(\text{CH}_3\text{CH}_2\text{O}) = -25 \pm 8\text{ kJ mol}^{-1}$ [34].

^k No dipole moment data available; the calculated rate is the Langevin rate coefficient.

the flow tube—an effect which depends on mass but in the opposite sense to that of discrimination in the detector. Nevertheless, diffusional losses are unlikely to have much effect on the branching ratios presented here because of the large masses involved. It is worth noting, however, that care must be taken when using the standard technique [26] to determine the product ratios allowing for mass discrimination of the detection system only. Importantly, for negative ion work, the Faraday plate detector is indirectly used to determine whether electron detachment occurs. A decrease in the current at the Faraday plate, subsequent to the introduction of the neutral reagent into the flow tube, is attributed to the production of free electrons which diffuse quickly to the walls of the instrument before they can be detected. However, a decrease in the Faraday plate current will also occur if the parent anion is converted in the reaction to a daughter anion of smaller mass. This is a result of the greater diffusional loss of the daughter anion to the SIFT walls compared with the

parent anion. Hence care must be taken when looking for electron detachment processes when dealing with negative ion–molecule reactions. In all the studies presented here, no decrease in the Faraday plate current was detected, suggesting that if electron detachment did occur it was slight.

3. Results and discussion

To facilitate discussion, the neutral reactant molecules have been placed into one of two groups I and II: (I) CH_3Br , CH_2Br_2 , CHBrCl_2 , CHBr_2Cl , $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{Cl}$ (the hydrogen-containing halo-carbons), and (II) CF_3Br , CF_2Br_2 , CFBr_3 , CBrClF_2 , CFBr_2Cl , CCl_3Br and $\text{CF}_2\text{BrCF}_2\text{Br}$ (the fully halogenated halocarbons). The experimental rate coefficients and the anion product distributions for the O_2^- , $\text{O}_2^{\cdot-}$ and OH^- anion reactions with the group I molecules are listed

Table 2

Compilation of the measured rate coefficients k_{exp} and product anion distributions for the reactions of O_2^- with the series of halogenated compounds in Group I investigated using the SIFT apparatus at 300 K. The calculated collisional rate coefficients k_{calc} are also presented. The rate coefficients (experimental and calculated) are in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The experimental results are considered accurate to $\pm 20\%$

Molecule	Products	Suggested neutrals	Product percentages	Reaction enthalpy $\Delta H/\text{kJ mol}^{-1}$	k_{exp}	k_{calc}
CH_3Br	Br^-	$+\text{CH}_3\text{O}_2^{\text{a}}$	100	–105	1.3	1.8
CH_2Br_2	Br^-	$+\text{CH}_2\text{O}+\text{OBr}^{\text{b}}$	100	–154	1.6	1.8
CHBrCl_2	Br^-	$+\text{CCl}_2\text{O}+\text{OH}^-$	91	–303	1.3	
	Cl^-	$+\text{CBrClO}^{\text{c}}+\text{OH}^-$	4	(–264)		
	CHBrCl_2^-	$+\text{O}_2$	4	$\Delta H_f(\text{CHBrCl}_2^-) < -91$		
	BrCl^{d}	$+\text{CClO}^{\text{e}}+\text{OH}^-$	1	$< 1 \pm 16$		
CHBr_2Cl	Br^-	$+\text{CBrClO}^{\text{c}}+\text{OH}^-$	95	(–190)	1.0	
	Cl^-	$+\text{CBr}_2\text{O}+\text{OH}^-$	5	–268		
$\text{C}_2\text{H}_5\text{Br}$	Br^-	$+\text{CH}_3\text{O}^-+\text{CH}_2\text{O}$	100	–201	1.3	1.8
$\text{CH}_2\text{BrCH}_2\text{Br}$	Br^-	$+\text{Br}^-+\text{CH}_2\text{O}+\text{CH}_2\text{O}$	85	–238	1.9	1.5 ^f
	Br_2^-	$+\text{CH}_2\text{O}+\text{CH}_2\text{O}$	15	–346		
$\text{CH}_2\text{BrCH}_2\text{Cl}$	Br^-	$+\text{Cl}^-+\text{CH}_2\text{O}+\text{CH}_2\text{O}$	93	–180	1.9	1.4 ^f
	Cl^-	$+\text{Br}^-+\text{CH}_2\text{O}+\text{CH}_2\text{O}$	7	–204		

^a $H_f(\text{CH}_3\text{O}_2) = 28 \text{ kJ mol}^{-1}$ [35].

^b $H_f(\text{OBr}^-) = 126 \text{ kJ mol}^{-1}$ [33].

^c $H_f(\text{CBrClO}) = -167 \pm 1 \text{ kJ mol}^{-1}$ estimated from Br/Cl exchange in $\text{CBr}_2\text{O}/\text{CCl}_2\text{O}$.

^d $H_f(\text{BrCl}^-) \leq -107 \pm 21 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^-+\text{CBr}_2\text{ClF}$.

^e $H_f(\text{CClO}^-) = -22 \pm 3 \text{ kJ mol}^{-1}$ [36].

^f No dipole moment data available; the calculated rate is the Langevin rate coefficient.

Table 3

Compilation of the measured rate coefficients k_{exp} and product anion distributions for the reactions of OH^- with the series of halogenated compounds in Group I investigated using the SIFT apparatus at 300 K. The calculated collisional rate coefficients k_{calc} are also presented. The rate coefficients (experimental and calculated) are in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The experimental results are considered accurate to $\pm 20\%$

Molecule	Products	Suggested neutrals	Product percentages	Reaction enthalpy $\Delta H/\text{kJ mol}^{-1}$	k_{exp}	k_{calc}
CH_3Br	Br^-	$+\text{CH}_3\text{OH}$	100	-240	2.3	2.3
CH_2Br_2	CHBr_2^{a}	$+\text{H}_2\text{O}$	95	-65	1.5	2.3
	Br^-	$+\text{HBr}+\text{CH}_2\text{O}$	5	-221		
CHBrCl_2	$\text{CBrCl}_2^{\text{b}}$	$+\text{H}_2\text{O}$	96	< -158	1.2	
	Br^-	$+\text{H}_2\text{O}+\text{CCl}_2$	4	-106		
CHBr_2Cl	$\text{CBr}_2\text{Cl}^{\text{c}}$	$+\text{H}_2\text{O}$	96	$< -36 \pm 8$	1.2	
	Br^-	$+\text{HBr}+\text{CHClO}^{\text{d}}$	3	(-288)		
	Cl^-	$+\text{HBr}+\text{CHBrO}^{\text{e}}$	1	(-228)		
$\text{C}_2\text{H}_5\text{Br}$	Br^-	$+\text{CH}_2\text{O}+\text{CH}_4$	100	-197	2.3	2.7
$\text{CH}_2\text{BrCH}_2\text{Br}$	Br^-	$+\text{CH}_2\text{O}+\text{CH}_3\text{Br}$	89	-228	2.2	1.9 ^h
	HOBr^{f}	$+\text{CH}_2\text{BrCH}_2^{\text{g}}$	11	< -32		
$\text{CH}_2\text{BrCH}_2\text{Cl}$	Br^-	$+\text{CH}_2\text{O}+\text{CH}_3\text{Cl}$	68	-180	2.3	1.9 ^h
	Cl^-	$+\text{CH}_2\text{O}+\text{CH}_3\text{Br}$	32	-150		

^a $H_f(\text{CHBr}_2^-) = 40 \text{ kJ mol}^{-1}$ determined from $H_f(\text{CHBr}_2) = 227 \text{ kJ mol}^{-1}$ and $\text{EA}(\text{CHBr}_2) = 1.94 \text{ eV}$ [32].

^b $H_f(\text{CBrCl}_2^-) \leq -102 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CBrCl}_3$.

^c $H_f(\text{CBr}_2\text{Cl}^-) \leq 78 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{O}^- + \text{CHBr}_2\text{Cl}$.

^d $H_f(\text{CHClO}) = -164 \pm 1 \text{ kJ mol}^{-1}$ estimated from H/Cl exchange in $\text{CH}_2\text{O}/\text{CCl}_2\text{O}$.

^e $H_f(\text{CHBrO}) = -111 \pm 1 \text{ kJ mol}^{-1}$ estimated from H/Br exchange in $\text{CH}_2\text{O}/\text{CBr}_2\text{O}$.

^f $H_f(\text{HOBr}^-) \leq -387 \pm 20 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CBr}_3\text{F}$.

^g $H_f(\text{CH}_2\text{BrCH}_2) = 141 \pm 16 \text{ kJ mol}^{-1}$, estimated using the C–Br bond strength [37], the electron affinity of Br and the exothermicity of the Br^- channel from electron attachment to $\text{CH}_2\text{BrCH}_2\text{Br}$ [38,39].

^h No dipole moment data available; the calculated rate is the Langevin rate coefficient.

in Tables 1–3, respectively, and in Tables 4–6 for the reactions with the group II molecules, respectively. For those brominated molecules with known polarisabilities and (for the polar molecules) known dipole moments, the calculated collisional rate coefficients k_{calc} are also given in the tables for comparison with the experimental values. These were calculated using the Langevin theory for non-polar molecules [27] or the average dipole orientation theory for those reactions involving polar molecules [28]. Also presented in the tables are suggested neutrals, inferred where possible from mass balance and thermodynamics and the enthalpies of the reactions (estimated values are given in brackets). Thermochemical data used to determine these enthalpies have mainly been taken from the compilation by Lias et al. [29], but also from Refs. [30–44] (see Tables 1–6 for details).

3.1. Group I reactions

3.1.1. CH_3Br

The reactions of O^- , O_2^- and OH^- with CH_3Br are all fast, resulting in Br^- being the major (O^- reaction) or the only (O_2^- and OH^- reactions) ionic product. Formation of the Br^- anion presumably takes place via an $\text{S}_{\text{N}}2$ mechanism, because dissociative electron transfer (DET), defined as $\text{A}^- + \text{BC} \rightarrow \text{A} + (\text{BC}^-)^* \rightarrow \text{A} + \text{B}^- + \text{C}$, to form Br^- and CH_3 is endothermic for the three reactant anions; CH_3Br has an electron affinity of $0.4 \pm 0.1 \text{ eV}$ [32], lower than those of O ($1.46 \pm 0.01 \text{ eV}$) and OH^- ($1.829 \pm 0.010 \text{ eV}$), and comparable with that of O_2 ($\approx 0.45 \text{ eV}$) [37]. In comparison, electron attachment, defined as: $\text{e}^- + \text{BC} \rightarrow (\text{BC}^-)^*$, to CH_3Br leads to Br^- as the only observed anionic product [45].

