

# Selected ion flow tube study of the reactions of $O^-$ and $O_2^-$ with $CHCl_2F$ , $CHClF_2$ , $CHF_3$ , $CH_2ClF$ , $CH_2F_2$ , $CH_3F$ , $CHF_2CHF_2$ , $CH_2FCF_3$ , and $CH_3CHF_2$

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Received 17 January 1997; accepted 12 February 1997

## Abstract

In this paper we report the reactions of  $O^-$  and  $O_2^-$  with several saturated hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) in a 0.5 Torr helium buffer gas at about 300 K using a selected ion flow tube. The reaction rate coefficients and branching ratios determined for the large number of reactions studied are presented.  $O^-$  is found to react with all the molecules studied, and several distinct reaction processes are observed. These include nucleophilic attack on chlorine, nucleophilic attack on carbon, and hydrogen, proton, and  $H_2^+$  abstraction. Nucleophilic attack on carbon is found to dominate the  $O_2^-$  reactions with the HCFCs. Bimolecular reactions of  $O_2^-$  with the HFCs do not occur. © 1997 Elsevier Science B.V.

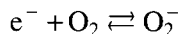
**Keywords:** Ion/molecule reactions; Selected ion flow tube; Hydrochlorofluorocarbons; Hydrofluorocarbons

## 1. Introduction

The understanding of many of the sensitive techniques and the instrumentation used for trace gas detection, which are based on ionic reactions, critically depends on our knowledge of the ion chemistry involved. Examples are instruments such as the electron capture detector (ECD) [1,2], the ion mobility spectrometer (IMS) [3,4], and the chemical ionisation mass spectrometer (CIMS) [5–8]. The response of all these instruments depends on electron–molecule and ion–molecule reactions of both thermalised and energetic charged particles. In negative ion mode

$O^-$ ,  $OH^-$ , and  $O_2^-$  are commonly used as the active anions, either directly as in the case for the IMS and the CIMS or indirectly for the ECD. A number of recent studies by us [9–11] have illustrated the complex ion chemistry occurring in IMS systems.

The ECD is sensitive to many chlorofluorocarbons (CFCs) by electron attachment, whereas many of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) do not have a response in the ECD. A response can be obtained by doping the buffer gas, for example with  $O_2$  or  $N_2O$  [1]. For  $O_2$  doping, taking a simplistic view, an equilibrium is rapidly established:



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When the  $O_2^-$  anions are consumed by reaction with a compound, this equilibrium rapidly responds, reducing the electron concentration, so giving an ECD signal. The removal of  $O^-$  by reactions can be exploited in a similar manner.  $O^-$  is generally formed by dissociative electron attachment to  $N_2O$ , and because of its high reactivity this allows the ECD to give a response to many compounds. Whilst these simple mechanisms afford an understanding of the enhancement of the ECD response, an earlier study of ours [12] has suggested that other factors, in particular reactions of non-thermal electrons and anions, need to be taken into account to explain some of the observations.

This paper reports the reactions of thermalised  $O^-$  and  $O_2^-$  with a number of hydrogen and halogen containing saturated molecules which do not have a large response in the ECD under normal (undoped) operation; namely,  $CHCl_2F$ ,  $CHClF_2$ ,  $CHF_3$ ,  $CH_2ClF$ ,  $CH_2F_2$ ,  $CH_3F$ ,  $CHF_2CHF_2$ ,  $CH_2FCF_3$ , and  $CH_3CHF_2$ . These reactions have been studied using the selected ion flow tube (SIFT) technique at a temperature of about 300 K. Many of the reactions are reported here for the first time, and, until recently, no studies of these or closely related compounds have been undertaken with a SIFT apparatus. Using a flowing afterglow apparatus, Tanaka et al. [13] studied the reactions of  $O^-$  with the chemical series  $CH_3X$ , where X is F, Cl, and Br, and Streit [14] investigated the reactions of  $O^-$  and  $O_2^-$  with  $CHBr_3$ . Of more relevance to this study, Dawson and Jennings [15] employed an ion cyclotron resonance (ICR) mass spectrometer to examine the production of radical anions from the reactions of  $O^-$  with  $CH_2F_2$  and  $CH_3F$ . Most recently Morris et al. [16] have investigated the reactions of  $O^-$  and  $O_2^-$  with several halogenated molecules including  $CH_2FCF_3$  and  $CHBrF_2$  using a SIFT. The reactions of  $O^-$  and  $O_2^-$  with a number of CFCs and related compounds have already been studied by us, and are the subject of a publication [12].

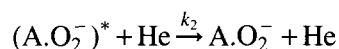
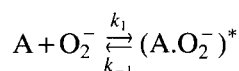
## 2. Experimental details

The SIFT apparatus, experimental technique, and analysis of data have been extensively reviewed [17]. Therefore, only a brief description of the points that are pertinent to this study are presented here. The anions were created in a high pressure ion source;  $O^-$  by dissociative electron attachment to  $N_2O$ , and  $O_2^-$  from electron attachment to  $O_2$  in an oxygen/nitrogen ( $\sim 1/5$ ) mix. 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 ( $\sim 150 \text{ Torr l s}^{-1}$ ) at a pressure of 0.5 Torr. Neutral reagents were injected into the flow tube in a controlled manner to give a reactant neutral number density up to  $\sim 10^{12} \text{ cm}^{-3}$ . The precursor and product anions were sampled through a Faraday plate (at the detection end of the flow tube), mass analysed using a second quadrupole mass spectrometer, and detected by a channeltron electron multiplier. The decrease in the reactant anion signal was monitored at different neutral flows (i.e. for a large range of neutral reagent concentration) to obtain the reaction rate coefficient. Branching ratios of the product anions were obtained by extrapolating to zero neutral reactant number density to take account of possible secondary reactions. The mass discrimination of the detection system was corrected for by using a standard method as described by Adams and Smith [18]. Values of reaction rate coefficients and product percentages are considered to be accurate to  $\pm 20\%$ , although they are generally reproducible to better than this.

The Faraday plate current is a measure of the total charge reaching the end of the flow tube. However, the number of charged species reaching the Faraday plate is always less than the number of ions injected into the flow, because only a fraction of the charged particles will be incident on the plate and because of diffusional losses. The radial diffusion of electrons is very rapid, so that every encounter leading to electron

detachment effectively decreases the number of charge carriers by one. Hence, the branching ratio for electron detachment can be obtained from the maximum observed decrease in the plate current. Ion–molecule reactions do not change the number of charged species. However, an ion–molecule reaction can change the current measured at the Faraday plate, because the rate of diffusion is dependent on the mass of the anion. Thus, a reaction which produces an anion of heavier mass than the reactant anion will lead to a decrease in the diffusional loss of anions and hence an increase in the Faraday plate current. An approximate correction derived from a simple model has been applied to the Faraday plate measurements to prevent this diffusional mass discrimination effect from distorting the branching ratios for electron detachment determined in this work. A more detailed treatment of the effects of diffusional loss upon the kinetic analysis will be the subject of a future communication [19].

Some association reactions were observed with  $O_2^-$ . For these the mechanism is:



and the overall rate of reaction is:

$$d[O_2^-]/dt = -\{k_2 k_1 [He]/(k_{-1} + k_2 [He])\} [A][O_2^-]$$

It is usual to define an effective two-body rate coefficient:

$$k_2^{\text{eff}} = k_2 k_1 [He]/(k_{-1} + k_2 [He])$$

For some of the ternary processes the pressure dependence of  $k_2^{\text{eff}}$  was determined by varying the helium pressure in the SIFT over the range 0.3 to 0.75 Torr.  $k_2^{\text{eff}}$  is directly proportional to the helium number density in the pressure ‘unsaturated’ region ( $k_{-1} \gg k_2 [He]$ ), and a three body association rate coefficient is quoted:

$$k_3 = k_2(k_1/k_{-1})$$

As the helium pressure increases,  $k_2^{\text{eff}}$  ceases to increase linearly with helium number density, passing through a ‘fall-off’ region ( $k_{-1} \sim k_2 [He]$ ), before levelling out to a constant value ( $k_1$ ) in the pressure ‘saturated’ region ( $k_{-1} \ll k_2 [He]$ ). For the reactions of  $O_2^-$  with  $CHF_2CHF_2$ ,  $CH_2FCF_3$ , and  $CH_3CHF_2$  it was difficult to show conclusively that the reactions were taking place in the ‘unsaturated’ region. For these reactions, the effective two-body rate coefficient is quoted at a particular pressure of helium.

### 3. Results and thermochemical analysis

The measured rate coefficients ( $k_{\text{exp}}$ ), the collisional rate coefficients ( $k_c$ , calculated using the average dipole orientation (ADO) theory [20], with dipole moments and polarisabilities taken from [21]), and the product branching ratios from the reactions studied are summarised in Table 1. Tables 2 and 3 summarise and compare the  $O^-$  and  $O_2^-$  reaction pathways, respectively, from this study and from our earlier study [12]. Table 4 summarises new thermochemical data deduced from our results.

The thermochemical analysis and preliminary discussion of the reaction pathways to form the various products in the reactions follow. Our analysis is restricted to enthalpy and we have ignored possible entropic factors. Entropic factors will oppose the endothermicity for reactions in which there is an increase in the number of species between reactants and products. For most of the observed reactions in this study there is either no change or an increase in the number of species. The enthalpies of formation for anions and neutrals at 298 K are taken from Lias et al. [22] unless otherwise stated. For the reaction pathways which were not observed, and where the required thermochemical data are available, Tables 2 and 3 indicate whether the pathway is exothermic (exo) or endothermic (endo).

Table 1

The experimental rate coefficients,  $k_{\text{exp}}$ , and the product ion distributions (percentages) for the reactions of  $\text{O}^-$  and  $\text{O}_2^-$  with the series of molecules investigated in this study

