Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 233 (2004) 259–265

www.elsevier.com/locate/ijms

Electron attachment to and anion reactions with SF_5Cl: electron-swarm and selected ion flow tube studies

C.A. Mayhew*, A. Critchley, G.K. Jarvis

Molecular Physics Group, Schools of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Received 15 September 2003; accepted 23 December 2003

Professor Tilmann Märk has made outstanding contributions to the fields of electron attachment processes and ion-molecule reactions, and is a source of great inspiration to all working in those scientific areas. It is therefore a great pleasure to dedicate this paper, which deals with both electron attachment processes and ion-molecule reactions, to Tilmann on the occasion of his 60th birthday.

Abstract

The first investigation of non-thermal electron attachment to SF_5Cl in a swarm environment is reported here. An electron swarm mass spectrometer, the drift tube of which operates in an atmospheric pressure of N_2 or Ar, has been used to obtain the data. Experimental attachment rate coefficients, k_a, and the anion products resulting from electron attachment are reported. k_a is observed to decrease as the mean electron energy increases. The estimated thermal (300 K) electron attachment rate constant is $k_{th} \approx (1.3 \pm 0.4) \times 10^{-8}\,cm^3\,s^{-1}$, which is significantly less than the expected s-wave capture rate. The mass spectra obtained show a number of anions resulting from electron attachment, namely F_2^-, SF_4^-, SF_5^- and SF_5Cl^-, with SF_5^- and SF_5Cl^- being the only anions observed as the mean electron energy approaches zero. Anion reactions with SF_5Cl made it difficult to accurately assign branching ratios, and therefore only a qualitative description of the results will be presented here. Anion reactions with SF_5Cl are of general interest and make interesting comparisons with anion reactions involving SF_6. In this paper, we also present the results of a selected ion flow tube study investigating the 300 K reactions of SF_5Cl with a number of anions; O_2^-, SF_6^-, OH^-, CF_3^-, F^-, Cl^- and SF_5^-.

Keywords: Electron attachment; Branching ratios; Anion reactions

1. Introduction

Electron attachment to SF_6 has been extensively studied, mainly because of the use of SF_6 in plasma-etching applications in industry [1,2] and as an insulating dielectric [3,4]. Electron attachment data need to be incorporated into models used to characterise gaseous discharges and industrial plasmas. Comparisons of electron attachment to related molecules and derivatives of SF_6 provide interesting insights into the physical and chemical molecular properties of electron attachment, improve our understanding of this fundamental process, are informative and are of general interest. Towards this goal, we have recently reported electron attachment to a series of homologous molecule SF_6, SeF_6, and TeF_6 and a derivative of SF_6, SF_5CF_3, using a non-thermal electron-swarm technique [5,6]. It is found that SF_6 attaches electrons much more rapidly than either SeF_6 or TeF_6, with the attachment being dominated by the capture of near zero-energy electrons. In each case the dominant anion product is XF_6^- (X = S, Se, Te), accompanied by XF_5^-. SF_5CF_3 is also found to attach electrons most rapidly for near-zero electron energy with the estimated thermal electron attachment rate constant being approximately 25% of that for SF_6, and producing only one observed anion product, SF_5^-, i.e., the parent anion $(SF_5CF_3^-)^*$ is not sufficiently long-lived to be detected [6]. These results have been confirmed by a beam study investigating low energy electron attachment to SF_5CF_3 [7]. In this paper, we present an electron attachment study to another derivative of SF_6, namely SF_5Cl.

Only two previous studies have investigated the electron attachment properties of SF_5Cl [8,9], and both of these used low-pressure electron beam techniques. Whilst these provide details of the product anions as a function of electron energy,

---

* Corresponding author.
E-mail address: c.mayhew@bham.ac.uk (C.A. Mayhew).

1387-3806/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.ijms.2003.12.031

no information is available on the electron attachment rate coefficients. Swarm techniques are more amenable to determining absolute electron attachment rate coefficients. Furthermore, electron swarm environments are characterised by multiple collisions, which can play a stabilising role and are more characteristic of plasmas and gas discharges.