The other products observed for the O^- reaction, CHBr^- (40%) and OH^- (3%), result from

Table 4

Compilation of the measured rate coefficients k_{exp} and product anion distributions for the reactions of O^- with the series of halogenated compounds in Group II investigated using the SIFT apparatus at 300 K. The calculated collisional rate coefficients k_{calc} are also presented. The rate coefficients (experimental and calculated) are in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The experimental results are considered accurate to $\pm 20\%$

Molecule	Products	Suggested neutrals	Product percentages	Reaction enthalpy $\Delta H/\text{kJ mol}^{-1}$	k_{exp}	k_{ADO}
CF_3Br	Br^-	$+\text{F} + \text{CF}_2\text{O}$	38	-235	1.7	1.8 ^b
	OBr^- ^a	$+\text{CF}_3$	31	-19		
	F^-	$+\text{Br} + \text{CF}_2\text{O}$	24	-232		
	BrF^- ^c	$+\text{CF}_2\text{O}$	7	-402		
CF_2Br_2	Br^-	$+\text{Br} + \text{CF}_2\text{O}$	50	-467	1.9	1.9
	OBr_2^-	$+\text{CF}_2$	43	$\Delta H_f(\text{Br}_2\text{O}^-) < -66$		
	OBr^- ^a	$+\text{CF}_2\text{Br}^{\text{d}}$	7	-29		
CFBr_3	CFBr_2^- ^e	$+\text{OBr}^-$ ^a	80	$< -59 \pm 29$	2.2	
	OBr^- ^a	$+\text{CFBr}_2$	11	$\Delta H_f(\text{CFBr}_2) < -27$		
	Br^-	$+\text{Br} + \text{CFBrO}^{\text{f}}$	9	(-350)		
CCl_3Br	CBrCl_2^- ^g	$+\text{OCl}^{\text{h}}$	71	$< -66 \pm 5$	1.8	2.1 ⁱ
	CCl_3^-	$+\text{OBr}^-$ ^a	11	-81		
	OBr^- ^a	$+\text{CCl}_3$	10	-87		
	OCl^- ^h	$+\text{CCl}_2\text{Br}^{\text{j}}$	5	-53 ± 12		
	Br^-	$+\text{Cl} + \text{CCl}_2\text{O}$	1	-337		
	Cl^-	$+\text{Br} + \text{CCl}_2\text{O}$	1	-400		
	Cl_2^-	$+\text{CBrClO}^{\text{k}}$	≈ 1	(-464)		
CBrClF_2	OBrCl^-	$+\text{CF}_2$	80	$\Delta H_f(\text{BrClO}^-) < -125 \pm 20$	1.7	
	OBr^- ^a	$+\text{CF}_2\text{Cl}^-$	11	-146		
	Br^-	$+\text{Cl} + \text{CF}_2\text{O}$	6	-402		
	BrCl^- ^l	$+\text{CF}_2\text{O}$	2	< -417		
	Cl^-	$+\text{Br} + \text{CF}_2\text{O}$	1	-425		
$\text{CFBr}_2\text{Cl}^{\text{m}}$	OBr_2^- ⁿ	$+\text{CFCl}$	47	($< -20 \pm 42$)	1.7	
	CFBr_2^- ^e	$+\text{OCl}^{\text{h}}$	27	($< -146 \pm 33$)		
	CFBrCl^- ^o	$+\text{OBr}^-$ ^a	16	(-59 ± 36)		
	OBr^- ^a	$+\text{CFBrCl}^{\text{p}}$	4	(-98 ± 13)		
	BrCl^- ^l	$+\text{CFBrO}^{\text{f}}$	2	(< -411)		
	Br^-	$+\text{Cl} + \text{CFBrO}^{\text{f}}$	2	(-403)		
	OCl^- ^h	$+\text{CFBr}_2^{\text{q}}$	≈ 1	($< -72+13$)		
$\text{CF}_2\text{BrCF}_2\text{Br}$	Cl^-	$+\text{Br} + \text{CFBrO}^{\text{f}}$	≈ 1	(-426)	2.4	
	Br^-	$+\text{Br} + \text{CF}_2\text{O} + \text{CF}_2$	72	-265		
	OBr_2^- ⁿ	$+\text{C}_2\text{F}_4$	21	< -66		
	OBr^- ^a	$+\text{CF}_2\text{BrCF}_2^{\text{r}}$	7	-29 ± 16		

^a $H_f(\text{OBr}^-) = -101 \text{ kJ mol}^{-1}$ determined from $H_f(\text{OBr}) = 126 \text{ kJ mol}^{-1}$, $\text{EA}(\text{OBr}^-) = -2.35 \text{ eV}$ [33].

^b Polarisability of $\text{CF}_3\text{Br} = 6.78 \text{ \AA}^3$ [3].

^c $H_f(\text{BrF}^-) = -384 \text{ kJ mol}^{-1}$ [3].

^d $H_f(\text{CF}_2\text{Br}^-) = -226 \pm 16 \text{ kJ mol}^{-1}$ [40].

^e $H_f(\text{CFBr}_2^-) \leq -313 \pm 15 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CFBr}_3$.

^f $H_f(\text{CFBrO}^-) = -377 \pm 1 \text{ kJ mol}^{-1}$, estimated from F/Br exchange in $\text{CF}_2\text{O}/\text{CBr}_2\text{O}$.

^g $H_f(\text{CBrCl}_2^-) \leq -102 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CBrCl}_3$.

^h $H_f(\text{OCl}^-) = -118 \text{ kJ mol}^{-1}$, determined from $H_f(\text{OCl}) = 101 \text{ kJ mol}^{-1}$ and $\text{EA}(\text{OCl}) = 2.37 \text{ eV}$ [33].

ⁱ Polarisability and dipole moment of $\text{CCl}_3\text{Br} = 12 \text{ \AA}^3$ and 0.2 D [41].

^j $H_f(\text{CBrCl}_2^-) = 130 \pm 8 \text{ kJ mol}^{-1}$ determined using the C–Cl bond strength [37], the electron affinity of Cl and the exothermicity of the Cl^- channel from electron attachment to CBrCl_3 [42].

^k $H_f(\text{CBrClO}^-) = -167 \pm 1 \text{ kJ mol}^{-1}$, estimated from Br/Cl exchange in $\text{CBr}_2\text{O}/\text{CCl}_2\text{O}$.

^l $H_f(\text{BrCl}^-) \leq -107 \pm 21 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CBr}_2\text{ClF}$.

^m $H_f(\text{CFBr}_2\text{Cl}^-) = -181 \pm 13 \text{ kJ mol}^{-1}$, estimated using the average value from (i) F/Cl exchange calculated from CCl_4/CF_4 and $\text{CF}_2\text{Cl}_2/\text{CF}_4$ in CBr_2F_2 , (ii) Cl/Br exchange calculated from $\text{CCl}_4/\text{CBr}_4$ and $\text{CBr}_2\text{Cl}_2/\text{CCl}_4$ with CFCl_3 , and (iii) F/Br exchange calculated from $\text{CF}_2\text{Br}_2/\text{CF}_4$ and $\text{CF}_2\text{Br}_2/\text{CBr}_4$ with CF_2BrCl .

ⁿ $H_f(\text{OBr}_2^-) \leq -66 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{O}^- + \text{CF}_2\text{Br}_2$.

H_2^+ and H transfer, respectively. Although not observed, the abstraction of Br \cdot to produce $\text{BrO}^- + \text{CH}_3$ is exothermic ($\Delta H = -25 \text{ kJ mol}^{-1}$). Therefore, it appears that nucleophilic attack by O^- on the carbon, leading to the Br^- product, and on hydrogen, leading to the CHBr^- and OH^- products, is more favoured than attack on the bromine. Our measured rate coefficient for the O^- reaction is an order of magnitude larger than that reported by Futrell and Tiernan ($2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [18] and is also larger than that reported by Tanaka et al., ($1.1 \pm 0.1 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$) [19]. Furthermore, Futrell and Tiernan report OH^- as the major product (52%), with CHBr^- (33%) and Br^- (14%) being the minor products. Discrepancies between our results and those of Futrell and Tiernan are likely to be due to the differences in collisional energies of anions with neutral molecules within the tandem mass spectrometer compared with those within the SIFT. Tanaka et al. observe Br^- , CHBr^- and OH^- as products from the reaction with O^- , but do not present distribution data.

Our measured rate coefficient for the O_2^- reaction is in exact agreement with that determined by McDonald and Chowdhury [20] using a FA. For the OH^- reaction, our rate coefficient is higher than those published by Bohme and MacKay, ($1.0 \pm 0.2 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$) [21], and Tanaka et al., ($0.99 \pm 0.09 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$) [19], although it is in better agreement with the results of Olmstead and Brauman, ($1.9 \pm 0.4 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$) [22], and DePuy et al., ($2.2 \pm 0.2 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$) [23].

3.1.2. CH_2Br_2

O^- reacts with CH_2Br_2 with a rate coefficient

approximately 50% of the collisional value. The three observed ionic products, Br^- (52%), CHBr_2^- (38%) and BrO^- (10%), are formed via nucleophilic substitution, proton transfer and Br abstraction mechanisms, respectively. Energetically it is possible to form the Br_2^- molecular anion and formaldehyde (H_2CO) but no Br_2^- was observed, although it is possible that Br^- could be formed from dissociation of $(\text{Br}_2^-)^*$. The decomposition of Br_2^- to $\text{Br}^- + \text{Br}^\cdot$ requires 110 kJ mol^{-1} , and redistribution of the available energy from the reaction of O^- with CH_2Br_2 within an intermediate complex, and then between the products according to the number of degrees of freedom, would provide only 61 kJ mol^{-1} , leaving the decomposition endothermic. Therefore, for Br_2^- to be an intermediate in the formation of Br^- , it must be formed with considerably more internal energy than expected from simple equipartition of energy ideas, and then all the Br_2^- would have to dissociate to Br^- and Br. Thus, the formation of Br^- is unlikely to be from the decomposition of Br_2^- . Decomposition of $(\text{CHBr}_2^-)^*$ to Br^- and CHBr_2^\cdot is endothermic, as too is DET. Hydrogen abstraction leading to OH^- and CHBr_2^- is exothermic ($\Delta H = -18 \text{ kJ mol}^{-1}$) but is not observed.