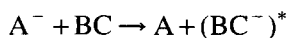
Reactant molecule	$\text{O}^-$ reaction	$\text{O}_2^-$ reaction	Reactant molecule	$\text{O}^-$ reaction	$\text{O}_2^-$ reaction
$\text{CHCl}_2\text{F}$ (HCFC-21)	2.0(–9) [2.1(–9)] $\text{Cl}^-$ 42% $\text{OCl}^-$ 5% $\text{ClF}^-$ 3% $\text{CCl}_2\text{F}^-$ 50%	5.9(–10) [1.6(–9)] $\text{Cl}^-$ 100%	$\text{CHF}_2\text{CHF}_2^{\text{a}}$	1.9(–9)  $\text{e}^-$ 85% $\text{F}^-$ 4% $\text{HF}_2^-$ 2% $\text{C}_2\text{F}_4\text{O}^-$ 9%	$k_2^{\text{eff}} = 1.9(–10)$ at 0.49 Torr He $\text{C}_2\text{H}_2\text{F}_4\text{O}_2^-$ 100%
$\text{CHClF}_2$ (HCFC-22)	2.4(–9) [2.2(–9)] $\text{F}^-$ 5% $\text{Cl}^-$ 55% $\text{HClO}^-$ 15% $\text{CClF}_2^-$ 25%	5.2(–10) [1.7(–9)] $\text{Cl}^-$ 84% $\text{HClO}_2^-$ 16%	$\text{CH}_2\text{FCF}_3^{\text{a,b}}$ (HFC-134a)	3.2(–9)  $\text{C}_2\text{F}_4^-$ 100%	$k_2^{\text{eff}} = 9.5(–11)$ at 0.49 Torr He $\text{C}_2\text{H}_2\text{F}_4\text{O}_2^-$ 100%
$\text{CHF}_3$ (HFC-23)	1.9(–9) [2.1(–9)] $\text{e}^-$ 30% $\text{OH}^-$ 4% $\text{F}^-$ 16% $\text{HF}_2^-$ 3% $\text{CF}_3^-$ 47%	$k_3 = 5(–28)$ 100% $\text{CHF}_3\text{O}_2^-$	$\text{CH}_3\text{CHF}_2^{\text{a}}$ (HFC-152)	2.2(–9)  $\text{e}^-$ 65% $\text{H}_2\text{O.F}^-$ 25% $\text{C}_2\text{H}_2\text{F}_2^-$ 10%	$k_2^{\text{eff}} = 1.1(–11)$ at 0.49 Torr He $\text{CH}_3\text{CHF}_2\text{O}_2^-$ 100%
$\text{CH}_2\text{ClF}^{\text{a}}$ (HCFC-31)	2.4(–9)  $\text{Cl}^-$ 55% $\text{CFCl}^-$ 45%	1.0(–9)  $\text{Cl}^-$ 100%			
$\text{CH}_2\text{F}_2^{\text{a}}$ (HFC-32)	1.8(–9)  $\text{e}^-$ 38% $\text{OH}^-$ 25% $\text{CF}_2^-$ 37%	$k_3 = 1.5(–28)$  $\text{CH}_2\text{F}_2\text{O}_2^-$ 100%			
$\text{CH}_3\text{F}$ (HFC-41)	1.4(–9) [2.4(–9)] $\text{OH}^-$ 68% $\text{F}^-$ 1% $\text{CHF}^-$ 31%	$\text{CH}_3\text{F.O}_2^-$ 100% (See text)			

<sup>a</sup>The polarisabilities of these molecules are unknown.

<sup>b</sup>The dipole moment of this molecule is unknown.

The  $k_{\text{exp}}$  values are quoted as, for example, 1.9(–9) meaning  $1.9 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and below them in square brackets in the same style are the collisional rate coefficients,  $k_{\text{c}}$ , calculated using the ADO formulation [20]. The estimated uncertainty in the measured rate coefficients is  $\pm 20\%$ . For association reactions, the three body rate coefficient is given when a study of the pressure dependence of the effective bimolecular rate coefficient,  $k_2^{\text{eff}}$ , has clearly demonstrated that the process occurs in the unsaturated region (see text) and is represented by  $k_3$  (units of  $\text{cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$ ), otherwise  $k_2^{\text{eff}}$  is given at a particular helium pressure.

Before starting a discussion of the various reactions, it will be useful to give a set of working definitions of the signatures of the reaction mechanisms mentioned in the following text. Electron transfer simply means that the electron on the reactant anion is transferred to the neutral:



If the exothermicity of this reaction pathway is sufficient the resulting product anion may dissociate:



and this is referred to as dissociative electron transfer. Note that the electron transfer could take place by a long range process (as implied

Table 2

Summary of reaction pathways for the reactions of  $O^-$  with the molecules presented in this study and from an earlier study of ours on a number of halogenated methanes [12]

Molecule	C Nu	Cl Nu	H abstraction	H <sup>+</sup> abstraction	H <sub>2</sub> <sup>+</sup> abstraction	e <sup>-</sup> detachment	Others
CHCl <sub>3</sub> F	45	5	Exo	50	–	Exo	
CHClF <sub>2</sub>	60	15 (HClO <sup>-</sup> )	Exo	25	–	Exo	
CHF <sub>3</sub>	19	–	4	47	–	30	
CH <sub>2</sub> ClF	55	Uncertain <sup>a</sup>	Exo	Unknown <sup>b</sup>	45	Exo	
CH <sub>2</sub> F <sub>2</sub>	Exo	–	25	Uncertain <sup>c</sup>	37	38	
CH <sub>3</sub> F	1	–	68	Unknown <sup>d</sup>	31	Uncertain <sup>e</sup>	
CHF <sub>2</sub> CHF <sub>2</sub>	15	–	Unknown <sup>f</sup>	Unknown <sup>f</sup>	Unknown <sup>f</sup>	85	
CH <sub>2</sub> FCF <sub>3</sub>	Exo	–	Endo	Endo <sup>g</sup>	100	Unknown <sup>h</sup>	
CH <sub>3</sub> CHF <sub>2</sub>	Exo	–	Exo	Unknown <sup>i</sup>	10	65	25 (H <sub>2</sub> O.F <sup>-</sup> )
CCl <sub>4</sub>	20	80	–	–	–	Exo	
CCl <sub>3</sub> F	40	60	–	–	–	Exo	
CCl <sub>2</sub> F <sub>2</sub>	60	40	–	–	–	Exo	
CClF <sub>3</sub>	100	Endo	–	–	–	Endo <sup>j</sup>	
CF <sub>4</sub>	Exo	–	–	–	–	Endo	
CHCl <sub>3</sub>	32	20	Exo	48	–	Exo	
CH <sub>2</sub> Cl <sub>2</sub>	19	1	Exo	25	55	Exo	
CH <sub>3</sub> Cl	40	Uncertain <sup>k</sup>	45	Endo	15	Endo	

<sup>a</sup> $O^- + CH_2ClF \rightarrow OCl^- + CH_2F$   $\Delta H = 2 \pm 12$  kJ mol<sup>-1</sup>.

<sup>b</sup>Heat of formation of CHClF<sup>-</sup> is unknown,  $\Delta H = 192 + \Delta_f H(CHClF^-)$  kJ mol<sup>-1</sup>.

<sup>c</sup> $O^- + CH_2F_2 \rightarrow CHF_2^- + OH$   $\Delta H = 20 \pm 29$  kJ mol<sup>-1</sup>.

<sup>d</sup>Heat of formation of CH<sub>2</sub>F<sup>-</sup> is unknown,  $\Delta H = 178 + \Delta_f H(CH_2F^-)$  kJ mol<sup>-1</sup>.

<sup>e</sup> $O^- + CH_3F \rightarrow e^- + CHF + H_2O$   $\Delta H = 6 \pm 12$  kJ mol<sup>-1</sup>.

<sup>f</sup>Heats of formation of CHF<sub>2</sub>CHF<sub>2</sub> and CF<sub>2</sub>CF<sub>2</sub> both unknown.

<sup>g</sup> $O^- + CH_2FCF_3 \rightarrow CHF_2CF_3^- + OH$   $\Delta H = 22 \pm 19$  kJ mol<sup>-1</sup>.

<sup>h</sup>Heat of formation of CF<sub>3</sub>CF is unknown,  $\Delta H = 546 + \Delta_f H(CF_3CF)$  kJ mol<sup>-1</sup>.

<sup>i</sup>Heat of formation of CH<sub>3</sub>CF<sub>2</sub> is unknown,  $\Delta H = 432 + \Delta_f H(CH_3CF_2)$  kJ mol<sup>-1</sup>.

<sup>j</sup>Taking EA(ClF) = 2.9 ± 0.2 eV.

<sup>k</sup> $O^- + CH_3Cl \rightarrow OCl^- + CH_3$   $\Delta H = 12 \pm 18$  kJ mol<sup>-1</sup>.

The numbers refer to the total percentage branching ratios for the various channels. C Nu and Cl Nu refer to nucleophilic attack on carbon and chlorine, respectively. An indication as to whether a particular reaction pathway, which is not observed, is exothermic (exo) or endothermic (endo) is given.

above) or alternatively through a collision complex:



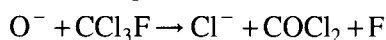
The mechanism referred to in the text as nucleophilic attack on an atom 'X' in the neutral molecule is defined by the resulting product to which A or A<sup>-</sup> is bound. For example (taken from [12]):



and



are nucleophilic attack on chlorine, whereas

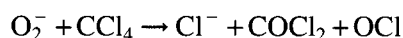


(or COClF + Cl) (35%)

and



are nucleophilic attack on carbon. There is, of course, some ambiguity with this working definition when dealing with molecular anions. For example, is the reaction:



to be defined as nucleophilic attack on carbon or chlorine? Under these circumstances we will refer to the process as nucleophilic attack on carbon, because a carbon–chlorine bond has been broken.

Hydrogen, proton, and H<sub>2</sub><sup>+</sup> abstraction are, respectively:



Table 3

Summary of reaction pathways for the reactions of  $O_2^-$  with the molecules presented in this study and from an earlier study of ours on a number of halogenated methanes [12]

Molecule	C Nu	$HClO_2^-$	$e^-$ transfer <sup>a</sup>	Three body association
$CHCl_2F$	100	Exo <sup>b</sup>		Exo
$CHClF_2$	84	16		Exo
$CHF_3$	Exo	–		100
$CH_2ClF$	100	Exo <sup>b</sup>		Exo
$CH_2F_2$	Exo	–		100
$CH_3F$	Exo	–		100
$CHF_2CHF_2$	Unknown <sup>c</sup>	–		100
$CH_2FCF_3$	Exo	–		100
$CH_3CHF_2$	Exo	–		100
$CCl_4$	100	–	Exo	Exo
$CCl_3F$	90	–	10	Exo
$CCl_2F_2$	50	–	50	Exo
$CClF_3$	<sup>d</sup>	–		<sup>d</sup>
$CF_4$	Endo	–		Exo
$CHCl_3$	100	Exo <sup>b</sup>	Exo	Exo
$CH_2Cl_2$	100	Endo		Exo
$CH_3Cl$	100	Endo		Exo

<sup>a</sup> The electron affinities for the molecules of this study and the majority of molecules from the previous study [12] are unknown.

<sup>b</sup> This assumes that  $\Delta_f H(HClO_2^-) < -321 \text{ kJ mol}^{-1}$ .

<sup>c</sup>  $\Delta_f H(CHF_2CHF_2)$  and  $\Delta_f H(CF_2CF_2)$  are unknown.

<sup>d</sup> For this molecule two and three body processes are in competition.

The numbers refer to the total percentage branching ratios for the various channels. C Nu refers to nucleophilic attack on carbon. An indication as to whether a particular reaction pathway, which is not observed, is exothermic (exo) or endothermic (endo) is given.

and



In our experiments the product anions are identified by mass analysis. The product neutrals are not identified but are inferred through a combination of thermochemistry and mass balance. There are inevitably some reactions for which the observations and thermochemistry are compatible with more than one set of neutral products. When this is the case the most likely exothermic reaction pathways leading to the observed anion product are given.

### 3.1. $O^-$ reactions

The rate coefficients and branching ratios for the reactions with the molecules of this study are given in Table 1. Table 2 summarises the  $O^-$  reaction pathways and includes results from an earlier study of ours for  $O^-$  reactions with a series of halogenated methanes [12].