2. Experimental details

The electron-swarm technique [10,11] and our apparatus [5,12,13] have been described in the literature. In brief, an electric potential is applied along a drift tube creating a uniform electric field, *E*, drawing electrons towards a Faraday plate detector. An electron energy distribution is established, determined by a dynamic balance between the kinetic energy gained from the electric field and energy loss through multiple collisions with the buffer gas (either Ar or N_2 of number density *N*). The shape of this energy distribution depends on *E*/*N*, the type of buffer gas used, and the temperature. For fixed *N*, higher electric field strengths lead to higher mean electron energies. For a given *E/N*, use of Ar as the buffer gas results in an electron swarm with higher mean electron energies than provided by N_2. The studies presented here cover $E/N = 0.4 \times 10^{-18}$ to 15×10^{-18} V cm^2 for N_2 ($\bar{\varepsilon} = 0.04$–0.4 eV) and 0.4×10^{-18} to 6×10^{-18} V cm^2 for Ar ($\bar{\varepsilon}$ range of 0.5–1.9 eV).

Electrons can be distinguished from anions, formed by electron attachment, by a simple timing arrangement in which the electrons are admitted into the drift tube as a short (1–2 ms) pulse. The large mass difference between electrons and anions ensures that anions arrive at the end of the drift tube after the electrons and over a far broader time window. We can thus monitor the attenuation of electron pulses as a function of the admitted reactant gas concentration with little interference from product anions. The density reduced electron attachment coefficient, α, is determined as a function of *E/N*. Multiplication of α with the mean electron drift speed gives the electron attachment rate constant, k_a, as a function of *E/N* (and hence mean electron energy).

A small orifice in the Faraday plate allows anions formed within the drift tube to enter a differentially pumped region leading to a quadrupole mass spectrometer. Anions formed from electron attachment and secondary anions, resulting from subsequent anion-molecule reactions, can thus be monitored. In this mode of operation electrons are admitted continuously into the drift tube, i.e., the investigation of the product anions takes place during a completely separate experiment from the electron attachment rate measurements. Different *E/N* values are used and coarser steps in the electron mean energy are taken. Branching ratios are obtained by extrapolating product anion signals to zero neutral attaching gas number density. This takes into account any reactions of the product anions with the neutral attaching gas. Branching ratios were measured with the detection quadrupole mass spectrometer operating at its lowest resolution. This reduced mass discrimination effects. Nevertheless, even when operating in this mode there is still great uncertainty associated with the measurement of branching ratios because of the need to allow for secondary reactions and because as the *E*/*N* is reduced the anion signal intensity dramatically decreases. As a result of these problems only a qualitative description of the branching ratios will be presented here.

The sample of SF_5Cl was commercially purchased (Apollo Scientific Limited) with a stated purity of 97%, and was used without further purification. We were unable to obtain any information on the possible impurities within our sample from the supplier. Stainless steel cylinders (volume $\sim 2 \times 10^3$ cm^3), which have been silcosteel treated (Restek Corporation) to passivate the surfaces, were used to store the SF_5Cl gas in concentrations of typically a few hundred ppm in nitrogen or argon gas at a total pressure of about 2 atm. Gases in the cylinders were continuously mixed by a small circulation pump to ensure homogeneity. Even with the use of specially treated containers, we noted that the SF_5Cl sample deteriorated with time, presumably because of reactions of SF_5Cl with the surfaces. Therefore, samples were prepared and used as quickly as possible. New samples were prepared on a routine basis.

3. Results and discussion

3.1. Electron attachment rate constants

The SF_5Cl electron attachment rate constants determined in this study are presented in Fig. 1 as a function of mean electron energy and the results are summarised in Table 1. These rate constants were calculated from our measured density normalised electron attachment coefficients. Electron drift velocities needed for this calculation were taken from tables provided by Hunter et al. [14]. As observed for