O_2^- reacts with CH_2Br_2 to form Br^- via nucleophilic attack on carbon. Although DET yielding Br^- is thermoneutral, with $\Delta H = 3 \pm 4 \text{ kJ mol}^{-1}$, and hence cannot be completely ruled out, it is nevertheless unlikely that it competes with nucleophilic substitution. In comparison, electron attachment to CH_2Br_2 forms the Br^- anion and the $\text{CH}_2\text{Br}^\cdot$ radical [45].

The OH^- reaction yields two anionic products, namely CHBr_2^- , by proton transfer, and Br^- by nucleophilic substitution, DET to form Br^-

^o $H_f(\text{CFBrCl}^-) \leq -258 \pm 16 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CFBr}_2\text{Cl}$.

^p $H_f(\text{CFBrCl}^-) = -63 \text{ kJ mol}^{-1}$, estimated from the average Br/Cl exchange in $\text{CBr}_3/\text{CCl}_3$, $\text{CHBr}_2/\text{CHCl}_2$ and $\text{CH}_2\text{Br}/\text{CH}_2\text{Cl}^-$ and average Br/F exchanges in CBr_3/CF_3 , $\text{CHBr}_2/\text{CHF}_2$ and $\text{CH}_2\text{F}/\text{CH}_2\text{F}^-$.

^q $H_f(\text{CFBr}_2^-) \leq -27 \text{ kJ mol}^{-1}$, determined from the exothermicity of the Br^- channel from electron attachment to CFBr_3 [38].

^r $H_f(\text{CF}_2\text{BrCF}_2^-) = -609 \pm 16 \text{ kJ mol}^{-1}$ from the use of the C–Br bond strength [37], the electron affinity of Br and the exothermicity of the Br^- channel from electron attachment to $\text{CF}_2\text{BrCF}_2\text{Br}$ [38,39].

Table 5

Compilation of the measured rate coefficients k_{exp} and product anion distributions for the reactions of O_2^- with the series of halogenated compounds in Group II investigated using the SIFT apparatus at 300 K. The calculated collisional rate coefficients k_{calc} are also presented. The rate coefficients (experimental and calculated) are in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The experimental results are considered accurate to $\pm 20\%$

Molecule	Products	Suggested neutrals	Product percentages	Reaction enthalpy $\Delta H/\text{kJ mol}^{-1}$	k_{exp}	k_{calc}
CF_3Br	CF_3Br^-	$+\text{O}_2$	53	-48	1.1	1.3 ^b
	Br^-	$+\text{CF}_3\text{O}_2^{\text{a}}$	47	-139		
CF_2Br_2	Br^-	$+\text{CF}_2\text{O}+\text{OBr}^{\text{c}}$	100	-306	0.98	1.4
CFBr_3	Br^-	$+\text{CFBrO}^{\text{d}}+\text{OBr}^{\text{c}}$	100	(-186)	1.9	
CCl_3Br	Br^-	$+\text{CCl}_3+\text{O}_2$	95	-49	1.3	1.6 ^e
	Cl^-	$+\text{CCl}_2\text{Br}^{\text{f}}+\text{O}_2$	5	-12		
CBrClF_2	Br^-	$+\text{CF}_2\text{O}+\text{OCl}^{\text{g}}$	≈ 89	-272	1.2	
	CF_2BrCl^-	$+\text{O}_2$	10	$\Delta H_f(\text{CF}_2\text{BrCl}^-) < -480$		
	BrO_2^-	$+\text{CF}_2\text{Cl}^{\text{h}}$	≈ 1	$\Delta H_f(\text{BrO}_2^-) < -205$		
$\text{CFBr}_2\text{Cl}^{\text{h}}$	Br^-	$+\text{CFCIO}+\text{OBr}^{\text{c}}$	95	-290	1.2	
	Cl^-	$+\text{CFBrO}^{\text{d}}+\text{OBr}^{\text{c}}$	5	(-255)		
$\text{CF}_2\text{BrCF}_2\text{Br}$	Br_2^-	$+\text{CF}_2\text{O}+\text{CF}_2\text{O}$	94	-659	1.9	
	Br^-	$+\text{Br}^{\cdot}+\text{CF}_2\text{O}+\text{CF}_2\text{O}$	6	-550		

^a $H_f(\text{CF}_3\text{O}_2) = -618 \text{ kJ mol}^{-1}$ [43].

^b Polarisability of $\text{CF}_3\text{Br} = 6.78 \text{ \AA}^3$ [3].

^c $H_f(\text{OBr}^{\cdot}) = 126 \text{ kJ mol}^{-1}$ [33].

^d $H_f(\text{CFBrO}) = -377 \pm 1 \text{ kJ mol}^{-1}$, estimated from F/Br exchange in $\text{CF}_2\text{O}/\text{CBr}_2\text{O}$.

^e Polarisability and dipole moment of $\text{CCl}_3\text{Br} = 12 \text{ \AA}^3$ and 0.2 D [41].

^f $H_f(\text{CCl}_2\text{Br}^{\cdot}) = 130 \pm 8 \text{ kJ mol}^{-1}$, determined using the C–Cl bond strength [37], the electron affinity of Cl and the exothermicity of the Cl^- channel from electron attachment to CBrCl_3 [42].

^g $H_f(\text{OCl}^{\cdot}) = -118 \text{ kJ mol}^{-1}$, determined from $H_f(\text{OCl}^{\cdot}) = 101 \text{ kJ mol}^{-1}$ and $\text{EA}(\text{OCl}) = 2.37 \text{ eV}$ [33].

^h $H_f(\text{CFBr}_2\text{Cl}) = -181 \pm 13 \text{ kJ mol}^{-1}$ estimated using the average from (i) F/Cl exchange calculated from CCl_4/CF_4 and $\text{CF}_2\text{Cl}_2/\text{CF}_4$ in CBr_2F_2 , (ii) Cl/Br exchange calculated from $\text{CCl}_4/\text{CBr}_4$ and $\text{Br}_2\text{Cl}_2/\text{CCl}_4$ with CFCl_3 , and (iii) F/Br exchange calculated from $\text{CF}_2\text{Br}_2/\text{CF}_4$ and $\text{CF}_2\text{Br}_2/\text{CBr}_4$ with CF_2BrCl .

being endothermic. The product distribution shows that the less exothermic proton transfer channel is much faster than the thermodynamically more favoured nucleophilic substitution channel. The formation of Br^- via the dissociation of $(\text{CHBr}_2)^+$ can be ruled out, as the channel is endothermic, i.e. $\text{OH}^- + \text{CH}_2\text{Br}_2 \rightarrow \text{Br}^- + \text{CHBr} + \text{H}_2\text{O}$, with $\Delta H = 78 \text{ kJ mol}^{-1}$, where $\Delta H_f(\text{CHBr}) = 373 \pm 18 \text{ kJ mol}^{-1}$ [30].

3.1.3. CHBrCl_2

The major pathway for the O^- reaction produces CBrCl_2^- by proton transfer. Four minor ionic species, Br^- (5%), Cl^- (3%), BrCl^- (3%) and Cl_2^- ($\approx 1\%$) are also produced, probably via nucleophilic attack on carbon. An alternative exothermic route to the production of Br^- is via the decomposition of $(\text{CBrCl}_2)^+$, i.e.

$\text{O}^- + \text{CHBrCl}_2 \rightarrow (\text{CBrCl}_2)^+ + \text{OH}^- \rightarrow \text{Br}^- + \text{CCl}_2 + \text{OH}^-$, $\Delta H = -70 \text{ kJ mol}^{-1}$. It is uncertain whether Cl^- can be produced by a similar route, as $\Delta H_f(\text{CBrCl})$ is unknown. However, it should be noted that for such a small branching percentage associated with Cl^- , an impurity in our sample reacting with the anion with unit efficiency could be forming the Cl^- product. It cannot be ruled out that the formation of Br^- and Cl^- results from the decomposition of $(\text{BrCl}^-)^+$ and $(\text{Cl}_2^-)^+$, although the dihalides must both be formed from the reaction with an excess of energy greater than equipartition of energy suggests. Although a possible reaction channel yielding BrO^- and CHCl_2 is exothermic by 52 kJ mol^{-1} , the absence of any BrO^- as an ionic product suggests that proton transfer is kinetically favoured over the transfer of a heavy Br

Table 6

Compilation of the measured rate coefficients k_{exp} and product anion distributions for the reactions of OH^- with the series of halogenated compounds in Group II investigated using the SIFT apparatus at 300 K. The calculated collisional rate coefficients k_{calc} are also presented. The rate coefficients (experimental and calculated) are in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the three-body rate [] is in units of $10^{-26} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. The experimental results are considered accurate to $\pm 20\%$.