Table 4

Thermodynamic bounds established from the thermochemistry of the reported reactions

Enthalpies of formation		
Species	$\Delta_f H(298\text{ K})\text{ (kJ mol}^{-1}\text{)}^{-1}$	
$\text{CCl}_2\text{F}^-$	$< -268^a$	
$\text{CHF}_2\text{CHF}_2$	$> -1009^b$	
$\text{CClF}^-$	$< +89^c$	
$\text{C}_2\text{H}_2\text{F}_2^-$	$< -151^d$	
$\text{CH}_2\text{CF}$	$< +195^e$	
$\text{HClO}_2^-$	$< -321^f$	
Electron affinities		
Species	EA(298 K) (kJ mol <sup>-1</sup> )	EA(298 K) eV
HClO	$> +110^g$	$> 1.14$
CHClF	$< +174^h$	$< 1.80$

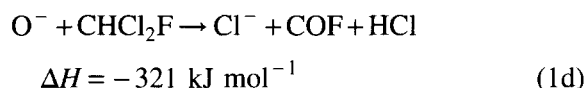
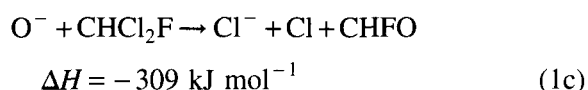
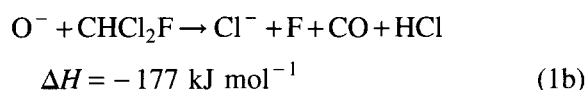
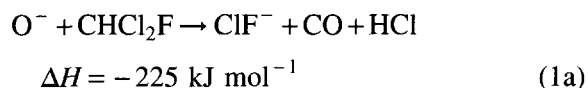
<sup>a</sup> Determined from  $O^- + CCl_3F \rightarrow CCl_2F + OCl$  [12].

<sup>b–g</sup> From reactions (4e), (7d), (9a), (9e), (11b) and (2h), respectively.

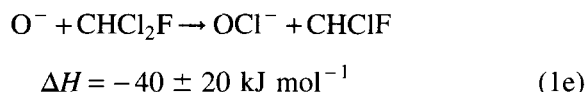
<sup>h</sup> See Section 4.2.

### 3.1.1. $\text{CHCl}_2\text{F}$

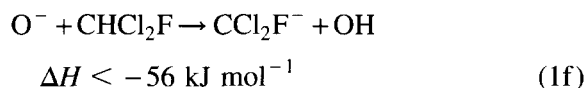
The reaction with  $\text{O}^-$  is fast, with a rate coefficient of  $2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The anion products observed are  $\text{Cl}^-$  (42%),  $\text{OCl}^-$  (5%),  $\text{ClF}^-$  (3%), and  $\text{CCl}_2\text{F}^-$  (50%). Nucleophilic attack on carbon can lead to the formation of the  $\text{ClF}^-$  and  $\text{Cl}^-$  anions:



$\text{OCl}^-$  is formed by nucleophilic attack on chlorine, via the following reaction pathway:

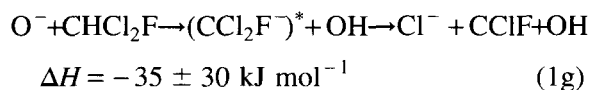


Proton abstraction to form the neutral OH leads to the major product  $\text{CCl}_2\text{F}^-$ . The enthalpy of formation of  $\text{CCl}_2\text{F}^-$  is not known, but the results from the reaction of  $\text{O}^-$  with  $\text{CCl}_3\text{F}$  [12] suggest a value of  $< -268 \text{ kJ mol}^{-1}$ . Hence, the exothermicity of the proton abstraction reaction must be at least  $56 \text{ kJ mol}^{-1}$ :



The possible competing channel of hydrogen abstraction to form  $\text{OH}^- + \text{CCl}_2\text{F}$  is not observed although it is exothermic by  $37 \text{ kJ mol}^{-1}$ .

Proton abstraction could also be responsible for the production of  $\text{Cl}^-$  via the formation of OH and  $\text{CClF}$ :

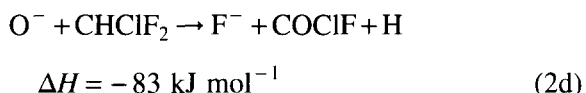
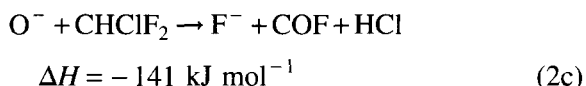
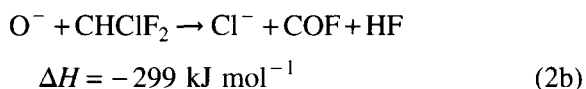
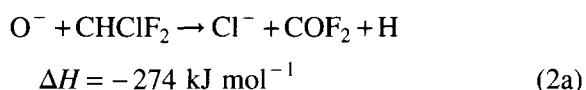


Non-dissociative electron transfer is not observed, and the reaction pathway of dissociative electron transfer to form  $\text{Cl}^- + \text{CHClF}_2 + \text{O}$  is endothermic by  $90 \text{ kJ mol}^{-1}$ .

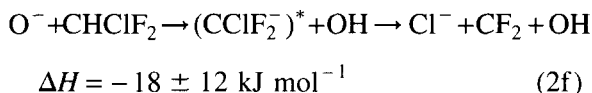
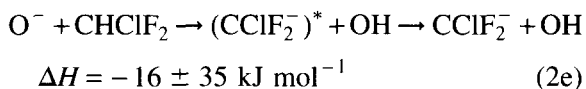
### 3.1.2. $\text{CHClF}_2$

Within experimental error, the rate coefficient for the reaction between  $\text{O}^-$  and  $\text{CHClF}_2$  is collisional ( $k_c = 2.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), and yields the products  $\text{F}^-$  (5%),  $\text{Cl}^-$  (55%),  $\text{HClO}^-$  (15%), and  $\text{CClF}_2^-$  (25%).

Dissociative electron transfer to produce  $\text{F}^-$  or  $\text{Cl}^-$  is endothermic. The product anions can, however, be formed following nucleophilic attack on carbon:



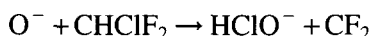
Proton abstraction can lead to the  $\text{CClF}_2^-$  product, fragmentation of which could lead to the production of  $\text{Cl}^-$ , providing a carbene is produced:



The corresponding hydrogen abstraction pathway to form  $\text{OH}^- + \text{CClF}_2$  is not observed, although it is exothermic by  $36 \text{ kJ mol}^{-1}$ .

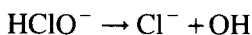
Nucleophilic attack on chlorine leads to the formation of  $\text{HClO}^-$ , the pathway being driven by the formation of a carbene through the

reaction:



$$\Delta H = -\text{EA}(\text{HClO}) + 93 \text{ kJ mol}^{-1} \quad (2\text{g})$$

The lowest energy fragmentation pathway for  $\text{HClO}^-$  is:



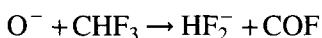
$$\Delta H = \text{EA}(\text{HClO}) - 110 \text{ kJ mol}^{-1} \quad (2\text{h})$$

Thus our observation of  $\text{HClO}^-$  requires that the electron affinity HClO is greater than 1.14 eV.

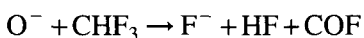
### 3.1.3. $\text{CHF}_3$

The rate coefficient for the  $\text{O}^-$  reaction with  $\text{CHF}_3$  is approximately at the collisional value. The anion products of the reaction are  $\text{OH}^-$  (4%),  $\text{F}^-$  (16%),  $\text{HF}_2^-$  (3%), and  $\text{CF}_3^-$  (47%), with electron detachment accounting for the remaining 30%.

Nucleophilic attack on carbon can lead to two of the product anions, and the possible reaction pathways are:

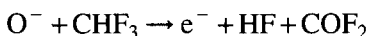


$$\Delta H = -271 \text{ kJ mol}^{-1} \quad (3\text{a})$$



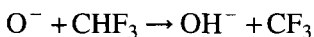
$$\Delta H = -110 \text{ kJ mol}^{-1} \quad (3\text{b})$$

A possible reaction pathway culminating in electron detachment is:

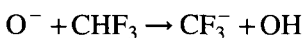


$$\Delta H = -326 \text{ kJ mol}^{-1} \quad (3\text{c})$$

The other two anion products,  $\text{OH}^-$  and  $\text{CF}_3^-$ , are formed by hydrogen and proton abstraction, respectively:



$$\Delta H = -10 \pm 8 \text{ kJ mol}^{-1} \quad (3\text{d})$$

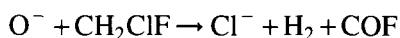


$$\Delta H = -22 \pm 14 \text{ kJ mol}^{-1} \quad (3\text{e})$$

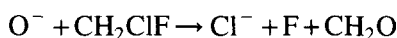
Dissociative electron transfer is endothermic for the pathways leading to  $\text{F}^-$ ,  $\text{CF}_3^-$ , and  $\text{HF}_2^-$ .

### 3.1.4. $\text{CH}_2\text{ClF}$

The  $\text{O}^-$  reaction has a rate coefficient of  $2.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Only two anion products are observed:  $\text{Cl}^-$  (55%) and  $\text{CClF}^-$  (45%). Dissociative electron transfer cannot account for these products; the reaction pathways being endothermic (unless  $\Delta_f H(\text{CClF}^-) < -402 \text{ kJ mol}^{-1}$ , which is unlikely). A number of other reaction pathways are energetically feasible. For example, nucleophilic attack on carbon can lead to the  $\text{Cl}^-$  anion:

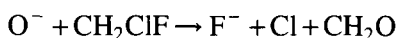


$$\Delta H = -249 \text{ kJ mol}^{-1} \quad (4\text{a})$$



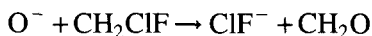
$$\Delta H = -104 \text{ kJ mol}^{-1} \quad (4\text{b})$$

That no  $\text{F}^-$  is observed may indicate that  $\text{Cl}^-$  is not produced through reaction pathway (4b), since the analogous reaction producing  $\text{F}^-$  is only marginally less exothermic:



$$\Delta H = -83 \text{ kJ mol}^{-1} \quad (4\text{c})$$

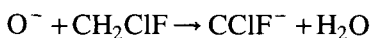
This conclusion is further supported by the observation that no  $\text{ClF}^-$  is formed, although the reaction pathway is exothermic:



$$\Delta H = -151 \text{ kJ mol}^{-1} \quad (4\text{d})$$

from which the  $\text{ClF}^-$  could have enough energy to fragment to  $\text{Cl}^-$  (+ F) or  $\text{F}^-$  (+ Cl).

$\text{H}_2^+$  abstraction, to give water as a neutral product, results in the formation of  $\text{CClF}^-$ :

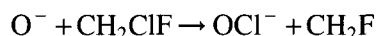


$$\Delta H = \Delta_f H(\text{CClF}^-) - 89 \text{ kJ mol}^{-1} \quad (4\text{e})$$

The reaction to produce  $\text{OCl}^-$  and  $\text{CH}_2\text{F}$  by nucleophilic attack on chlorine is, within



experimental error, thermoneutral:



$$\Delta H = 2 \pm 12 \text{ kJ mol}^{-1} \quad (4f)$$

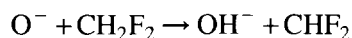
where the enthalpy has been calculated using  $\Delta_f H(\text{OCl}^-) = -118 \text{ kJ mol}^{-1}$  from Gilles et al. [23], and thus it is uncertain whether  $\text{OCl}^-$  is an energetically viable product.