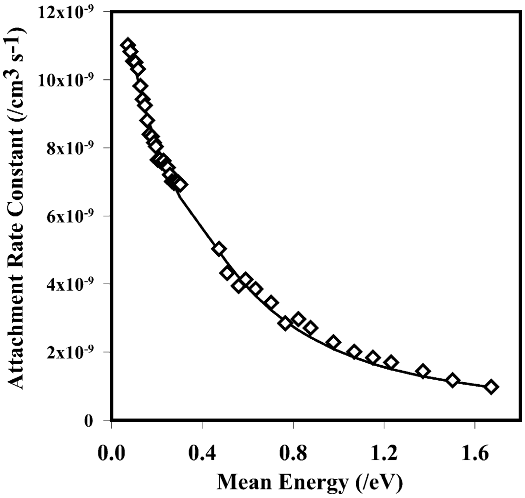

Fig. 1. Electron attachment rate constants for SF_5Cl in a buffer gas of N_2 (<0.4 eV) and Ar (>0.4 eV).

Table 1
Electron attachment rate constants $k_a(E/N)$ for SF_5Cl in N_2 and Ar buffer gases as a function of E/N and mean electron energy $\bar{\varepsilon}$

SF_5Cl/N_2			SF_5Cl/Ar		
E/N ($\times 10^{-18}$ V cm^2)	$\bar{\varepsilon}$ (eV)	k_a ($\times 10^{-8}$ cm^3 s^{-1})	E/N ($\times 10^{-18}$ V cm^2)	$\bar{\varepsilon}$ (eV)	k_a ($\times 10^{-8}$ cm^3 s^{-1})
1.47	0.073	1.102	0.31	0.474	0.503
1.76	0.084	1.083	0.37	0.510	0.432
2.05	0.095	1.054	0.47	0.560	0.394
2.35	0.106	1.051	0.53	0.591	0.413
2.64	0.117	1.031	0.62	0.635	0.385
2.93	0.127	0.982	0.78	0.703	0.345
3.23	0.138	0.942	0.93	0.765	0.285
3.52	0.147	0.925	1.09	0.823	0.297
3.81	0.157	0.881	1.24	0.877	0.271
4.11	0.168	0.840	1.55	0.977	0.229
4.40	0.178	0.833	1.86	1.069	0.201
4.70	0.188	0.815	2.17	1.151	0.184
4.99	0.196	0.804	2.49	1.231	0.170
5.28	0.203	0.765	3.11	1.372	0.144
5.58	0.212	0.766	3.73	1.502	0.117
5.87	0.221	0.757	4.66	1.672	0.098
6.16	0.230	0.762			
6.46	0.239	0.748			
6.75	0.248	0.742			
7.04	0.257	0.721			
7.34	0.266	0.701			
7.63	0.276	0.697			
7.92	0.285	0.700			
8.22	0.294	0.699			
8.51	0.303	0.692			

SF_6, the electron attachment rate constant associated with SF_5Cl decreases with increasing mean electron energy, but its value at low mean electron energies is significantly less than the expected s-wave capture value. Extrapolation of the electron attachment rate constant data to a mean electron energy of 0.038 eV provides as an estimate of the thermal (300 K) electron attachment rate constant; $k_{th} \approx (1.3 \pm 0.4) \times 10^{-8}$ cm^3 s^{-1}. By the very nature of the extrapolation, the error on k_{th} is relatively large. We are currently modifying our instrument so that thermal electron attachment rate constants can be readily determined.

The similarity in the dependence of the rate constants as a function of mean electron energy to that for electron attachment to SF_6, means that the electron attachment cross section for SF_5Cl peaks at ~0 eV, but its value will be smaller at 0 eV than that for SF_6. Deconvolution of our rate coefficient data permits an estimation of the cross section for electron capture at zero electron energy to be approximately 1×10^{-15} cm^2, which is two orders of magnitude smaller than that determined for SF_6 ($\sigma(\varepsilon = 0) \sim 1 \times 10^{-13}$ cm^2).