Molecule	Products	Suggested neutrals	Product percentages	Reaction enthalpy $\Delta H/\text{kJ mol}^{-1}$	k_{exp}	k_{calc}
CF_3Br	Br^-	$+\text{CF}_3\text{OH}^{\text{a}}$	100	$=333$	0.0029	1.7^{b}
	$\text{CF}_3\text{Br}\cdot\text{OH}^-$	Three-body reaction	=	≤ -787	[1.1]	
CF_2Br_2	HOBr_2^{c}	$+\text{CF}_2$	94	$\leq -36 \pm 14$	1.6	1.9
	Br^-	$+\text{HBr}+\text{CF}_2\text{O}$	6	$=373$		
CFBr_3	CFBr_2^-	$+\text{HOBr}^{\text{d}}$	62	$\Delta H_f(\text{CFBr}_2^-) \leq -313 \pm 15$	1.9	
	HOBr_2^{c}	$+\text{CFBr}^{\text{e}}$	29	$(\Delta H_f(\text{Br}_2\text{OH}^-) \leq -347)$		
	Br^-	$+\text{HBr}+\text{CFBrO}^{\text{f}}$	8	(-253)		
	HOBr^-	$+\text{CFBr}_2^{\text{g}}$	≈ 1	$\Delta H_f(\text{BrOH}^-) \leq -346 \pm 8$		
CCl_3Br	CCl_3^-	$+\text{HOBr}^{\text{d}}$	64	-21 ± 35	1.8	2.1^{h}
	OBr^-	$+\text{CHCl}_3$	19	$=26$		
	Cl^-	$+\text{HBr}+\text{CCl}_2\text{O}$	10	$=303$		
	CBrCl_2^-	$+\text{HOCl}$	4	$\Delta H_f(\text{CBrCl}_2^-) \leq -102$		
	Br^-	$+\text{HCl}+\text{CCl}_2\text{O}$	3	$=346$		
CBrClF_2	HOBrCl^-	$+\text{CF}_2$	75	$\Delta H_f(\text{BrClOH}^-) \leq -370$	0.0028	
	Br^-	$+\text{HCl}+\text{CF}_2\text{O}$	18	$=370$		
	Cl^-	$+\text{HBr}+\text{CF}_2\text{O}$	7	$=328$		
	$\text{CF}_2\text{BrCl}\cdot\text{OH}^-$	Three-body reaction	=	$=575$	[2.4]	
$\text{CFBr}_2\text{Cl}^{\text{j}}$	HOBr_2^{c}	$+\text{CClF}$	82	$\leq -49 \pm 32$	1.1	
	CBrClF^-	$+\text{HOBr}^{\text{d}}$	7	$(\Delta H_f(\text{CBrClF}^-) \leq -258 \pm 16)$		
	Br^-	$+\text{HBr}+\text{CClFO}$	4	$=376$		
	Br_2^-	$+\text{HCl}+\text{CFO}^-$	3	(-159)		
	CBr_2F^-	$+\text{HOCl}$	1	(-73 ± 20)		
	BrCl^-	$+\text{HBr}+\text{CFO}^-$	≈ 1	$(\Delta H_f(\text{BrCl}^-) \leq -107 \pm 21)$		
	OBr^-	$+\text{CHBrClF}^{\text{l}}$	1	(-6 ± 14)		
	Cl^-	$+\text{HBr}+\text{CFBrO}^{\text{f}}$	1	(-322)		
	HOBr_2^{c}	$+\text{C}_2\text{F}_4$	60	$=44$	2.4	
$\text{CF}_2\text{BrCF}_2\text{Br}$	Br^-	$+\text{CF}_2\text{O}+\text{CHF}_2\text{Br}^{\text{m}}$	40	$=352$		

^a $H_f(\text{CF}_3\text{OH}) = -907 \text{ kJ mol}^{-1}$ [43].

^b Polarisability of $\text{CF}_3\text{Br} = 6.78 \text{ \AA}^3$ [3].

^c $H_f(\text{HOBr}_2^-) \leq -347 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CFBr}_3$.

^d $H_f(\text{HOBr}) = -60 \pm 7 \text{ kJ mol}^{-1}$ [44].

^e $H_f(\text{CFBr}) \leq -26 \text{ kJ mol}^{-1}$, estimated from the observation of Br_2^- from electron attachment to CFBr_3 [38].

^f $H_f(\text{CFBrO}) = -377 \pm 1 \text{ kJ mol}^{-1}$, estimated from F/Br exchange in $\text{CF}_2\text{O}/\text{CFBr}_2\text{O}$.

^g $H_f(\text{CFBr}_2^-) \leq -27 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{O}^- + \text{CFBr}_3$.

^h Polarisability and dipole moment of $\text{CCl}_3\text{Br} \approx 12 \text{ \AA}^3$ and 0.2 D [41].

ⁱ $H_f(\text{OBr}^-) = -101 \text{ kJ mol}^{-1}$, determined from $H_f(\text{OBr}) = 126 \text{ kJ mol}^{-1}$ and $\text{EA}(\text{OBr}) = 2.35 \text{ eV}$ [33].

^j $H_f(\text{CFBr}_2\text{Cl}^-) = -181 \pm 13 \text{ kJ mol}^{-1}$, estimated using the average values from (i) F/Cl exchange calculated from CCl_4/CF_4 and $\text{CF}_2\text{Cl}_2/\text{CF}_4$ in CBr_2F_2 , (ii) Cl/Br exchange calculated from $\text{CCl}_4/\text{CBr}_4$ and $\text{CBr}_2\text{Cl}_2/\text{CCl}_4$ with CFCl_3 , and (iii) F/Br exchange calculated from $\text{CF}_2\text{Br}_2/\text{CF}_4$ and $\text{CF}_2\text{Br}_2/\text{CBr}_4$ with CF_2BrCl .

^k $H_f(\text{CFBr}_2^-) = -313 \pm 15 \text{ kJ mol}^{-1}$, an upper limit estimated from the reaction of $\text{OH}^- + \text{CFBr}_3$.

^l $H_f(\text{CHBrClF}) = -223 \pm 6 \text{ kJ mol}^{-1}$, estimated using the average F/Cl exchange from $\text{CHCl}_2/\text{CHF}_3$ in CHBrF_2 .

^m $H_f(\text{CHF}_2\text{Br}) = -425 \text{ kJ mol}^{-1}$ [10].

atom. In addition, the proton transfer channel is more exothermic.

The major ionic product from the O_2^- reaction is Br^- (91%). Traces of Cl^- (4%), $CHBrCl_2^-$ (4%) and $BrCl^-$ (1%) are also observed. Although the DET channel ($\Delta H = -14 \text{ kJ mol}^{-1}$) leading to Br^- , $CHCl_2$ and O_2 is possible, the competitive S_N2 channel may well be the major mechanism for the formation of Br^- . Certainly it is more favoured in terms of reaction thermodynamics, and the observation of other anion products implies that an intimate interaction takes place, so that nucleophilic processes can or do compete with electron transfer.

The two products from the OH^- reaction are $CBrCl_2^-$ (96%), by proton transfer, and Br^- (4%). Two mechanisms are possible for the production of Br^- , i.e. S_N2 and/or by the less exothermic pathway resulting from the decomposition of $(CBrCl_2)^*$, i.e. $OH^- + CHBrCl_2 \rightarrow H_2O + (CBrCl_2)^* \rightarrow Br^- + CCl_2 + H_2O$ ($\Delta H = -58 \pm 16 \text{ kJ mol}^{-1}$). Br^- formation via DET is endothermic by 120 kJ mol^{-1} .

3.1.4. $CHBr_2Cl$

O^- reacts with $CHBr_2Cl$ to yield five ionic species; CBr_2Cl^- (47%), Br^- (20%), BrO^- (20%), ClO^- (10%) and Cl^- (3%). CBr_2Cl^- , BrO^- and ClO^- are formed via the abstractions of a proton, Br and Cl, respectively. Both Br^- and Cl^- may be formed either via nucleophilic substitution or by the decomposition of $(CBr_2Cl)^*$. It is observed that the percentages of BrO^- and ClO^- decrease with increasing $CHBr_2Cl$ number density, whereas the CBr_2Cl^- signal increases. This suggests that there are secondary reactions of both BrO^- and ClO^- with $CHBr_2Cl$, leading to the production of CBr_2Cl^- .

Only two ionic products, Br^- (95%) and Cl^- (5%), are observed for the O_2^- reaction with $CHBr_2Cl$. It is unknown whether Br^- can result from DET because of the uncertainty in the enthalpy of the reaction, whereas the production of Cl^- via DET is definitely endothermic

($\Delta H = 33 \pm 8 \text{ kJ mol}^{-1}$). We therefore suggest that nucleophilic attack on carbon is the most probable reaction mechanism for the production of both these anions.

OH^- reacts to yield CBr_2Cl^- (96%) as the major product by proton transfer. Traces of Br^- (3%) and Cl^- (1%) are also observed, and these may be formed via the decomposition of $(CBr_2Cl)^*$ or by nucleophilic substitution. DET leading to Br^- or Cl^- is endothermic.

3.1.5. C_2H_5Br

Ethyl bromide reacts rapidly with O^- , yielding Br^- (96%) and $C_2H_4Br^-$ (4%) anions. $C_2H_4Br^-$ is formed via a proton transfer mechanism. Two mechanisms can be proposed for the Br^- formation. One is S_N2 and the second is elimination from $(C_2H_4Br)^*$ following proton transfer to O^- , i.e. $O^- + C_2H_5Br \rightarrow OH^- + (C_2H_4Br)^* \rightarrow Br^- + C_2H_4 + OH^-$ ($\Delta H = -168 \text{ kJ mol}^{-1}$) with a small percentage of $(C_2H_4Br)^*$ stabilised by collisional or radiative relaxation and detected. To ascertain which mechanism is responsible for the formation of Br^- from the reaction between O^- and C_2H_5Br , it would be desirable to determine whether ethylene or $CH_3CH_2O^-$ is produced, and/or to ascertain if an increase in buffer gas pressure changes the product distribution by enhancing the collisional relaxation of $(C_2H_4Br)^*$ before decomposition. (It is worth noting that in the reaction of F^- with C_2H_5Cl , leading to the anion Cl^- , the neutral products have been positively identified, with the result that the substitution channel leading to C_2H_5F is preferred over the elimination channel leading to $C_2H_4 + HF$ [46,47]). DET to produce Br^- is endothermic and can therefore be ruled out as a reaction pathway. The abstraction of a hydrogen or bromine atom leading to the production of OH^- or BrO^- , respectively, is energetically allowed but is not observed. However, in the tandem mass spectrometric study [18], H-atom abstraction was found to be a significant channel (39%), with the only other channel being nucleophilic displacement to

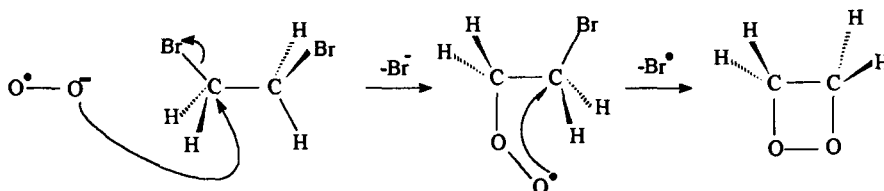
form Br^- . In addition, discrepancies exist in the values of the reaction rate coefficient between this study ($(2.0 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and that by Futrell and Tiernan [18] ($3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). These disagreements may be rationalised, as for the differences in the results for the $\text{O}^-/\text{CH}_3\text{Br}$ reaction, by considering the fact that anions in a tandem mass spectrometer usually possess higher translational energies than those in a SIFT apparatus.