Hydrogen abstraction, to produce  $\text{OH}^-$  (and  $\text{CHClF}$ ), is not observed although it is energetically allowed with  $\Delta H = -89 \text{ kJ mol}^{-1}$ . Proton abstraction is not observed. However, the lack of thermochemical data for the heat of formation of  $\text{CHClF}^-$  makes it impossible to determine if this reaction pathway is exothermic.

### 3.1.5. $\text{CH}_2\text{F}_2$

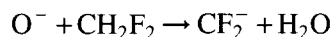
The reaction with  $\text{O}^-$  has a rate coefficient of  $1.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The anion products from this reaction are (at about 300 K)  $\text{OH}^-$  (25%) and  $\text{CF}_2^-$  (37%); electron detachment making up the remaining 38%. Using an ICR apparatus, Dawson and Jennings [15] observed the anion products  $\text{OH}^-$  and  $\text{CF}_2^-$  in a 60:40 ratio. The difference in the  $\text{OH}^-/\text{CF}_2^-$  ratio between the two studies most likely results from differences in the translational energies of the reactant ions in the two apparatuses.

Hydrogen abstraction yields  $\text{OH}^-$  in the reaction:



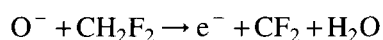
$$\Delta H = -29 \pm 10 \text{ kJ mol}^{-1} \quad (5a)$$

$\text{H}_2^+$  abstraction produces  $\text{CF}_2^-$ . Using 0.18 eV as the electron affinity of  $\text{CF}_2$  (Murray et al. [24]) gives  $\Delta_f H(\text{CF}_2^-) = -222 \pm 12 \text{ kJ mol}^{-1}$ , which in turn gives:



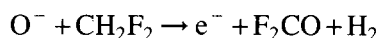
$$\Delta H = -119 \text{ kJ mol}^{-1} \quad (5b)$$

$\text{H}_2^+$  abstraction can also lead to electron detachment:

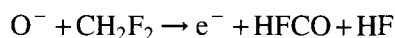


$$\Delta H = -102 \text{ kJ mol}^{-1} \quad (5c)$$

There are other thermochemically possible pathways to electron detachment via nucleophilic attack on carbon:



$$\Delta H = -295 \text{ kJ mol}^{-1} \quad (5d)$$



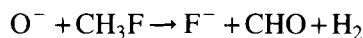
$$\Delta H = -305 \text{ kJ mol}^{-1} \quad (5e)$$

Exothermic pathways via nucleophilic attack on carbon exist for the production of  $\text{F}^-$  ( $+\text{COF} + \text{H}_2$ ,  $\Delta H = -79 \text{ kJ mol}^{-1}$ ),  $\text{F}_2^-$  ( $+\text{CH}_2\text{O}$ ,  $\Delta H = -61 \text{ kJ mol}^{-1}$ ), and  $\text{HF}_2^-$  ( $+\text{CHO}$ ,  $\Delta H = -293 \text{ kJ mol}^{-1}$ ), but none of these anions are observed.

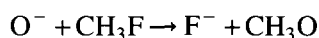
The proton abstraction reaction to produce  $\text{CHF}_2^-$  and  $\text{OH}$  has an enthalpy of  $20 \pm 29 \text{ kJ mol}^{-1}$ . Exothermic proton abstraction reaction channels are normally efficient, so the failure to observe  $\text{CHF}_2^-$  as a product may be taken to indicate that this pathway is endothermic.

### 3.1.6. $\text{CH}_3\text{F}$

Three anion products are observed for the reaction of  $\text{O}^-$  with  $\text{CH}_3\text{F}$ , which has a rate coefficient of  $1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The products are  $\text{OH}^-$  (68%),  $\text{CHF}^-$  (31%), and  $\text{F}^-$  (1%). Using a flowing afterglow, Tanaka et al. [13] report a rate coefficient of  $1.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and products  $\text{OH}^-$  (98%),  $\text{F}^-$  (1%), and  $\text{CHF}^-$  (1%), but they noted that there were problems in determining the branching ratio to  $\text{CHF}^-$  (which has the same  $m/e$  value as  $\text{O}_2^-$ ). Dawson and Jennings [15] just report the two major products— $\text{OH}^-$  (80%) and  $\text{CHF}^-$  (20%). Although, for such a small product yield,  $\text{F}^-$  could be produced via a fast (i.e. close to collisional) reaction with some impurity, nucleophilic attack on carbon can produce  $\text{F}^-$  (dissociative electron transfer being endothermic) via the following pathways:

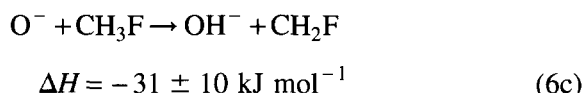


$$\Delta H = -65 \text{ kJ mol}^{-1} \quad (6a)$$

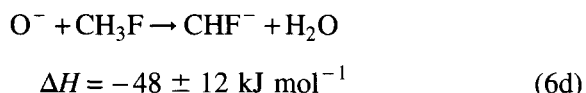


$$\Delta H = -95 \text{ kJ mol}^{-1} \quad (6b)$$

but clearly this does not compete favourably with hydrogen abstraction:



$\text{H}_2^+$  abstraction yields  $\text{CHF}^-$ :

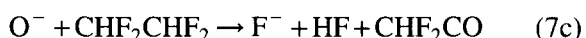
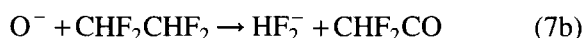


where the enthalpy of reaction (6d) has been determined using a value for the heat of formation of  $\text{CHF}^-$  obtained from the electron affinity of CHF (0.557 eV) reported by Murray et al. [24].

### 3.1.7. $\text{CHF}_2\text{CHF}_2$

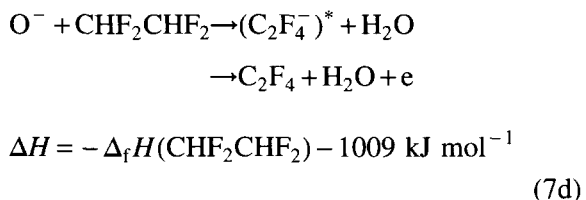
The  $\text{O}^-$  reaction results in four charged products. The dominant pathway leads to electron detachment (85%). The three anion products observed are  $\text{F}^-$  (4%),  $\text{HF}_2^-$  (2%), and  $\text{C}_2\text{F}_4\text{O}^-$  (9%). The reaction rate coefficient is  $1.9 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The reaction schemes we suggest for each of the anion products all involve nucleophilic attack on carbon:



Reactions (7b) and (7c) both involve nucleophilic attack at one of the carbons, but reaction (7a) must involve the attack by  $\text{O}^-$  on both carbons. No enthalpies for the reactions are given because the heats of formation of  $\text{CHF}_2\text{CHF}_2$ ,  $\text{C}_2\text{F}_4\text{O}^-$ , and  $\text{CHF}_2\text{CO}$  are unknown.

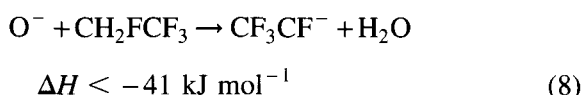
We propose that the electron detachment channel is a result of  $\text{H}_2^+$  abstraction:



although the intermediate  $\text{C}_2\text{F}_4^-$  anion is not observed.

### 3.1.8. $\text{CH}_2\text{FCF}_3$

The rate coefficient for this reaction is  $3.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Morris et al. [16] find the rate coefficient to be even larger than our value at  $4.3 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Unusually, only one product is observed, namely  $\text{CF}_3\text{CF}^-$ , resulting from  $\text{H}_2^+$  abstraction, and this is in agreement with the result of Morris et al. [16]. Using values for the enthalpy of formation of  $\text{CH}_2\text{FCF}_3$  and  $\text{CF}_3\text{CF}^-$  reported in Morris et al. [16] as  $-896 \text{ kJ mol}^{-1}$  and  $< -587 \text{ kJ mol}^{-1}$ , respectively, gives for the reaction:

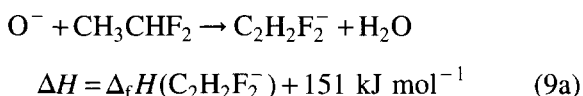


There are other exothermic reaction pathways involving nucleophilic attack on carbon, for example giving  $\text{CF}_3^-$  ( $+\text{COF} + \text{H}_2$ ,  $\Delta H = -35 \pm 16 \text{ kJ mol}^{-1}$ ) and  $\text{COF}^-$  ( $+\text{CF}_3 + \text{H}_2$ ,  $\Delta H = -116 \text{ kJ mol}^{-1}$ ), but these are not observed.

### 3.1.9. $\text{CH}_3\text{CHF}_2$

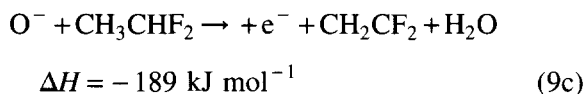
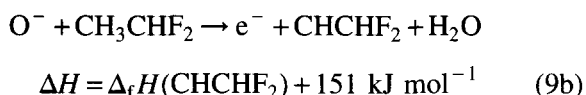
The anion products from the  $\text{O}^-$  reaction are  $\text{H}_2\text{O.F}^-$  (25%) and  $\text{C}_2\text{H}_2\text{F}_2^-$  (10%) with electron detachment making up the remaining 65%. The reaction rate coefficient is  $2.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

$\text{H}_2^+$  abstraction leading to  $\text{C}_2\text{H}_2\text{F}_2^-$  and  $\text{H}_2\text{O}$  is only exothermic if the  $\text{C}_2\text{H}_2\text{F}_2^-$  anion has an enthalpy of formation  $< -151 \text{ kJ mol}^{-1}$ :

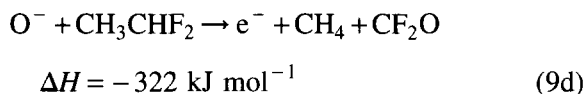


From a comparison of reactions with related compounds, there are two likely structures of  $\text{C}_2\text{H}_2\text{F}_2^-$ . One is the carbene anion  $\text{CHCHF}_2^-$ , produced when  $\text{H}_2^+$  is abstracted from the carbon to which the three hydrogens are bonded. The other is  $\text{CH}_2\text{CF}_2^-$ , produced when a hydrogen is abstracted from one of the carbons and  $\text{H}^+$  is abstracted from the other.

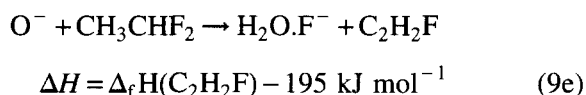
Reaction (9a) could also lead to electron detachment:



However, it should be noted that energetically nucleophilic attack on carbon could also result in electron detachment:

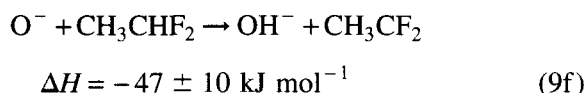


For the formation of the anion product  $\text{H}_2\text{O.F}^-$ :



either a major rearrangement takes place, or there is a concerted making and breaking of several bonds. A study of the reaction using the isotopomer  $\text{CH}_3\text{CDF}_2$  would be of interest in elucidating the reaction mechanism.