It is of interest to compare the above observations with another swarm study of ours, in which we investigated electron attachment to the series of molecules $CHCl_2F$, $CHClF_2$, and CHF_3 [13]. In the case of SF_6, we have just noted that replacement of an F atom by Cl leads to a large decrease in the density normalised electron attachment coefficient (and related quantities). In contrast, replacing Cl by F in $CHCl_2F$, to give $CHClF_2$, leads to a large decrease in α, and the mean electron energy has to be increased in order to observe electron attachment. In the case of CHF_3, we were unable to detect any attachment. Thus,

$$\alpha(SF_6) > \alpha(SF_5Cl)$$

but

$$\alpha(CHF_3) < \alpha(CHClF_2) < \alpha(CHCl_2F)$$

3.2. Products of electron attachment to SF_5Cl

SF_5Cl is observed to undergo dissociative electron attachment through a number of channels. In comparison, whilst SF_5CF_3 also extensively fragments upon electron attachment, it does so only through one channel leading to the product anion SF_5^- over the range of mean electron energies we investigated [6]. Sailer et al. [7] have ascribed this difference to the so-called electron capacity [15] of the substitute Cl as opposed to CF_3, which is a measure of the localization of the electron charge in the primary step of electron capture to the neutral molecule.

A typical mass spectrum of the anion products resulting from electron attachment to SF_5Cl is illustrated in Fig. 2. This mass spectrum was recorded with a reactant gas number density of 1.2×10^{11} molecules cm^{-3} in a buffer gas of N_2 at atmospheric pressure and at an E/N of 4.4×10^{-18} V cm^2 (corresponding to a mean electron energy of 0.18 eV). The resolution of the mass spectrometer was

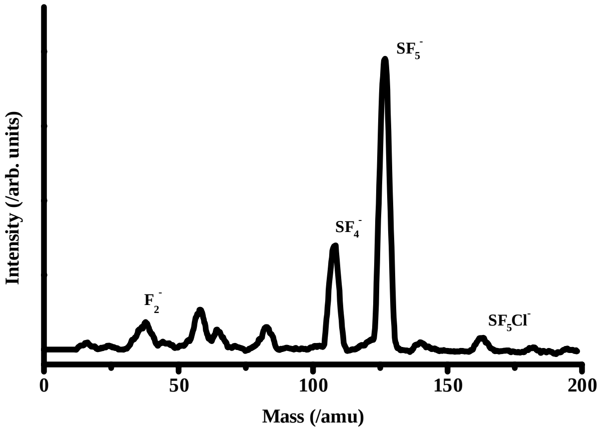

Fig. 2. Mass spectrum of the anion products resulting from electron attachment to SF_5Cl taken at an E/N of 4.4×10^{-18} V cm^2 (corresponding to a mean electron energy of 0.18 eV) and $[SF_5Cl] = 1.2 \times 10^{11}$ molecules cm^{-3} in a buffer gas of N_2. (Note that SF_4^- reacts with SF_5Cl to give SF_5^-, which leads to a larger SF_5^- intensity than results from electron attachment.)

set at its lowest possible value to minimise mass discrimination effects. As can be seen from Fig. 2, the two dominant product anions observed are SF_4^- and SF_5^-. Other smaller peaks in the mass spectrum are assigned to be F_2^- and SF_5Cl^-. It is possible that a peak at $m/z = 81$ amu results from an ion-molecule reaction leading to SO_2F^-. There are unassigned peaks at $m/z \sim 60$, 70, and 140 amu, but the branching ratios associated with these, like that associated with $m/z = 81$, extrapolate to zero as the concentration of the reactant molecule decreases. Therefore, these peaks are believed to be a result of reactions of the anion products with trace molecules present in our system.

Anion-molecule reactions were also observed to occur between SF_4^- and SF_5Cl leading to SF_5^-:

$$SF_4^- + SF_5Cl \rightarrow SF_5^- + SF_4Cl,$$
$$\Delta H = \Delta_f H(SF_4Cl) + 6.33\,\text{eV} \tag{1}$$

which indicates that $\Delta_f H(SF_4Cl) < -6.33$ eV. With the exception of $\Delta_f H(SF_5Cl) = -985$ kJ mol^{-1}, which was determined by us from a study investigating cation reactions with SF_5Cl [16], all other heats of formation used to determine the enthalpy of reaction (1), and all other reactions listed in this paper were taken from the NIST Webbook [17].