Ethyl bromide undergoes efficient nucleophilic substitution when reacting with O_2^- to form Br^- , DET leading to this anion being endothermic by $9 \pm 2 \text{ kJ mol}^{-1}$.

Br^- is also the only observed ionic product from the reaction with OH^- . Although proton transfer is not observed, Br^- could be produced via the decomposition of $(\text{C}_2\text{H}_4\text{Br})^*$, as the reaction channel is exothermic, $\text{OH}^- + \text{C}_2\text{H}_5\text{Br}$

$\text{CH}_2\text{BrCH}_2\text{Br}$ having been determined to be $141 \pm 16 \text{ kJ mol}^{-1}$ using the C–Br bond strength, the electron affinity of Br and the exothermicity of the Br^- channel from electron attachment to $\text{CH}_2\text{BrCH}_2\text{Br}$ [38,39]).

The reaction with O_2^- proceeds to produce Br^- (85%) and Br_2^- (15%). These two anions are also observed from electron attachment to this molecule [39,40], with Br^- also being the major product (97%) [38]. However, although DET to form Br_2^- is exothermic, DET to form Br^- is nearly thermoneutral and could be endothermic with $\Delta H = 9 \pm 16 \text{ kJ mol}^{-1}$. Therefore, to account for the large Br^- signal from the O_2^- reaction, we propose that nucleophilic attack of O_2^- on a carbon rather than electron transfer is the initial step. The second step is the displacement of a Br atom on the adjacent carbon atom by oxygen, as illustrated below:



$\rightarrow (\text{C}_2\text{H}_4\text{Br})^* + \text{H}_2\text{O} \rightarrow \text{Br}^- + \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ with $\Delta H = -203 \text{ kJ mol}^{-1}$. Therefore, it cannot be established whether this mechanism or nucleophilic attack is the major production route to Br^- , although the lack of any observed $\text{C}_2\text{H}_4\text{Br}^-$ might suggest that the nucleophilic attack mechanism is preferred. Br^- cannot be produced by DET, this being endothermic by 143 kJ mol^{-1} . Our measured reaction rate coefficient is in good agreement with that of $(2.6 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained in the study by DePuy et al. [23].

3.1.6. $\text{CH}_2\text{BrCH}_2\text{Br}$

O^- reacts with $\text{CH}_2\text{BrCH}_2\text{Br}$ to produce Br^- only. This product probably results from nucleophilic attack on carbon, as the production of Br^- via DET is endothermic (the heat of formation of

The final neutral product is probably formaldehyde H_2CO . Obviously, the above reaction mechanism preferentially yields Br^- because of the consecutive ejection of Br^- and Br^\cdot , whereas the small amount of Br_2^- may still be produced via the competing electron transfer mechanism, presumably within the reaction complex.

The observed products from the OH^- reaction are Br^- (89%) and BrOH^- (11%). The production of Br^- could take place via several competing mechanisms. For example, the decomposition of $(\text{C}_2\text{H}_3\text{Br}_2)^*$, resulting from proton transfer, to Br^- is exothermic, i.e. $\text{OH}^- + \text{CH}_2\text{BrCH}_2\text{Br} \rightarrow (\text{C}_2\text{H}_3\text{Br}_2)^* + \text{H}_2\text{O} \rightarrow \text{Br}^- + \text{C}_2\text{H}_3\text{Br} + \text{H}_2\text{O}$ with $\Delta H = -200 \text{ kJ mol}^{-1}$. There are also several exothermic nucleophilic attack mechanisms, e.g. $\text{OH}^- + \text{CH}_2\text{BrCH}_2\text{Br} \rightarrow \text{Br}^- + \text{CH}_2\text{O} + \text{CH}_3\text{Br}$, with $\Delta H = -183 \text{ kJ mol}^{-1}$, or

the elimination of Br^- from $(\text{C}_2\text{H}_4\text{Br}^-)^*$, following extraction of Br^+ by OH^- , $\text{OH}^- + \text{CH}_2\text{BrCH}_2\text{Br} \rightarrow \text{BrOH} + (\text{C}_2\text{H}_4\text{Br}^-)^* \rightarrow \text{Br}^- + \text{BrOH} + \text{C}_2\text{H}_4$, with $\Delta H = -45 \text{ kJ mol}^{-1}$.

3.1.7. $\text{CH}_2\text{ClCH}_2\text{Br}$

Reactions of O^- , O_2^- and OH^- with $\text{CH}_2\text{ClCH}_2\text{Br}$ produce the same two ionic products, namely Br^- and Cl^- , with Br^- being the dominant product for each of the reactant anions; 68% (O^-), 93% (O_2^-) and 62% (OH^-). As DET pathways are endothermic, the two ion products can be produced only via nucleophilic attack mechanisms. In comparison, Br^- (80%) and Cl^- (20%) are also the only observed ion products from electron attachment to $\text{CH}_2\text{ClCH}_2\text{Br}$ [39].

3.2. Group II reactions

3.2.1. CF_3Br

O^- is found to react with CF_3Br with a rate coefficient of $(1.7 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in good agreement with values reported by Morris $((1.4 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ [3] and by Streit $((1.3 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ [9]. F^- (24%), Br^- (38%), BrO^- (31%) and BrF^- (7%) are the observed ionic products, which are the same as those observed by Morris but with different reported percentages [3]. BrO^- is formed via Br abstraction by O^- . It is likely that Br^- and F^- are formed via nucleophilic substitution, as DET is endothermic. It cannot be ruled out that Br^- and F^- could be formed from the decomposition of nascent $(\text{BrF}^-)^*$ (formed via the concerted breaking of C–F and C–Br bonds and the formation of C=O and Br–F bonds), although BrF^- would have to acquire an energy in excess of 250 kJ mol^{-1} for this to occur.

For the reaction of O_2^- with CF_3Br , the measured rate coefficient is $(1.1 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with two other published values of $(1.0 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [3] and $(1.1 \pm 0.3) \times 10^{-9} \text{ cm}^3$

$\text{molecule}^{-1} \text{ s}^{-1}$ [9]. Furthermore, the two anionic products we observe are also reported by Morris, with a similar product distribution, CF_3Br^- (55%), by electron transfer, and Br^- (45%) [3]. The production of Br^- via the decomposition of $(\text{CF}_3\text{Br}^-)^*$ is endothermic by 19 kJ mol^{-1} , and so Br^- must be produced exclusively via nucleophilic attack. This differs from electron attachment to CF_3Br , which is known to produce Br^- as the only ionic product [45]. That non-dissociative electron transfer and nucleophilic attack products are observed implies that the transfer mechanism is occurring not via a long-range process, but through a reaction complex, so that the short-range nucleophilic attack mechanisms can compete with it.

The bimolecular reaction with OH^- , forming Br^- by nucleophilic attack on carbon, is slow and is in competition with a fast three-body associative reaction forming $\text{CF}_3\text{Br} \cdot \text{OH}^-$. Electron transfer from OH^- , leading to the production of CF_3Br^- , is endothermic by 86 kJ mol^{-1} . In a recent study by Staneke et al. [24], no products from this reaction were observed. It was suggested that this is because the presence of the fluorines in CF_3Br alters the charge distribution of the molecule, such that $\text{S}_\text{N}2$ attack by OH^- on carbon is hindered.

3.2.2. CF_2Br_2

O^- is found to react at the collisional rate coefficient with CF_2Br_2 , leading to the ionic products Br^- (50%), Br_2O^- (43%) and BrO^- (7%). The abstraction of two bromine atoms from CF_2Br_2 results in the formation of Br_2O^- , which is enhanced by the formation of stable difluorocarbene ($:\text{CF}_2$). The formation of both Br^- and BrO^- from the decomposition of $(\text{Br}_2\text{O}^-)^*$ can be discounted, as the processes are endothermic by $\Delta H = 77$ and $\Delta H = 163 \text{ kJ mol}^{-1}$, respectively. Thus, the production of all the observed anions occurs via competing nucleophilic attack mechanisms.

The O_2^- reaction with CF_2Br_2 , as found for the electron attachment process [38], produces

only Br^- . DET to produce Br^- cannot be ruled out, the enthalpy change being $\Delta H = -18 \pm 16 \text{ kJ mol}^{-1}$. However, there are far more exothermic nucleophilic attack channels available for the production of Br^- .

The observed ionic products from the reaction with OH^- are Br_2OH^- (94%) and Br^- (6%). In comparison, Staneke et al. observe only Br_2OH^- as a product from this reaction [24]. The formation of a stable $:\text{CF}_2$ carbene is important to the abstraction of two Br atoms by OH^- from the CF_2Br_2 molecule. Br^- cannot be formed from the decomposition of $(\text{Br}_2\text{OH}^-)^*$ because of the endothermicity of the process or from DET ($\Delta H = 146 \text{ kJ mol}^{-1}$). This leaves nucleophilic attack on carbon as the only possible mechanism for the production of Br^- .

3.2.3. CFBr_3

O^- reacts quickly with CFBr_3 to yield CFBr_2^- (80%), BrO^- (11%) and Br^- (9%) as the ionic products. The first two products are linked to each other via a single electron switch process and proceed via Br^+ and Br^\cdot abstraction, respectively. The formation of Br^- from the decomposition of $(\text{CFBr}_2)^*$ cannot be ruled out because of the uncertainties in $\Delta H_f(\text{CFBr}) < -26 \text{ kJ mol}^{-1}$ [38], but it could equally be a result of nucleophilic attack on carbon.

The efficient reaction of O_2^- with CFBr_3 occurs most probably via nucleophilic attack, with Br^- as the only ionic product. Uncertainties in the enthalpy of the DET channel, because of the unknown heat of formation of CFBr_2 ($\Delta H_f < -27 \text{ kJ mol}^{-1}$ [38]), means that this channel cannot be ruled out as a route to produce Br^- . In comparison, instead of producing Br^- only, electron attachment to CFBr_3 yields both Br^- (90%) and Br_2^- (10%) [38].