The hydrogen abstraction reaction:



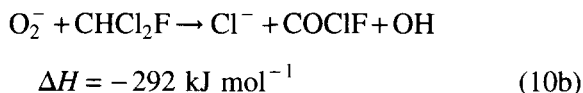
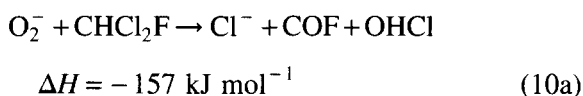
is exothermic, but is not observed. The enthalpy of formation of  $\text{CH}_3\text{CF}_2^-$  is unknown so that it cannot be determined if the proton abstraction channel, which is also not observed, is exothermic or endothermic.

### 3.2. $\text{O}_2^-$ reactions

The reaction rate coefficients and branching ratios for the reactions with the molecules in this study are included in Table 1. Table 3 summarises the  $\text{O}_2^-$  reaction pathways and includes results from an earlier study of ours for the reactions of  $\text{O}_2^-$  with a series of halogenated methanes [12].

#### 3.2.1. $\text{CHCl}_2\text{F}$

For this reaction the rate coefficient is  $5.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is less than 50% of the ADO value. The only observed product is  $\text{Cl}^-$ , which probably arises from nucleophilic attack on carbon:

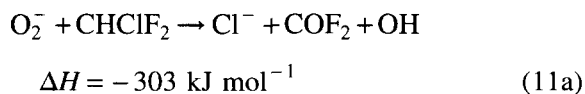


The parallel pathway of reaction (10b) leading to  $\text{OH}^-$  (+  $\text{Cl}^-$  +  $\text{COCIF}$ ) is exothermic ( $\Delta H = -120 \text{ kJ mol}^{-1}$ ), but no  $\text{OH}^-$  is observed. The production of  $\text{Cl}^-$  by dissociative electron transfer cannot be ruled out, but is unlikely because the enthalpy of the reaction is only  $9 \pm 8 \text{ kJ mol}^{-1}$ , and for such a low enthalpy a non-dissociative electron transfer product should also be observed.

There are other exothermic reaction pathways resulting from nucleophilic attack on carbon which lead to the products  $\text{F}^-$  (+ $\text{COCl}_2$  +  $\text{OH}$ ,  $\Delta H = -107 \text{ kJ mol}^{-1}$ ) or  $\text{Cl}_2^-$  (+ $\text{COF}$  +  $\text{OH}$ ,  $\Delta H = -45 \pm 25 \text{ kJ mol}^{-1}$ ) but neither of these are observed. (Note that the production of  $\text{OH}^-$  rather than  $\text{F}^-$  or  $\text{Cl}_2^-$  is endothermic.)

#### 3.2.2. $\text{CHClF}_2$

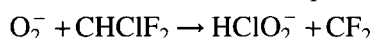
$\text{O}_2^-$  reacts with  $\text{CHClF}_2$  to produce two products,  $\text{Cl}^-$  (84%) and  $\text{HClO}_2^-$  (16%) with a rate coefficient of  $5.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This reaction rate coefficient is substantially below the collisional value. Nucleophilic attack on carbon seems the most likely route to  $\text{Cl}^-$  possibly via the reaction path:



The parallel reaction to form  $\text{OH}^-$  (+  $\text{COF}_2$  +  $\text{Cl}^-$ ) is exothermic by  $130 \text{ kJ mol}^{-1}$ , but does not appear to compete with  $\text{Cl}^-$  production. Dissociative

electron transfer to form  $\text{Cl}^- + \text{CHF}_2$  is endothermic by  $62 \text{ kJ mol}^{-1}$ .

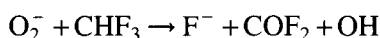
The only other observed anion product  $\text{HClO}_2^-$  must be formed with the production of  $\text{CF}_2$ :



$$\Delta H = \Delta_f H(\text{HClO}_2^-) + 321 \text{ kJ mol}^{-1} \quad (11b)$$

### 3.2.3. $\text{CHF}_3$

No bimolecular process is observed for the reaction with  $\text{O}_2^-$ , although nucleophilic attack on carbon is exothermic:

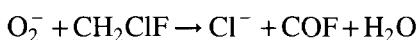


$$\Delta H = -113 \text{ kJ mol}^{-1} \quad (12)$$

Instead a three body association leading to  $\text{CHF}_3\text{O}_2^-$  takes place with a rate coefficient of  $5 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$  (as determined from a study of the pressure dependence of the effective bimolecular rate coefficient).

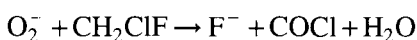
### 3.2.4. $\text{CH}_2\text{ClF}$

The  $\text{O}_2^-$  reaction with  $\text{CH}_2\text{ClF}$  proceeds at  $1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Nucleophilic attack on carbon can result in the observed single anion product  $\text{Cl}^-$ :

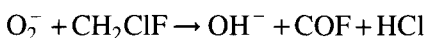


$$\Delta H = -341 \text{ kJ mol}^{-1} \quad (13a)$$

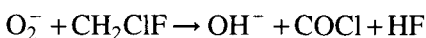
There are energetically feasible reaction pathways to other anion products, for example:



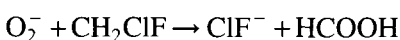
$$\Delta H = -251 \text{ kJ mol}^{-1} \quad (13b)$$



$$\Delta H = -101 \text{ kJ mol}^{-1} \quad (13c)$$



$$\Delta H = -170 \text{ kJ mol}^{-1} \quad (13d)$$



$$\Delta H = -271 \text{ kJ mol}^{-1} \quad (13e)$$

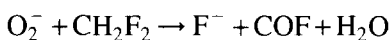
but none of these product anions are observed.

Electron transfer and subsequent decomposition of the parent ion into  $\text{Cl}^- + \text{CH}_2\text{F}$  is endothermic by  $43 \pm 11 \text{ kJ mol}^{-1}$ . Non-dissociative electron transfer is not seen, and whether this is energetically possible is uncertain because the electron affinity of  $\text{CH}_2\text{ClF}$  is unknown.

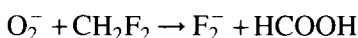
### 3.2.5. $\text{CH}_2\text{F}_2$

The reaction of  $\text{O}_2^-$  with  $\text{CH}_2\text{F}_2$  results in one product, namely the association product  $\text{CH}_2\text{F}_2\text{O}_2^-$ . From a study of the pressure dependence of the effective bimolecular rate coefficient, the three body association was found to occur in the pressure 'unsaturated' region, with a rate coefficient of  $1.5 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-2}$ .

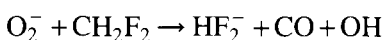
Several bimolecular reaction pathways are exothermic, but are not observed, including:



$$\Delta H = -171 \text{ kJ mol}^{-1} \quad (14a)$$



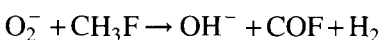
$$\Delta H = -181 \text{ kJ mol}^{-1} \quad (14b)$$



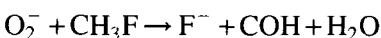
$$\Delta H = -260 \text{ kJ mol}^{-1} \quad (14c)$$

### 3.2.6. $\text{CH}_3\text{F}$

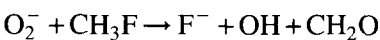
No bimolecular reactions of  $\text{O}_2^-$  with  $\text{CH}_3\text{F}$  are observed, although the following reaction pathways are energetically allowed:



$$\Delta H = -23 \pm 16 \text{ kJ mol}^{-1} \quad (15a)$$



$$\Delta H = -157 \text{ kJ mol}^{-1} \quad (15b)$$



$$\Delta H = -28 \pm 14 \text{ kJ mol}^{-1} \quad (15c)$$

Based on our results for the other HFCs we expected to observe the formation of the association product  $\text{CH}_3\text{F.O}_2^-$  ( $m/e = 66$ ) from the reaction of  $\text{O}_2^-$  with  $\text{CH}_3\text{F}$ . An initial attempt to detect this product was unsuccessful. By operating the SIFT apparatus with very high concentrations of  $\text{CH}_3\text{F}$  in the flow tube ( $[\text{CH}_3\text{F}] \approx 10^{14}$  molecules  $\text{cm}^{-3}$ ,  $p(\text{He}) = 0.6$  Torr) we were able to detect a signal due to product anions with  $m/e = 66$ . However, most of the  $\text{O}_2^-$  remained unreacted, and products at  $m/e = 50$  ( $\text{CF}_2^-$ ?,  $\text{H}_2\text{O.O}_2^-$ ?) and 75 were observed. These products are believed to be formed from the reactions of  $\text{O}_2^-$  with impurities in the  $\text{CH}_3\text{F}$  sample. Thus, we are unable to provide an upper limit to the three body rate coefficient for the association of  $\text{O}_2^-$  with  $\text{CH}_3\text{F}$ .

### 3.2.7. $\text{CHF}_2\text{CHF}_2$ , $\text{CH}_2\text{FCF}_3$ , and $\text{CH}_3\text{CHF}_2$

The only product observed for the reaction of  $\text{O}_2^-$  with these fluorinated ethanes is the association product. As mentioned earlier, we were unable to determine if the reactions proceed in the unsaturated region, and the values reported in Table 1 are the effective second order rate coefficients obtained at a helium pressure of 0.49 Torr.

Morris et al. [16] report the reaction of  $\text{O}_2^-$  with  $\text{CH}_2\text{FCF}_3$ , and also find that it proceeds exclusively by association. A study of the pressure dependence of the effective bimolecular rate coefficient by Morris et al. (0.29–0.53 Torr) showed some indication of fall-off behaviour. Although there is fair agreement for the rate coefficients between the two studies, our value ( $9.5 \times 10^{-11}$  molecule $^{-1}$   $\text{cm}^3$   $\text{s}^{-1}$ ,  $p(\text{He}) = 0.49$  Torr) is smaller than that reported by Morris et al. ( $1.3 \times 10^{-10}$  molecule $^{-1}$   $\text{cm}^3$   $\text{s}^{-1}$ ,  $p(\text{He}) = 0.43$  Torr) at nearly the same helium buffer gas pressure.

## 4. Discussion of the $\text{O}^-$ results

The chemistry of the reactions of  $\text{O}^-$  with the various halogenated methanes and ethanes is

very diverse. The results show that, providing the reaction pathway is at least slightly exothermic, the enthalpy of the reaction plays no part in determining the efficiency of the reaction pathway, and that other factors are important.

For a particular reaction, the collisional rate coefficient ( $k_c$ ) may be estimated by the ADO capture theory [20], and we have found that for all the reactions with  $\text{O}^-$  the overall rate coefficient ( $k_{\text{exp}}$ ):

$$k_{\text{exp}} \approx k_c \quad (16)$$

The interest is then in the mechanisms of the reactions, which are revealed in the product anion branching ratios. There are two limiting views of how the reaction proceeds. The first is that reaction is direct occurring at the initial region of contact between the ion and molecule, with immediate release of the product anion. This will occur when the barrier to reaction is low. The induced and permanent dipole moments of the molecule do influence the direction of approach of the ion, so a key signature would be the observation of a branching ratio which correlated with the direction of the dipole moment of the molecule relative to the location of the required region of impact for a particular channel. The alternative view is of a long-lived complex, in which the path for break up of the complex will be determined by the barriers between the complex and the various thermodynamically accessible products. The structures and energetics of the transition states will now be the key to interpreting the branching ratios. We have built up a substantial body of experimental data for the reactions of  $\text{O}^-$  with halogenated methanes and ethanes, and there have been some theoretical studies, from which some interesting trends are starting to emerge. There are clearly many factors to be considered. We believe that both the direct and long-lived complex mechanisms are involved. In this paper we highlight some of the trends we have identified, and offer possible interpretations. In a future publication we will examine in detail all of

the available information, from both experiment and theory, to produce a detailed and coherent mechanistic picture of the reactions of  $O^-$  with halogenated compounds in the gas phase.