The direct effect of reaction (1) on our branching ratios is that the SF_5^-/SF_4^- signal ratio will be concentration dependent. Therefore, it was essential to extrapolate product anion intensities to zero SF_5Cl concentration in order to determine branching ratios. In practice, this is extremely difficult, especially at low E/N values, because the anion signals dramatically decrease as E/N is reduced. This resulted in much uncertainty associated with the branching ratios. Nevertheless, we can be definite about a number of observations. Firstly that the branching ratios smoothly transfer over from the N_2 to the Ar data, indicating that the electron attachment process is independent of the buffer gas. Secondly, as the mean electron energy tends to zero, the branching ratio associated with the SF_4^- product anion extrapolates to zero percent, in agreement with the thermodynamics ($e^-(0\,\text{eV}) + SF_5Cl \rightarrow SF_4^- + ClF$, $\Delta H = 0.31 \pm 0.29$ eV), as too does the branching ratio associated with F_2^-. (The observation of the F_2^- product anion implies that SF_3Cl must be the neutral product and that $\Delta H(SF_3Cl) < -7.2$ eV.) Thirdly, two product anions remain as the mean electron energy tends to 0 eV, namely SF_5Cl^- (~10%) and SF_5^- (~90%). This is in agreement with a very recent and on-going study of ours in which the electrons in our swarm environment are maintained at a thermal (300 K) energy distribution.

Perhaps the most controversial result we obtained in terms of the product anions, was that for relatively minor changes in the mean electron energy the branching ratio associated with SF_4^- anion dramatically increased, with the result that SF_4^- anion became the dominant species above about 0.2 eV mean electron energies. We have not observed such dramatic changes in branching ratios before, and therefore we must be sceptical of the results, and they warrant some discussion.

That SF_5^- is the dominant anion at low mean electron energies is to be expected given that $EA(SF_5) = 3.8$ eV. As mentioned above, what is unexpected is the formation of SF_4^- at low mean electron energies given that $EA(SF_4) = 1.5$ eV [18]. The large differences in the electron affinities of SF_5 and SF_4 would lead one to expect that once formed SF_5Cl^- should naturally fall apart into SF_5^- and Cl. It is therefore appropriate at this stage to question the swarm results. Could the SF_4^- we observe be a result of collision-induced dissociation (CID) in the region between the drift tube and the quadrupole mass spectrometric region? Whilst CID can occur in our instrument, we were careful to keep this to a minimum by maintaining the voltage on the focussing lenses in our instrument to a minimum balanced with the requirement of obtaining a useable signal. Furthermore, in other studies we did not observe any dissociation of SF_5^- to $SF_4^- + F$ as a result of collisional processes [12]. Could an impurity in our sample result in the SF_4^- anion being produced? Again this is unlikely given the large branching ratio associated with the SF_4^- channel for mean energies above ~0.2 eV and that impurities are at less than the 3% level. Furthermore, thermal electron attachment studies using a flowing-afterglow Langmuir-probe apparatus by Miller et al. [18] show that electron attachment to SF_4 produces SF_4^-. Thus, if SF_4 was an impurity in our sample of SF_5Cl for example, we would expect to observe SF_4^- to remain as a major anion below 0.2 eV, which we do not. Could we have incorrectly assigned the peak in our mass spectrum? We cannot identify a different anion which would have a peak in the mass spectrum exactly 19 amu less than that associated with the SF_5^- product anion.

With the SF_4^- channel problem in mind, it is worth mentioning that energetics alone do not determine the direction of the dissociative electron attachment pathway.

Table 2
Thermochemistry related to electron attachment to SF_5Cl

Reaction $e^- + SF_5Cl \rightarrow$	Enthalpy of reaction (eV)
SF_5Cl^-	$-EA(SF_5Cl)$
$SF_5^- + Cl$	−1.75
$SF_4^- + ClF$	0.31 ± 0.29
$SF_4^- + F + Cl$	2.02
$F_2^- + SF_3Cl$	$\Delta H(SF_3Cl) + 7.2\,eV$
$F_2^- + SF_3 + Cl$	3.24
$F^- + SF_4Cl$	$\Delta H(SF_4Cl) + 7.6\,eV$
$Cl^- + SF_5$	−1.55
$ClF^- + SF_4$	0.23 ± 0.37

The enthalpies of the reactions have been determined for zero kinetic energy electrons.