OH^- reacts with CFBr_3 , leading to the formation of four ionic species, namely CFBr_2^- (62%), Br_2OH^- (29%), Br^- (8%) and BrOH^- ($< 1\%$). Staneke et al. observed the first three of these products; CFBr_2^- (60%), Br_2OH^- (30%) and Br^- (10%) [24]. The formation of Br^- from the

decomposition of $(\text{Br}_2\text{OH}^-)^*$ or $(\text{CFBr}_2)^*$ can be ruled out as these pathways are endothermic.

3.2.4. CBrCl_3

O^- reacts with CBrCl_3 to form the products CBrCl_2^- (71%), CCl_3^- (11%), BrO^- (10%) and ClO^- (5%). In addition, traces of Cl_2^- ($\approx 1\%$), Br^- ($\approx 1\%$) and Cl^- ($\approx 1\%$) are detected. It is obvious that the dominant reactions involve the nucleophilic abstraction of halogen atoms and cations. Nucleophilic attack on carbon seems to be suppressed, possibly because of the shielding of the C atom in CBrCl_3 by the four reactive halogen atoms. DET pathways leading to the production of Br^- , Cl^- and CCl_3^- are endothermic by 50 kJ mol^{-1} , 87 kJ mol^{-1} and 155 kJ mol^{-1} , respectively (where for the Cl^- channel the heat of formation for CBrCl_2^- has been determined to be 130 kJ mol^{-1} using the C–Cl bond strength (295 kJ mol^{-1}) [37], the electron affinity of Cl, and the exothermicity of electron attachment to CBrCl_3 [41]).

For the O_2^- reaction two ionic products are observed, Br^- (95%) and Cl^- (5%). Nucleophilic attack on carbon and electron transfer do have exothermic reaction channels to produce these products. Which of these two mechanisms is preferred (if any) is difficult to say; however, it is worth mentioning that electron attachment to CBrCl_3 also only yields Br^- and Cl^- , although the Cl^- channel is preferred (55%) [41]. We conclude that the reduced exothermicity in the O_2^- reaction, compared with the electron attachment process, results in the more exothermic channel leading to Br^- being favoured.

The OH^- reaction results in five ionic products: CCl_3^- (64%), BrO^- (19%), Cl^- (10%), CBrCl_2^- (4%) and Br^- (3%). The formation of Cl^- from the decomposition of $(\text{CCl}_3)^*$ is endothermic and hence cannot occur, $\Delta H = 52 \text{ kJ mol}^{-1}$. The formation of Br^- from the decomposition of $(\text{CBrCl}_2)^*$ is also impossible, $\Delta H = 66 \text{ kJ mol}^{-1}$. Formation of Cl^- or Br^- via nucleophilic attack on carbon by OH^- is possible but is almost certainly hindered by the four

surrounding halogen atoms. DET is endothermic to Br^- , CCl_3^- and Cl^- and does not occur. The observation of BrO^- implies that there is extraction of Br^+ with the subsequent proton transfer from BrOH to CCl_3^- . It was observed that as the number density of CBrCl_3 in the flow tube is raised, the percentage of CCl_3^- decreases and that of CBrCl_2^- increases, indicating that the following secondary reaction takes place: $\text{CCl}_3^- + \text{CBrCl}_3 \rightarrow \text{CBrCl}_2^- + \text{CCl}_4$, with $\Delta H < -15 \pm 28 \text{ kJ mol}^{-1}$. We have determined a rate coefficient of $(4.6 \pm 0.9) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for this reaction from the decreasing CCl_3^- signal as a function of CBrCl_3 number density.

3.2.5. CBrClF_2

Our measured rate coefficient for the reaction of O^- with CBrClF_2 is higher than that reported by Streit, $(7.2 \pm 2.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9]. Furthermore, there are discrepancies in the observed ionic products between the two studies which cannot be explained by the presence of both O^- and O_2^- anions simultaneously in the FA apparatus of Streit. The major ionic product we observe, but not observed by Streit, is BrClO^- . This is presumably formed from the simultaneous abstraction of Br and Cl from CBrClF_2 . The minor ionic products observed are BrO^- (11%), Br^- (6%), BrCl^- (2%), and Cl^- (1%). The formation of BrO^- , Br^- and Cl^- from the decomposition of $(\text{BrClO}^-)^*$ is endothermic, $\Delta H = 145$, $\Delta H = 13 \pm 14$ and $\Delta H = 23 \pm 14 \text{ kJ mol}^{-1}$, respectively. However, as has been suggested before, it cannot be ruled out that both Br^- and Cl^- are formed from the decomposition of $(\text{BrCl}^-)^*$ provided that BrCl^- is formed with a distribution of energies some of which are sufficient to result in dissociation.

The rate coefficient for the reaction between O_2^- and CBrClF_2 is significantly higher than that of $(5.2 \pm 1.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Streit [9]. Three ionic species, namely Br^- (89%), CBrClF_2^- (10%) and

$\text{O}_2 \cdots \text{Br}^-$ ($\approx 1\%$), are formed. The molecular anion CBrClF_2^- is formed via electron transfer from O_2^- to CBrClF_2 followed by collisional or radiative relaxation of nascent $(\text{CBrClF}_2^-)^*$. However, most of the $(\text{CBrClF}_2^-)^*$ is likely to decompose into Br^- , some of which may be clustered with O_2 generated from the electron transfer so as to produce $\text{O}_2 \cdots \text{Br}^-$ within the lifetime of the precursor ion–molecule complex $[\text{O}_2 \cdots \text{CBrClF}_2]$. Nucleophilic substitution may also be a reaction mechanism for Br^- production.

The bimolecular reaction of OH^- with CBrClF_2 , resulting in the products BrClOH^- (75%), Br^- (18%) and Cl^- (7%), is slow and is in competition with a fast three-body associative reaction. BrClOH^- is formed via abstraction of Br and Cl, the driving force for this process again being the formation of a stable difluorocarbene. The formation of the two halide anions, Br^- and Cl^- , from the decomposition of $(\text{BrClOH}^-)^*$ is endothermic by $\Delta H = 79$ and $\Delta H = 83 \text{ kJ mol}^{-1}$, respectively. Furthermore, DET leading to Cl^- or Br^- is endothermic. Therefore, both halide anions must be formed by nucleophilic attack on carbon.

3.2.6. CBr_2ClF

O^- reacts with CBr_2ClF to yield Br_2O^- (47%), CBr_2F^- (27%) and CBrClF^- (16%). Traces of BrO^- (4%), Br^- (2%), BrCl^- (2%), Cl^- (1%) and ClO^- (1%) are also observed. The formation of BrO^- from the decomposition of $(\text{Br}_2\text{O}^-)^*$ is endothermic by $\Delta H = +68 \text{ kJ mol}^{-1}$. Thus, the extraction of Br and of Br_2 is in competition. The observed Br^- can be formed via a variety of mechanisms; for examples the decomposition of $(\text{Br}_2\text{O}^-)^*$ and/or $(\text{CBrClF}^-)^*$ could lead to Br^- , e.g. $\text{O}^- + \text{CBr}_2\text{ClF} \rightarrow \text{Br}^- + \text{BrO}^- + \text{CFCl}$ ($\Delta H = -59 \text{ kJ mol}^{-1}$). It cannot be ruled out that Br^- is formed from the decomposition of $(\text{Br}_2^-)^*$, but this would require that all the $(\text{Br}_2^-)^*$ be formed with more than the 83 kJ mol^{-1} predicted by equipartition of energy within the reaction complex, and that none of the $(\text{Br}_2^-)^*$ is collisionally stabilised.

Two ionic species, namely Br^- (95%) and Cl^-

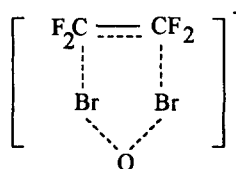
(5%), are observed for the reaction of O_2^- with CBr_2ClF . It is possible that both Br^- and Cl^- are formed via DET, e.g. $O_2^- + CBr_2ClF \rightarrow Cl^- + CBr_2F + O_2$ ($\Delta H \leq -31 \text{ kJ mol}^{-1}$), although there are competing exothermic nucleophilic attack pathways available.

OH^- reacts with CBr_2ClF to yield predominantly Br_2OH^- (82%) via abstraction of two bromine atoms, leaving a carbene $:CClF$. The abstraction of two bromine atoms may proceed in a stepwise fashion. The first step may be the abstraction of Br^\cdot by OH^- , forming an intermediate ionic complex $[HOBr^\cdot \cdots CBrClF^-]$. The second step may be the release of a Br^- from $CBrClF^-$, leading to the formation of a relatively stable $:CClF$ carbene and Br_2OH^- . Minor products observed are $CBrClF^-$ (7%) (via abstraction of Br^\cdot), Br^- (4%), Br_2^- (3%), and traces of CBr_2F^- (1%), $BrCl^-$ (1%), BrO^- (1%) and Cl^- (1%) were also observed. The Br^- anion could be produced via several channels; for example the decomposition of $(Br_2OH^-)^*$ or $(CBr_2F^-)^*$ may be exothermic, i.e. $OH^- + CBr_2ClF \rightarrow (Br_2OH^-)^* + CClF \rightarrow Br^- + BrOH + CClF$ with $\Delta H = 25 \pm 33 \text{ kJ mol}^{-1}$ and $OH^- + CBr_2ClF \rightarrow (CBr_2F^-)^* + ClOH \rightarrow Br^- + ClOH + CBrF$ with $\Delta H \leq -1 \pm 13 \text{ kJ mol}^{-1}$. It cannot be ruled out that the production of Br^- arises from the decomposition of $(Br_2^-)^*$ and $(BrCl^-)^*$. However, this requires $(Br_2^-)^*$ to be formed with more than the 32 kJ mol^{-1} predicted by the equipartition of energy, and the enthalpy of the decomposition channel of $(BrCl^-)^*$ has enough uncertainty to render it either just exothermic or just endothermic ($OH^- + CBr_2ClF \rightarrow Br^- + Cl + HBr + CFO$ ($\Delta H = 1 \pm 21 \text{ kJ mol}^{-1}$)). Nevertheless, there are several independent channels to the production of Br^- and Cl^- via nucleophilic attack on carbon.