#### 4.1. Nucleophilic attack on carbon

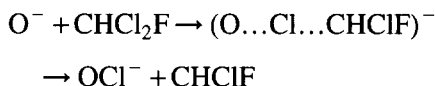
For the  $O^-$  reactions presented in this study, we suggest that nucleophilic attack on carbon is responsible for the production of  $Cl^-$ ,  $F^-$ , and  $ClF^-$ . It is also considered to be the mechanism resulting in electron detachment and the production of  $HF_2^-$  from the reaction with  $CHF_3$ , and the products  $HF_2^-$  and  $C_2F_4O^-$  from the reaction with  $CHF_2CHF_2$ . As discussed by us in an earlier paper [12] there is the possibility that the  $Cl^-$  and  $F^-$  anions are formed from the dissociation of excited  $Cl_2^*$  or  $ClF^*$  anions, which result from the initial nucleophilic attack. This requires a greater percentage of the energy from the reaction going to the anion product than is predicted from a simple statistical distribution of energy according to the number of degrees of vibrational freedom. Evidence for this pathway comes from the observation of the diatomic anions  $Cl_2^-$  (e.g. from  $CCl_2F_2$ ) and  $ClF^-$  (from  $CClF_3$ ) in addition to  $Cl^-$  and  $F^-$  [12]. The molecular anions will be formed with a distribution of internal energy, and a proportion of the anions will contain sufficient energy to dissociate. In this present study  $ClF^-$  is only observed from the reaction with  $CHCl_2F$ , where it is a minor product (3%). Since no  $F^-$  is produced in this reaction, perhaps the observed  $Cl^-$  has come from  $Cl_2^*$  and not  $ClF^*$ , although no  $Cl_2^-$  is observed.

From Table 2, which summarises the pathways for the reactions presented in this study and those from our earlier study [12], definite trends can be seen in the amount of nucleophilic attack on carbon in the fluorine substituted methane reactions. It is clearly a favourable mechanism when there is chlorine in the molecule, reflecting the proficiency of chlorine as a leaving group. This is consistent with nucleophilic attack on

carbon occurring via a long-lived complex. There are clear parallels with the  $S_N2$  mechanism of solution phase organic chemistry.

#### 4.2. Nucleophilic attack on chlorine

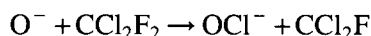
In this present study there is just one clear example of nucleophilic attack on chlorine, and this is the reaction of  $O^-$  with  $CHCl_2F$  to form  $OCl^-$ . We propose the following reaction pathway:



$$\Delta H = -40 \pm 20 \text{ kJ mol}^{-1} \quad (17a)$$

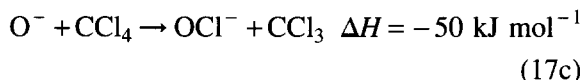
No  $CHClF^-$  was observed. Since in other reactions the parallel path of  $CX_3^-$  is observed if the channel is exothermic, this implies that the reaction pathway to  $CHClF^-$  is endothermic and we deduce that the electron affinity of  $CHClF$  is less than 1.8 eV.

For all the reactions studied which lead to  $OCl^-$ , reaction Eq. (17a) and the reactions of  $O^-$  with  $CCl_4$ ,  $CCl_3F$ ,  $CCl_2F_2$ , and  $CHCl_3$  [12], the associated exothermicity is low. For example:

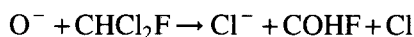


$$\Delta H = -14 \pm 19 \text{ kJ mol}^{-1} \quad (17b)$$

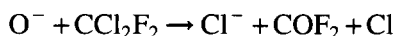
The most exothermic reaction leading to  $OCl^-$  is:



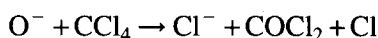
The exothermicities of (17a), (17b) and (17c) are low compared with the observed nucleophilic attack on carbon channels, for example:



$$\Delta H = -309 \text{ kJ mol}^{-1} \quad (17d)$$



$$\Delta H = -377 \text{ kJ mol}^{-1} \quad (17e)$$

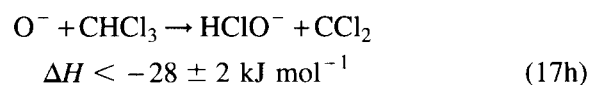
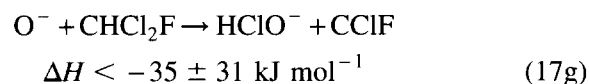


$$\Delta H = -337 \text{ kJ mol}^{-1} \quad (17f)$$

The production of  $\text{OCl}^-$  is a direct, simple stripping reaction. No or little molecular rearrangement is required and the energy barrier should be small. That nucleophilic attack on chlorine can compete with (the more exothermic) nucleophilic attack on carbon reflects the efficiency of a direct reaction relative to one through a long-lived complex. Nucleophilic attack on carbon requires considerably more rearrangement which is likely to result in a greater potential barrier along the reaction co-ordinate.

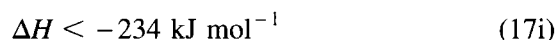
The yield of  $\text{OCl}^-$ , as expected, decreases with decreasing number of chlorine atoms in the chlorinated methanes. Furthermore, it is observed that the replacement of a fluorine with a hydrogen, whilst keeping the chlorine content the same, also reduces the yield of  $\text{OCl}^-$ . Such a replacement opens up other exothermic channels, notably hydrogen stripping reactions ( $\text{H}$ ,  $\text{H}^+$ , and  $\text{H}_2^+$  abstraction). The production of  $\text{OCl}^-$  is in competition with nucleophilic attack on carbon (via a long-lived complex) and with these various hydrogen stripping reactions (also direct). Many factors could thus have an influence on the relative yield of  $\text{OCl}^-$ . One factor, concentrating just on the direct pathways, is that changing F for the more electropositive H will change the charge distribution in the molecule and this may decrease the probability of the  $\text{O}^-$  being delivered to a Cl atom.

For the reaction with  $\text{CHClF}_2$  the interesting product  $\text{HClO}^-$  is observed (the reaction channel leading to  $\text{OCl}^-$  being endothermic ( $\Delta H = 35 \pm 19 \text{ kJ mol}^{-1}$ )). According to our working definition, this product corresponds to nucleophilic attack on chlorine. The limits on the heat of formation of  $\text{HClO}^-$ , derived from the reaction of  $\text{O}^-$  with  $\text{CHClF}_2$ , show that  $\text{HClO}^-$  could energetically be formed in the reactions of  $\text{O}^-$  with  $\text{CHCl}_2\text{F}$  and  $\text{CHCl}_3$ :

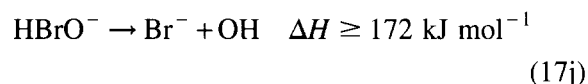


but it is not observed in either of these reactions. In our earlier study [12] the reaction of  $\text{O}^-$  with  $\text{CCl}_2\text{F}_2$  produced the related anion product  $\text{OCl}_2$  and (presumably) the neutral  $\text{CF}_2$ . The formation of difluorocarbene thus appears to be the driving force behind these reactions. That these reactions preferentially occur forming  $\text{CF}_2$ , and no other halogenated carbenes (such as  $\text{CClF}$  and  $\text{CCl}_2$  together with the corresponding anion products) is perhaps a consequence of the stronger effect that fluorine has in delocalising the charge distribution in the intermediate complex, therefore weakening the C–H and C–Cl bonds. The energetics of the transition states are now central to an interpretation of the observed reaction pathways; a pattern of behaviour which indicates that the reaction is governed by the break up of a long-lived complex.

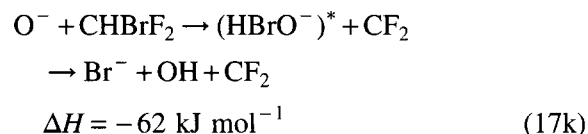
In comparison, for the reaction of  $\text{O}^-$  with  $\text{CHBrF}_2$ , Morris et al. [16] report products  $\text{F}^-$  (16%),  $\text{Br}^-$  (71%),  $\text{BrO}^-$  (11%), and  $\text{Br}^-\text{HF}$  (2%). Interestingly no  $\text{HBrO}^-$  was observed although the reaction channel is highly exothermic:



(The enthalpy of this reaction has been obtained using  $\Delta_f H(\text{HBrO}^-) < -346 \text{ kJ mol}^{-1}$  determined in a study of the reaction of  $\text{OH}^-$  with  $\text{CFBr}_3$  [25] and  $\Delta_f H(\text{CHBrF}_2) = -425 \text{ kJ mol}^{-1}$  [26].) However, if formed  $\text{HBrO}^-$  may have sufficient internal energy to dissociate:



overall



#### 4.3. $\text{H}$ , $\text{H}^+$ , and $\text{H}_2^+$ abstraction

The exothermicities of the observed  $\text{H}$ ,  $\text{H}^+$ , and  $\text{H}_2^+$  abstraction pathways are in general low. Like

the pathways leading to  $\text{OCl}^-$  they may be regarded as stripping reactions, and probably occur via a direct mechanism.

All the singly hydrogenated compounds studied reacted with  $\text{O}^-$  via proton abstraction, and all, except for the reaction with  $\text{CHClF}_2$ , with a product percentage of  $\sim 50\%$ . The smaller product percentage associated with the  $\text{CHClF}_2$  reaction (25%) can partially be attributed to the accessibility of the reaction pathway leading to the  $\text{HClO}^-$  anion (15%), which, as explained previously, occurs because of the favoured formation of a  $\text{CF}_2$  neutral.

$\text{H}_2^+$  abstraction occurs in the reactions with all of the methanes and ethanes which contain two or more H atoms. For all the methanes, except for  $\text{CH}_2\text{ClF}$ ,  $\text{H}_2^+$  abstraction occurs in competition with either  $\text{H}^+$  abstraction ( $\text{CH}_2\text{Cl}_2$ ) or H-atom abstraction ( $\text{CH}_2\text{F}_2$ ,  $\text{CH}_3\text{F}$ , and  $\text{CH}_3\text{Cl}$ ). For  $\text{CH}_2\text{ClF}$  only the  $\text{H}_2^+$  abstraction channel is observed, although the H atom abstraction channel is definitely exothermic. For the ethanes,  $\text{CH}_2\text{FCF}_3$  and  $\text{CH}_3\text{CHF}_2$ , the only reaction pathway involving the hydrogen atoms is  $\text{H}_2^+$  abstraction. For  $\text{CHF}_2\text{CHF}_2$ , we suggest that the major product (electron detachment) is a result of  $\text{H}_2^+$  abstraction, with the intermediate anion not being observed presumably because  $\text{CF}_2\text{CF}_2^-$  is unstable (unlike the  $\text{CFCF}_3^-$  product resulting from the reaction of  $\text{O}^-$  with  $\text{CH}_2\text{FCF}_3$ ) and this is discussed further below.