For example, the reaction leading to the Cl^- product anion is exothermic, but we did not observe this channel in our swarm measurements. Thus, other factors than overall energy play a role in determining the fragmentation pathway in dissociative electron attachment. Our swarm measurements suggest that once the transient parent anion is produced, it preferentially dissociates (at least for electron swarms whose mean electron energies are below 0.2 eV) with the electron being attached to the fragment with the greatest electron affinity, in this case SF_5, to the exclusion of the other fragment Cl (EA = 3.6 eV), despite the fact that difference in the enthalpies of the two channels is only 0.2 eV, i.e., the difference in the electron affinities of SF_5 and Cl:

$$e^- + SF_5Cl \rightarrow (SF_5Cl^-)^* \rightarrow SF_5^- + Cl, \quad \Delta H = -1.75\,\text{eV (channel observed)} \tag{2}$$

$$e^- + SF_5Cl \rightarrow (SF_5Cl^-)^* \rightarrow Cl^- + SF_5, \quad \Delta H = -1.55\,\text{eV (channel not observed)} \tag{3}$$

ΔH corresponds to the enthalpy of the reaction for zero kinetic energy electrons. Table 2 summarises the thermochemistry relating to the electron attachment to SF_5Cl.

Electron beam studies also found that dissociative electron attachment to SF_5Cl dominated the attachment process. However, interestingly the branching ratios of product anions are different to those that we obtained. At electron energies of ∼0 eV, Fenzlaff et al. [9] observed the following product anions and corresponding branching ratios (in brackets); SF_5Cl^- (<1%), SF_5^- (8%), ClF^- (15%), Cl^- (46%) and F^- (30%). At higher electron energies the anions SF_4^-, SF_3^-, SF_2^-, and F_2^- were observed, but with very small branching ratios. None of the major anion products observed in the beam study, which have resonances at electron energies of ∼0 eV, i.e., F^-, Cl^- and ClF^-, are observed in our swarm study. In the only other, and earlier, beam study by Harland and Thynne [8], low appearance energies for F^-, Cl^- and ClF^- fragments are not reported, and appearance energies of 3.2, 4.0, and 7.6 eV, respectively, are given.

A possible explanation of the discrepancy between the electron beam and our swarm measurements could be associated with the purity of the samples used in the beam studies. This present investigation of the product anions resulting from electron attachment to SF_5Cl highlights the experimental difficulties of working with a molecule such as SF_5Cl, and the need to reinvestigate electron attachment to SF_5Cl using electron beam techniques to help reconcile these interesting differences.

4. Anion-SF_5Cl reaction measurements

That we did not observe Cl^- as a product anion is surprising for two reasons. Firstly, dissociative electron attachment of low energy electrons to this product is exothermic. Secondly, Fenzlaff et al. observed Cl^- as the dominant anion product for electron energies of about 0 eV in their beam studies. To help shed some light on these differences we decided to study the reaction of an anion, which has a low electron detachment energy, with SF_5Cl. We therefore investigated the reaction with O_2^- as the reactant anion. O_2 has a low electron affinity (0.440 ± 0.006 eV). This makes O_2^- very reactive, and electron transfer should readily occur from O_2^- to a molecule which has an electron affinity greater than 0.440 eV. O_2^- represents in some sense an electron with negative energy, it is an electron donor, and makes an interesting comparison to free electron attachment. If Cl^- is observed as a product from the reaction of O_2^- with SF_5Cl, then we should expect to see Cl^- in our swarm study.