3.2.7. CF_2BrCF_2Br

O^- reacts with CF_2BrCF_2Br to produce three ionic products: Br^- (72%), Br_2O^- (21%) and BrO^- (7%). Abstraction of two bromine atoms

from CF_2BrCF_2Br , to produce Br_2O^- , probably occurs via a five-atom-centred transition state, as illustrated below:



The decomposition of $(Br_2O^-)^*$ to BrO^- is endothermic ($O^- + CF_2BrCF_2Br \rightarrow (Br_2O^-)^* + C_2F_4 \rightarrow BrO^- + Br + C_2F_4$ ($\Delta H = +33 \text{ kJ mol}^{-1}$)). Therefore, BrO^- is formed by nucleophilic attack of O^- on a Br atom in the CF_2BrCF_2Br molecule. Hence, the production of Br_2O^- and BrO^- takes place through two competing reaction channels. Br^- cannot be produced by DET because such a process is endothermic and thus must be formed via a nucleophilic attack mechanism. It cannot be ruled out that the decomposition of $(Br_2O^-)^*$ leads to $Br^- + BrO$ because the exothermicity of the reaction is $\Delta H = -65 \text{ kJ mol}^{-1}$.

O_2^- reacts with CF_2BrCF_2Br to produce two ion products only: Br_2^- (94%) and Br^- (6%). It is difficult to explain the much higher yield of Br_2^- than of Br^- from nucleophilic attack by O_2^- on a carbon atom in the CF_2BrCF_2Br molecule. The concerted displacement of Br_2^- by O_2^- , which would involve a six-atom-centred transition state, seems unlikely because of the rapid rotation of the two CF_2Br groups about the C–C single bond of CF_2BrCF_2Br at room temperature. Therefore, it is likely that the initial step is a single electron transfer within the ionic complex $[CF_2BrCF_2Br \cdots O_2^-]$, at a larger distance than required for nucleophilic attack of O_2^- on a carbon atom. The electron transfer causes the dissociation of $(CF_2BrCF_2Br^-)^*$, yielding a nascent $(Br_2^-)^*$, in a fashion similar to electron attachment to CF_2BrCF_2Br [38,39]. The $(Br_2^-)^*$ formed in this way will be energetically unable to dissociate to Br^- and Br ($\Delta H = 71 \text{ kJ mol}^{-1}$). One cannot say with any certainty that DET to produce Br^- ,

CF_2BrCF_2 and O_2 occurs because the heat of this reaction is $\Delta H = +9 \pm 16 \text{ kJ mol}^{-1}$. However, Br^- could be formed within the complex, to produce Br^- , Br^\cdot and $2\text{CF}_2\text{O}$, in a fashion similar to the reaction of O_2^- with $\text{CH}_2\text{BrCH}_2\text{Br}$. Therefore, it cannot be ruled out that $(\text{Br}_2^-)^*$ is an intermediate in the production of Br^- . It is interesting to compare the above results with those of electron attachment. Both anion products are observed in the electron attachment process, but Br^- is by far the dominant anion with a branching ratio of 80% [39]. This must be due to the fact that the formation of Br^- and CF_2BrCF_2 following electron attachment is exothermic, but for which in the O_2^- electron transfer reaction the exothermicity is reduced by the electron affinity of O_2 , possibly rendering the reaction endothermic. Electron attachment to form Br_2^- and C_2F_4 is energetically more favourable than the production of Br^- and CF_2BrCF_2 . However, the former would require a complex rearrangement of the molecular bonds, involving the bridging of the carbon–carbon bond in the $(\text{CF}_2\text{BrCF}_2\text{Br}^-)^*$ anion by the two bromine atoms, followed by the elimination of Br_2^- (which will have insufficient energy to dissociate to Br^- and Br^\cdot) and the formation of the π -bond in C_2F_4 . On the other hand, electron attachment to form Br^- and CF_2BrCF_2 requires only the breaking of one C–Br bond in $(\text{CF}_2\text{BrCF}_2\text{Br}^-)^*$ with the retention of the electron on the departing Br atom. Taking all the above considerations into account, it is therefore not too surprising that Br^- is the dominant anion in the electron attachment process and Br_2^- is the dominant anion in the O_2^- reaction.

OH^- has a fast reaction with $\text{CF}_2\text{BrCF}_2\text{Br}$ to produce two ionic species, Br^- (40%) and Br_2OH^- (60%). It is possible for the Br^- to come from the decomposition of $(\text{Br}_2\text{OH}^-)^*$, i.e. $\text{OH}^- + \text{CF}_2\text{BrCF}_2\text{Br} \rightarrow (\text{Br}_2\text{OH}^-)^* + \text{C}_2\text{F}_4 \rightarrow \text{Br}^- + \text{BrOH} + \text{C}_2\text{F}_4$ ($\Delta H = -6 \pm 11 \text{ kJ mol}^{-1}$). It is, however, more likely that the formation of Br^- occurs via a more exothermic nucleophilic attack mechanism. DET pathways leading to the production of Br^- or Br_2^- are endothermic.

4. Discussion

4.1. Electron transfer reactions

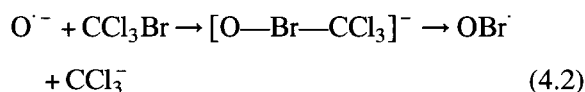
4.1.1. O^- and OH^- reactions

DET is endothermic for all the molecules studied. Energetically, non-dissociative electron transfer can be ruled out only in the reactions with CH_3Br and CF_3Br , because these are the only molecules studied with known electron affinities, $\text{EA}(\text{CH}_3\text{Br}) = 0.4 \pm 0.1 \text{ eV}$ [32] and $\text{EA}(\text{CF}_3\text{Br}) = 0.9 \pm 0.2 \text{ eV}$. However, even if non-dissociative electron transfer is exothermic to the other molecules, the lack of any parent anions indicates that it does not compete with nucleophilic attack. Thus electron transfer does not occur to any of the molecules studied.

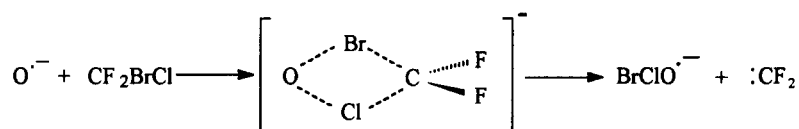
4.1.2. O_2^- reactions

Non-dissociative electron transfer is observed for the reactions with CF_3Br , CHBrCl_2 and CF_2BrCl . The electron affinities of the latter two molecules are not reported, but they must obviously be greater than 0.45 eV. Although CH_3Br has a similar electron affinity to O_2 , with the enthalpy of the reaction $\text{O}_2^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Br}^- + \text{O}_2$ being $\Delta H = 4 \pm 10 \text{ kJ mol}^{-1}$, no parent anion is observed. DET is exothermic to produce Br^- from the reaction with CF_2Br_2 , to produce Br^- and Cl^- from the reactions with CBrCl_3 and CBr_2ClF and to produce Br_2^- from the reactions with $\text{CF}_2\text{BrCF}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{Br}$. On the other hand, DET to produce Br^- is endothermic from the reactions with CH_3Br , $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_2\text{BrCH}_2\text{Cl}$ and CF_3Br , and is also endothermic to produce Cl^- from $\text{CH}_2\text{BrCH}_2\text{Cl}$. For the reactions with CH_2Br_2 , CHBrCl_2 , CHBr_2Cl , $\text{CH}_2\text{BrCH}_2\text{Br}$, CFBr_3 , CBrClF_2 and $\text{CF}_2\text{BrCF}_2\text{Br}$, errors in the reaction energetics make decisions on the production of Br^- by DET inconclusive. This is also true for Cl^- from CHBrCl_2 . The production of Cl^- via DET to CHBr_2Cl and CF_2BrCl is, however, definitely endothermic. When DET is endothermic, the observed atomic anion products must be pro-

duced via nucleophilic attack. Whether DET or nucleophilic attack is the preferred mechanism for the reactions when both are energetically viable is difficult to say. Electron transfer is usually a long-range process, i.e. transfer occurs at impact parameters considerably larger than those needed for nucleophilic attack. However, presumably only when the potential surface of the neutral is crossed at its minimum by that of the corresponding anions' potential surface, i.e. there is little or no activation energy, will this long-range electron transfer process occur with any efficiency. Nevertheless, if this is the case,



For many of the reactions, products such as OBr_2^- , OBrCl^- , HOBr_2^- and HOBrCl^- are observed, requiring the formation of difluorocarbene or tetrafluoroethene, with the exception of $\text{O}^{\cdot-}$ and OH^- with CFBr_2Cl (CFCl) and OH^- with CFBr_3 (CFBr). For the methanes, presumably this occurs via a four-atom-centred transition state as illustrated below for the reaction of $\text{O}^{\cdot-}$ with CF_2BrCl :

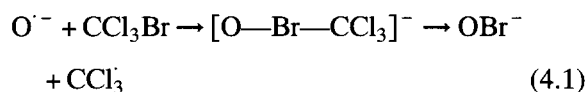


the long-range nature of the electron transfer mechanism leading to an excited parent anion, with sufficient energy to dissociate, will generally take place to the exclusion of other more intimate reaction pathways leading to the dissociative products; and this is unlikely for the majority of the neutral molecules studied here. We therefore conclude that when an electron transfer mechanism, leading to non-dissociative or dissociative products, is observed in parallel or in competition with nucleophilic attack, e.g. the reaction of O_2^- with CF_3Br , then these processes must both be proceeding through a reaction complex.

4.2. Nucleophilic attack on bromine and chlorine

4.2.1. $\text{O}^{\cdot-}$ and OH^- reactions

Attack on bromine and chlorine can be envisaged to proceed through an intermediate complex, followed by complex decomposition, for example:



Similarly, for the reaction with $\text{CF}_2\text{BrCF}_2\text{Br}$, a five-atom-centred transition state must be involved. When this type of reaction occurs, it is a substantial, if not dominant, mechanism. This is probably because of the presence of fluorine in the neutral product.

For some of the reactions with $\text{O}^{\cdot-}$, OBr^- (or OCl^-) is observed in addition to OBr_2^- (or OBrCl^-). It is thermodynamically impossible to produce these products via the dissociation of OBr_2^- etc. Therefore, when OBr_2^- and OBr^- are observed as products from the same reaction, they are produced via competing reaction pathways. Although the production of OBr^- etc. is endothermic via this mechanism, for some of these reactions the production of Br^- is exothermic. However, it is unlikely that $(\text{OBr}_2^-)^*$ etc. gain enough energy from the reaction to enable dissociation to take place. For the analogous reactions with OH^- , the $\Delta H_f(\text{OHBr}^-)$ is unreported and, therefore, no conclusions can be drawn concerning the energetics of the reactions.