#### 4.4. Electron detachment

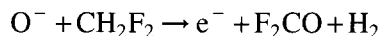
The general mechanism for reactive electron detachment involves the formation of an intermediate anion with energy in excess of its detachment threshold. Four of the systems presented in this paper exhibit an electron detachment channel, namely  $\text{O}^- + \text{CHF}_3$ ,  $\text{O}^- + \text{CH}_2\text{F}_2$ ,  $\text{O}^- + \text{CH}_3\text{CHF}_2$ , and  $\text{O}^- + \text{CHF}_2\text{CHF}_2$ , and it is interesting to speculate on the nature of the intermediate anion.

For  $\text{CHF}_3$  the proposed electron detachment pathway is:

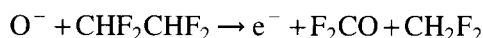


$$\Delta H = -326 \text{ kJ mol}^{-1} \quad (18a)$$

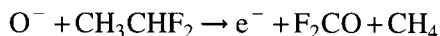
i.e. the reaction proceeds by nucleophilic attack on carbon. The H stripping reaction (3d) and (3e) are not sufficiently exothermic to produce intermediate anions ( $\text{OH}^-$  and  $\text{CF}_3^-$ ) with energies above their respective electron detachment thresholds. For the other three systems, the stripping channel,  $\text{H}_2^+$  abstraction (reactions (5c), (7d) and (9c)), is sufficiently exothermic to lead to electron detachment. More exothermic pathways to electron detachment have been identified, for example:



$$\Delta H = -295 \text{ kJ mol}^{-1} \quad (18b)$$



$$\Delta H = -\Delta_f H(\text{CHF}_2\text{CHF}_2) - 1201 \text{ kJ mol}^{-1} \quad (18c)$$



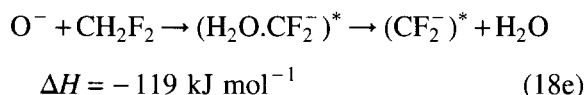
$$\Delta H = -322 \text{ kJ mol}^{-1} \quad (18d)$$

(Reaction pathway (18c) is  $192 \text{ kJ mol}^{-1}$  more exothermic than the  $\text{H}_2^+$  abstraction pathway (7d).) These pathways ((18b), (18c) and (18d)) may be classified as nucleophilic attack on carbon. They are very complex, involving substantial rearrangement, and the barriers are expected to be very high [27]. Instead, we propose that for the reactions of  $\text{O}^-$  with  $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_2\text{CHF}_2$ , and  $\text{CH}_3\text{CHF}_2$  electron detachment occurs following  $\text{H}_2^+$  abstraction. Stripping reactions in which  $\text{H}_2^+$  is transferred to  $\text{O}^-$  are well known for a variety of organic neutral reactants [16,28], and, when thermochemically allowed, are generally more efficient than intimate mechanisms, such as nucleophilic attack. Further, the  $\text{H}_2^+$  abstraction mechanism offers

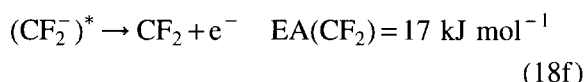


appealing explanations of many aspects of our observations.

For two of the systems ( $\text{O}^- + \text{CH}_2\text{F}_2$  and  $\text{O}^- + \text{CH}_3\text{CHF}_2$ ) the intermediate anion has been observed. In the case of  $\text{CH}_2\text{F}_2$  a carbene anion is proposed as the intermediate:



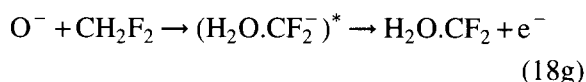
with a fraction of the intermediate carbene anions being formed with sufficient internal energy to autodetach vibrationally:



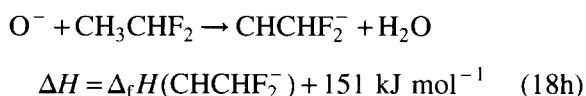
At 300 K the branching ratios for  $\text{CF}_2^-$  and electron detachment are 37% and 38%, respectively. With such a small molecule, it is unlikely that there will be sufficient time for any  $\text{CF}_2^-^*$ , which has enough internal energy to autodetach, to be collisionally stabilised by the helium in the flow tube. This implies that about half of the  $\text{CF}_2^-$  must be formed with internal energies below the detachment threshold. A comparison of the high exothermicity of reaction (18e) against the electron affinity of  $\text{CF}_2$ , shows that the production of excited  $\text{CF}_2^-$  is inefficient, and that the available energy is not shared equally between the two products. The observations can be explained by postulating that (18e) has an early transition state, with a small  $\text{H}\hat{\text{O}}\text{H}$  angle and long  $\text{O}-\text{H}$  distances, while the geometry of the  $\text{CF}_2$  unit is close to the equilibrium structure of  $\text{CF}_2^-$ . The passage to products through this transition state will naturally lead to the production of vibrationally excited  $\text{H}_2\text{O}$ , and  $\text{CF}_2^-$  with relatively little internal energy. There are obvious parallels with the dynamics of the reaction of the isoelectronic F atom with  $\text{CH}_2\text{F}_2$ , in which most of the exothermicity appears as vibrational excitation of the HF product [29].

A study of the temperature dependence (293–450 K) of the branching ratios, showed that as the temperature is raised, a decrease of the  $\text{CF}_2^-$

percentage signal occurs with an accompanying increase in the electron signal [30]. For example, at about 430 K the relative anion distribution is  $\text{OH}^-$  at 31%,  $\text{CF}_2^-$  at 16%, and  $\text{e}^-$  at 53%. From the observation that  $[\text{e}^-] \geq [\text{CF}_2^-]$  at all temperatures, Lee and Dyke [30] propose that there are two routes for electron production. One is the temperature dependent route just mentioned (reactions (18e) and (18f)), which is effectively vibrational autodetachment of  $\text{H}_2\text{O}...\text{CF}_2^-$  at large separations. The other is a temperature independent vibrational autodetachment of the complex  $\text{H}_2\text{O}.\text{CF}_2^-$ :



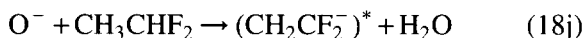
In the case of  $\text{CH}_3\text{CHF}_2$ ,  $\text{H}_2^+$  abstraction may result from two different pathways. One pathway is analogous to that described for the  $\text{CH}_2\text{F}_2$  molecule, and leads to a carbene anion:



The energy released in reaction (18h) will primarily appear as vibrational energy of the  $\text{H}_2\text{O}$  product, and only a fraction of the  $\text{CHCHF}_2^-$  carbene anions will contain sufficient energy to autodetach:

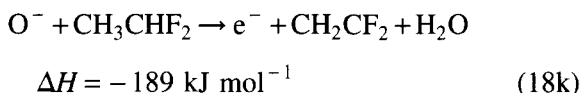


The other pathway is for a hydrogen atom to be abstracted from one of the carbons and  $\text{H}^+$  from the other:



At the transition state for this reaction the  $\text{H}_2\text{O}$  forms part of a five-membered ring, and its geometry is much closer to the equilibrium structure of  $\text{H}_2\text{O}$ . The reaction exothermicity will be distributed more evenly between the two products, and a high fraction of the intermediate anions will be formed with energies

above the detachment limit:



Overall the relative yield of electrons (65%) to anions ( $\text{C}_2\text{H}_2\text{F}_2^-$ ) (10%) is much higher than for the reaction of  $\text{O}^-$  with  $\text{CH}_2\text{F}_2$ , and this suggests that reaction pathway (18k) dominates, but not necessarily to the exclusion of (18h) followed by (18i), i.e. both pathways are likely to contribute to the removal of  $\text{O}^-$ .

Our interpretation is supported by the results from the reaction of  $\text{O}^-$  with  $\text{CHF}_2\text{CHF}_2$ , for which the dominant reaction channel is electron detachment (85%) and  $\text{C}_2\text{F}_4^-$  is not detected.  $\text{CHF}_2\text{CHF}_2$  cannot form a carbene anion intermediate by  $\text{H}_2^+$  abstraction without a major rearrangement, the only feasible  $\text{H}_2^+$  abstraction pathway is:



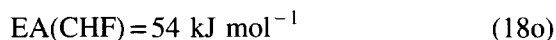
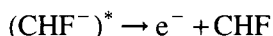
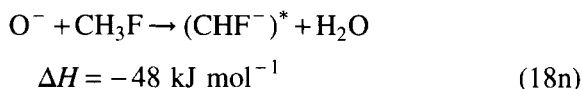
As stated above this pathway is expected to lead to the efficient production of excited anions, which then autodetach:



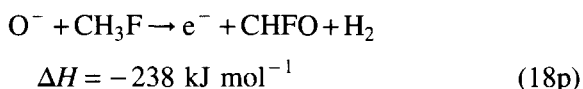
The proposed intermediate anion  $\text{CF}_2\text{CF}_2^-$  is not observed. However, the electron affinity of  $\text{CF}_2\text{CF}_2$  is believed to be close to zero and may be negative [31]. Thus, the formation of  $\text{CF}_2\text{CF}_2^-$  must necessarily result in detachment.

It is worthy of comment that several of the other molecules investigated, both in this study and in our earlier study [12], undergo  $\text{H}_2^+$  abstraction upon reaction with  $\text{O}^-$  ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{ClF}$ ,  $\text{CH}_3\text{F}$ , and  $\text{CH}_2\text{FCF}_3$ ), but for these molecules electron detachment does not occur. It must be presumed that the energy deposited in the carbene anion during the  $\text{H}_2^+$  abstraction is not sufficient to open the detachment channel. This cannot be confirmed for the majority of the reactions because not all the thermochemical values needed to determine the enthalpy of the reaction are known. Only for  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{F}$

are all the heats of formation known for the various products. For  $\text{CH}_3\text{F}$ , and in agreement with our proposition, the electron detachment channel is overall endothermic:

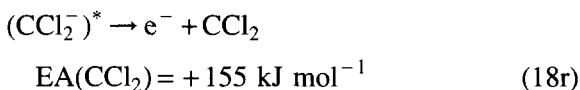
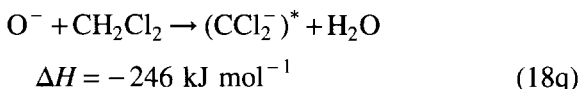


There is an exothermic pathway involving nucleophilic attack on carbon which could lead to electron detachment:

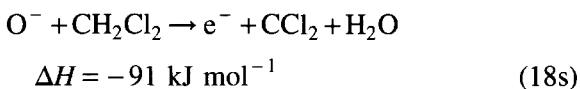


The failure to observe electron detachment shows that pathway (18p) does not occur. This supports our earlier assertion that reactions (18b), (18c) and (18d) are not the source of the electrons in the reactions of  $\text{O}^-$  with  $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_2\text{CHF}_2$ , and  $\text{CH}_3\text{CHF}_2$ , as well as the general observation that simple stripping reactions (here  $\text{H}_2^+$  abstraction) often occur in preference to far more exothermic, but also more intimate, pathways such as nucleophilic attack on carbon.

For  $\text{CH}_2\text{Cl}_2$  electron detachment is energetically feasible:



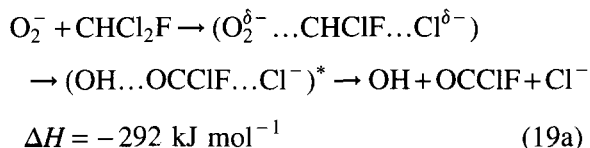
(where we have used the electron affinity of  $\text{CCl}_2$  from Murray et al. [24]). Overall:



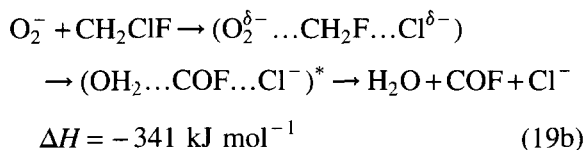
but is not observed, presumably because the internal energy deposited into  $(\text{CCl}_2)^-$  in reaction (18q) is always less than  $155 \text{ kJ mol}^{-1}$ .

## 5. Discussion of the O<sub>2</sub><sup>−</sup> results

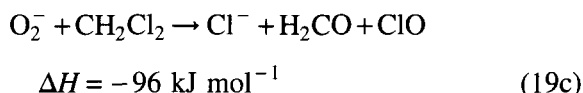
O<sub>2</sub><sup>−</sup> is less reactive than O<sup>−</sup>, and in many cases reacts only by association. The only reasonably efficient bimolecular reactions ( $k_{\text{exp}} \sim k_c$ ) involve the hydrochlorofluoromethanes. For these Cl<sup>−</sup> is produced almost exclusively. Dissociative electron transfer to form Cl<sup>−</sup> is endothermic in almost all of the reactions (or has extremely low exothermicity, as in the reaction of O<sub>2</sub><sup>−</sup> with CHCl<sub>2</sub>F), and can therefore be ruled out as a mechanism for the formation of Cl<sup>−</sup>. Instead, nucleophilic attack on carbon resulting in halide displacement with the cleavage of the oxygen–oxygen bond is proposed as the mechanism. This is in agreement with the conclusions reached from the study of the reactions of O<sub>2</sub><sup>−</sup> with the halogenated methanes presented in our earlier paper [12]. We do not observe the fission directly, but an exhaustive thermochemical analysis has established that the only Cl<sup>−</sup> displacement pathways which are exothermic require cleavage of the O–O bond. This fission is quite plausible, for it has been directly observed in the products of such diverse systems as the reaction of C<sub>3</sub>H<sub>3</sub><sup>−</sup> with O<sub>2</sub> [32] and in the reaction of O<sub>2</sub><sup>−</sup> with phenyl acetate [33]. In the case of the two singly hydrogenated species (CHCl<sub>2</sub>F and CHClF<sub>2</sub>) presented in this study, thermodynamic considerations suggest that the reaction proceeds by break up of a complex to produce an OH radical, for example:



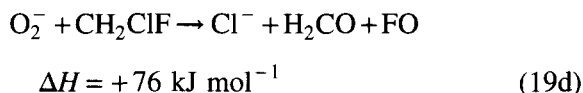
For CH<sub>2</sub>ClF the most exothermic pathway is to form H<sub>2</sub>O, releasing the observed Cl<sup>−</sup> product:



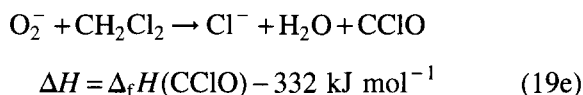
The analogous pathway suggested by us for the production of Cl<sup>−</sup> from the reaction of O<sub>2</sub><sup>−</sup> with CH<sub>2</sub>Cl<sub>2</sub> [12]:



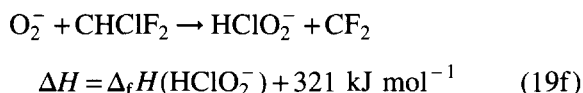
is thermodynamically closed for CH<sub>2</sub>ClF



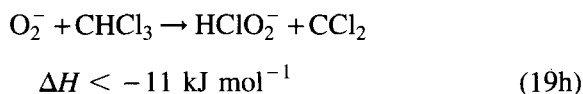
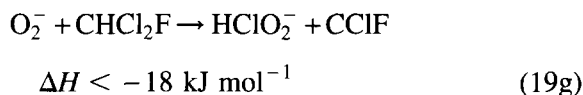
This may imply that the pathway to produce Cl<sup>−</sup> in the reaction of O<sub>2</sub><sup>−</sup> with CH<sub>2</sub>Cl<sub>2</sub> is via or in competition with the production of the neutrals H<sub>2</sub>O and CClO:



For the reaction with CHClF<sub>2</sub> the interesting product HClO<sub>2</sub><sup>−</sup> (16%) is observed in competition with the production of Cl<sup>−</sup> (84%):



Thus,  $\Delta_f H(\text{HClO}_2^-) < -321 \text{ kJ mol}^{-1}$ . This value can be used to assess the exothermicity of other reactions in which HClO<sub>2</sub><sup>−</sup> could be formed. In particular:



These pathways are clearly exothermic, yet HClO<sub>2</sub><sup>−</sup> is not an observed product for the reaction of O<sub>2</sub><sup>−</sup> with CHClF<sub>2</sub> or CHCl<sub>3</sub>. For the reaction of O<sup>−</sup> with CHClF<sub>2</sub> we have already suggested that the formation of HClO<sup>−</sup> is driven by the formation of CF<sub>2</sub>. It seems likely that this is also true for the reaction of O<sub>2</sub><sup>−</sup> with CHClF<sub>2</sub>. It is of note that a similar process was observed in a study by

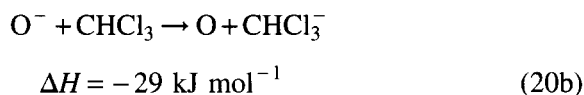
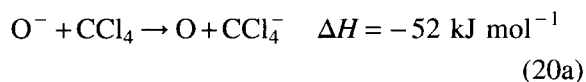
Morris et al. [16] for the reaction of  $\text{O}_2^-$  with  $\text{CHBrF}_2$ , where  $\text{HBrO}_2^-$  is the major product (71%).

It is worthy of comment that none of the  $\text{O}_2^-$  bimolecular reactions with the HCFCs results in fluorine containing anion products although exothermic reaction pathways for them are available. These are, however, usually less exothermic than the reaction pathways for the formation of chloride or chlorine containing anions from the partially chlorinated molecules. In addition the presence of fluorine in a methane molecule provides less steric hindrance to the carbon, than does the presence of chlorine. The process of nucleophilic attack on carbon is then more likely to proceed through the fluorinated side of a partially fluorinated and chlorinated methane, ejecting chlorine from the opposite side to the attack. This still does not explain the lack of reaction in the molecules that do not contain chlorine. Thus, an activation barrier to the rearrangements required in these reactions may also exist, which is too large to overcome at thermal energies unless the compound is chlorinated.

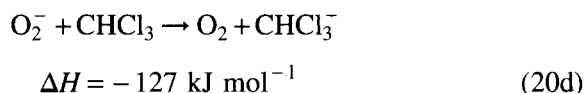
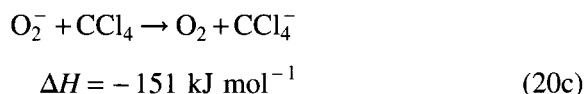
For the six HFCs studied, exothermic bimolecular reaction pathways exist, but do not take place, indicating that there is an activation barrier hindering these processes. With the exception of  $\text{CH}_3\text{F}$ , all associate with  $\text{O}_2^-$  at an observable rate.

## 6. Electron transfer

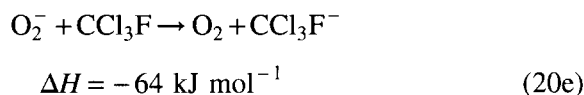
In no case was electron transfer observed. The electron affinities of the neutral molecules of this study are unknown. Therefore, we cannot determine if the electron transfer channels are open. For the molecules of our earlier study [12], some of their electron affinities are known, and the following channels are exothermic but not observed:



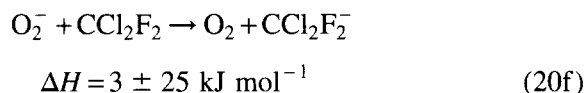
and



Only for the reactions:



and



is the electron transfer channel observed. With the possible exception of these two reactions, it appears that electron transfer does not compete favourably with other reaction pathways.

Dissociative electron transfer is only known to be exothermic for one of the reactions presented in this study—that of  $\text{O}_2^-$  with  $\text{CHCl}_2\text{F}$ . The product  $\text{Cl}^-$  was observed, but in view of the low exothermicity of this pathway ( $\Delta H = -9 \pm 8 \text{ kJ mol}^{-1}$ ) it seems more likely that the  $\text{Cl}^-$  has all been formed through nucleophilic attack on carbon.

## 7. Concluding remarks

Nucleophilic attack and  $\text{H}$ ,  $\text{H}^+$ , and  $\text{H}_2^+$  abstraction are the major mechanisms involved in the reactions of  $\text{O}^-$  with the molecules presented in this paper. Electron detachment, observed in the  $\text{O}^-$  reactions with  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_3\text{CHF}_2$ , and  $\text{CHF}_2\text{CHF}_2$ , is proposed to result from a product anion of the  $\text{H}_2^+$  abstraction channel gaining sufficient internal energy during the reaction process to autodetach. For the bimolecular

$O_2^-$  reactions studied in this and our earlier investigations the dominant mechanism is nucleophilic attack on carbon (invariably producing  $Cl^-$  by substitution). For  $O^-$  nucleophilic attack on carbon is in competition with various stripping reactions.

The nucleophilic attack pathways leading to halide displacement, particularly those observed with the  $O^-$  reactions, pose some interesting questions about the reaction dynamics. Simple systems have been studied with a view to predicting the efficiency of the  $S_N2$  pathway (for example, see references [34–36]), but usually where the reaction proceeds via a straightforward displacement of the leaving group by the nucleophile (i.e. no other reaction steps occur). To extend these ideas to the reactions studied here is more complicated. There is the obvious difficulty in calculating physical properties at the transition states. Furthermore, the collision geometry of the reactions is much more complicated, and there are other reaction pathways available, which may be preferred depending upon the orientation of the constituents within the collision complex. Such complexity is highlighted in the theoretical study by Lee and Dyke [30] on the reaction of  $O^-$  with  $CH_2F_2$  which reveals that this reaction occurs over a very complicated surface. Our study, with its detailed characterisation of the reaction pathways, is providing us with a unique opportunity to explore and investigate the various chemical and physical processes involved in anion–molecule reactions.

On a more applied theme, instrumentation, such as the ECD and IMS, and techniques such as negative ion chemical mass spectrometry, are not being used to the best of their potential, because of a lack of understanding of the fundamental ion–molecule reactions taking place. In part this is due to the complexity of response and the underlying richness of the chemistry; but it is this which leads to their considerable potential, potential which has yet to be fully realised. We are building up a detailed picture of the chemistry from which it will be

possible to obtain a better understanding of the separate techniques. This fundamental work will lead to the development of new detection and monitoring systems, combining the best aspects of the three existing techniques. Thus we view our studies of relatively simple ion–molecule reactions as an essential underpinning of the more applied work that is being performed to develop highly selective and sensitive monitors for toxic chemicals and pollutants in the atmosphere.

## Acknowledgements

CAM, RAK, and RP are grateful to the PLSD, (CBD), Porton Down, United Kingdom, for the financial support of this work. One of us (RP) would especially like to thank the CBD for a studentship and a postdoctoral fellowship. We thank Professor J. Dyke (University of Southampton) for helpful discussions.

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