Some separate comments are now made on the reactions of $\text{O}^{\cdot-}$ and OH^- with the molecules studied.

4.2.2. $O^{\cdot -}$ reactions

The production of $OBr^{\cdot -}$ is exothermic for all the molecules studied and is observed for all reactions, except for those with CH_3Br , $CHBrCl_2$, CH_2BrCH_2Br and CH_2BrCH_2Cl , for which no nucleophilic attack on bromine is observed. This is presumably because of an alternative proton transfer channel and/or less steric hindrance to attack on carbon. Nucleophilic attack on chlorine is observed for all but two of the chlorinated molecules, the exceptions being the reactions with CH_2BrCH_2Cl and $CHBrCl_2$.

The abstraction of $Br^{\cdot +}$ is found to be the more favoured mechanism over the abstraction of $Br^{\cdot -}$ when both are observed to occur. Similarly, for nucleophilic attack on chlorine, abstraction of $Cl^{\cdot +}$ is a more favoured mechanism than abstraction of $Cl^{\cdot -}$. Thus it appears that the carbon preferentially retains both the bonding electrons when the $C-Br/C-Cl$ bond is ruptured, indicating that the electron affinities of the carbon-containing neutral are greater than that of $OBr^{\cdot -}/OCl^{\cdot -}$.

4.2.3. $OH^{\cdot -}$ reactions

Abstraction of (only) $Cl^{\cdot -}$ is not observed from any of the chlorine-containing molecules, whereas extraction of $Br^{\cdot -}$ is observed from several of the molecules. One product of note, observed from the reaction with $CBrCl_3$ and $CFBr_2Cl$, is $OBr^{\cdot -}$ and not $HOBr^{\cdot -}$. To explain this product, we propose that a reaction complex is formed and that either hydrogen transfer or proton transfer from $OH^{\cdot -}$ to the methane under attack is occurring during the abstraction of $Br^{\cdot -}$ or $Br^{\cdot +}$, respectively. As the electron affinity of $OBr^{\cdot -}$ must be greater than that of $HOBr$, the preferred initial mechanism is extraction of $Br^{\cdot +}$ followed by proton transfer.

4.2.4. $O_2^{\cdot -}$ reactions

Although exothermic reaction pathways are available, nucleophilic attack on bromine or chlorine is not observed from the reactions with $O_2^{\cdot -}$. However, for some of the reactions, possible

neutral products are $OBr^{\cdot -}$ and $OCl^{\cdot -}$, although it is probable that these are formed only after preferential attack on carbon by $O_2^{\cdot -}$.

4.3. Nucleophilic attack on hydrogen

4.3.1. $O^{\cdot -}$ and $OH^{\cdot -}$ reactions

Attack on hydrogen-containing molecules can be envisaged to proceed through an intermediate complex. Proton transfer from the neutral molecule to the anion is the dominant process for the reactions with singly hydrogenated molecules. The minor reaction channels involve nucleophilic attack on carbon. In the reactions with the multiply hydrogenated methanes, proton transfer from CH_2Br_2 is observed to both $O^{\cdot -}$ and $OH^{\cdot -}$. Proton transfer from CH_3Br to $O^{\cdot -}$ and $OH^{\cdot -}$ is endothermic and is therefore not observed. Although proton transfer from CH_3Br to $O^{\cdot -}$ is endothermic, nucleophilic attack on hydrogen is still observed to occur, via the extraction of both $H^{\cdot -}$ (to form $OH^{\cdot -}$) and $H_2^{\cdot +}$ (to form H_2O). Unlike the singly hydrogenated methanes studied, it is important to note for the reactions of the multiply hydrogenated methanes that, although nucleophilic attack on hydrogen is observed, the most dominant reaction mechanism is nucleophilic attack on carbon. A possible reason for this is that the increased hydrogen content provides the attacking nucleophile with greater access to the carbon, i.e. there is less of a steric hindrance.

In the reactions with the hydrogenated ethanes, direct evidence of nucleophilic attack on hydrogen is observed only from the reaction of $O^{\cdot -}$ with C_2H_5Br , for which proton transfer occurs. However, it cannot be ruled out that the only other product observed ($Br^{\cdot -}$) in the reactions with both $O^{\cdot -}$ and $OH^{\cdot -}$, could result from initial proton transfer, followed by dissociation of the anion product.

4.3.2. $O_2^{\cdot -}$ reactions

Proton transfer from the multiply hydrogenated molecules to $O_2^{\cdot -}$ (forming HO_2) is endothermic and is therefore not observed. Of

the two singly hydrogenated molecules, proton transfer is exothermic from CHBrCl_2 but it is not observed.

4.4. Nucleophilic attack on carbon

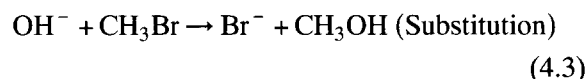
4.4.1. O^- reactions

For the reactions of the molecules investigated with O^- , seven of the observed anionic products are considered to result from nucleophilic attack by the anion on carbon; these are Br^- , Br_2^- , Cl^- , Cl_2^- , BrCl^- , F^- and BrF^- . A mixture of atomic and dihalide anion products was observed in our study of O^- and O_2^- with several CFCs [12]. There, we suggested that if each of these anions is produced independently from the same transition complex, then this would require the complex to have many exit pathways; and the simplicity of the systems under investigation mitigates against this. We also suggested that where the atomic and dihalide anions are observed as products from the same reaction, the atomic anions could be produced from the decomposition of the excited dihalide anion. We concluded that this was possible only if the dihalide anion was formed with more energy than predicted by the QET and the equipartition of energy. To resolve this, we suggested that the QET was not applicable because of how the bonds broke in the intermediate complex. As the bond(s) between the dihalide anion and the neutral gradually lengthen, bond breakage preferentially occurs closest to the neutral. This means that more of the energy contained in the bond is retained by the anion, suggesting that the dihalide anions are created with a distribution of energies, some with enough energy to result in dissociation [12]. In this study, this explains the observation of Br^- and F^- from $(\text{BrF}^-)^*$, from the reaction of O^- with CF_3Br and the observation of Br^- and Cl^- from $(\text{BrCl}^-)^*$, from the reactions of O^- with CF_2BrCl and CFBr_2Cl .

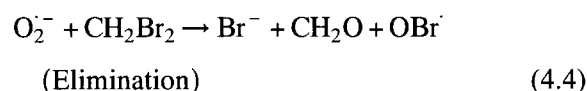
4.4.2. O_2^- and OH^- reactions

For the reactions with O_2^- and OH^- , nucleophilic attack is the only viable reaction mechanism. This leads to less diversity in the observed products. Br^- is the only atomic anion observed from the reactions with OH^- and, with the exception of the reaction with CHBrCl_2 (where BrCl^- is also observed), reactions with O_2^- produce only Br^- and Cl^- . Therefore, a simpler reaction process for nucleophilic attack by O_2^- and OH^- must be occurring than for O^- .

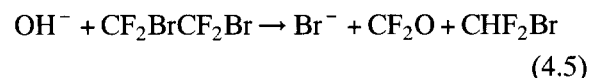
For the reactions with the methanes, this is envisaged to proceed through a complex which then dissociates to give Br^- and, to allow for an energetically favourable pathway, an alcohol or peroxide (substitution) or HBr (OBr^-) plus another neutral (elimination). For examples



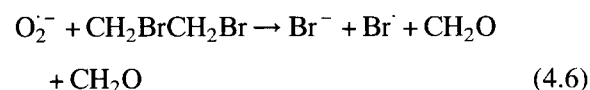
and



Similarly, the reactions with the ethanes probably proceed through a complex which then dissociates to give Br^- . For the reactions with OH^- , the most exothermic reaction pathways involve breaking the C–C bond in the ethane, with the O and H bonded to different carbons, e.g.



For the reactions with O_2^- , the most exothermic reactions again involve elimination of Br^- , with the subsequent elimination of Br^- and the breaking of the C–C bond with an O bonded to either carbon, e.g.



5. Summary

A comprehensive study of the reactions of O^- , O_2^- and OH^- with a variety of brominated compounds has been presented. With the exception of two reactions, namely OH^- with CF_3Br and with CF_2BrCl , the measured bimolecular rate coefficients are at, or close to, the collisional value. For the two slow bimolecular reactions, there is direct competition with fast ternary association reactions. For O_2^- , because of the low electron affinity of O_2 , electron transfer occurs for a significant number of reactions; non-dissociative electron transfer occurs in the reactions with CF_3Br , $CHBrCl_2$ and CF_2BrCl . It is also possible for a number of anion products to be produced by dissociative electron transfer from O_2^- , for the reactions with CF_2BrCF_2Br (Br_2^- , Br^-), CH_2BrCH_2Br (Br_2^- , Br^-), $CBrCl_3$ (Br^- , Cl^-), CF_2BrCl (Br^-), $CHBrCl_2$ (Br^-), $CHBr_2Cl$ (Br^-), CH_2Br_2 , CH_2Br_2 (Br^-), CF_2Br_2 (Br^-) and CBr_2ClF (Br^- , Cl^-), although nucleophilic attack can also explain these observed products. However, for some of the above mentioned reactions, nucleophilic attack pathways are definitely occurring in parallel with DET, suggesting that most of the reactions proceed through a reaction complex. Comparison of the number and variety of product channels shows that the strongest nucleophile in this study is O^- , followed closely by OH^- , with the weakest being O_2^- . This is simply because energetics demand that O^- and OH^- react by nucleophilic attack rather than by electron transfer processes. It is noticed from several reactions that the most favoured reaction channel is governed by the neutral rather than the anionic product. This is highlighted in the reactions of both O^- and OH^- with CF_2Br_2 , CF_2BrCl and CF_2BrCF_2Br . In all of these reactions the major neutral product is C_nF_{2n} ($n = 1, 2$), allowing the formation of products such as Br_2O^-/Br_2OH^- and $BrClO^-/BrClOH^-$.

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