Using a selected ion flow tube (SIFT), the reaction of O_2^- with SF_5Cl was investigated. The SIFT apparatus, experimental technique, and analysis of data have been extensively reviewed in the literature [19,20] and the reader is referred to those references for more details. We found that the reaction proceeds at a rate constant of $(1.3 \pm 0.3) \times 10^{-9}\,cm^{-3}\,s^{-1}$, which is close to the calculated collisional value, resulting in the anion products SF_5^- (86%), SF_5Cl^- (13%) and SOF_2^- (∼1%). The last proposed product anion is a result of a chemical reaction in which bonds are broken and formed, However, it has such a small branching ratio, that we cannot rule out that it is a result of reaction with an unknown impurity. Otherwise, the results are in agreement with our swarm measurements corresponding to mean electron energies at thermal energies. The observation of the first two products, SF_5^- (86%) and SF_5Cl^- (13%), implies that electron transfer takes place, and that the major channel is dissociative. The Cl^- channel, which is highly exothermic, is not observed, whilst the slightly more exothermic channel leading to SF_5^- is

$$O_2^- + SF_5Cl \rightarrow (SF_5Cl^-)^* \rightarrow Cl^- + SF_5 + O_2, \quad \Delta H = -107\,\text{kJ mol}^{-1} \tag{4}$$

$$O_2^- + SF_5Cl \rightarrow (SF_5Cl^-)^* \rightarrow SF^- + Cl + O_2, \quad \Delta H = -125\,\text{kJ mol}^{-1} \tag{5}$$

Table 3
300 K reaction rate coefficients and product anion distributions for the reactions of SF_5Cl with various negative ions

Reagent anion	Rate coefficient ($\times 10^{-9}$ cm^3 molecule^{-1} s^{-1})	Product anion (%)	Proposed neutral products	ΔH (kJ mol^{-1})
O_2^-	1.3 [1.6]	SF_5^- (86)	Cl + O_2	−125
		SF_5Cl^- (13)	O_2	$EA(O_2) - EA(SF_5Cl)$
		SOF_2^- (1)		
SF_6^-	0.04 [0.95]	SF_5Cl^- (100)		$EA(SF_6) - EA(SF_5Cl)$
OH^-	1.9 [2.1]	SF_5^- (62)	Cl + OH	9 ± 60
		SF_5Cl^- (28)	OH	$EA(OH) - EA(SF_5Cl)$
		$SClO^-$ (4)	HF + $2F_2$	$\Delta_f H(SClO^-) - 851$
		Cl^- (3)	SF_5 + OH	28 ± 60
		$F_2SH^-/ClFOH^-$ (2)		
		SF^- (1)		
CF_3^-	0.80 [1.1]	SF_5^- (100)	Cl + CF_3	7 ± 60
F^-	1.5 [2.0]	SF_5^- (100)	ClF	−91
Cl^-	0.94 [1.5]	SF_5^- (100)	Cl_2	−63
SF_5^-	0 [0.99]	n.r.		

The capture rate coefficients, calculated using parametrized fits to results from trajectory calculations [21], are presented in square brackets under the experimental values. The measured rate coefficients and product anion branching ratios are considered to be accurate to ±20%. The calculation for the collisional rate coefficients require as inputs the polarizability and dipole moment of the molecule. The polarizability of SF_5Cl has been estimated to be 8.38×10^{-30} m^3 using Miller and Savchik's empirical approach. At the Hartree–Fock level, the dipole moment for SF_5Cl has been calculated to be 0.93 D. The enthalpy of the reaction has been determined where possible.

i.e., as the transient negative ion $(SF_5Cl^-)^*$, formed by electron transfer from O_2^- to SF_5Cl begins to dissociate, the electron preferentially attaches itself to the SF_5 fragment rather than the Cl fragment. These results suggest that there is a potential energy barrier to the reaction channel leading to Cl^-, which must be sufficiently large to make even dissociative electron attachment to low energy free electrons via this channel impossible.

Anion reactions with SF_5Cl are of general interest and make interesting comparisons with anion reactions with SF_6. Therefore, in addition to the reaction of O_2^-, we have also investigated the reaction of SF_5Cl with a series of anions; SF_6^-, OH^-, CF_3^-, F^-, Cl^- and SF_5^-. The results for these, together with the O_2^- reactions are summarised in Table 3. The reaction with SF_6^- is of particular interest, because in contrast to the O_2^- reaction, this reaction proceeds at well below the collisional rate, with a reaction rate coefficient of $k = (4.0 \pm 0.8) \times 10^{-11}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, producing SF_5Cl^- exclusively via non-dissociative electron transfer:

$$SF_6^- + SF_5Cl \rightarrow SF_5Cl^- + SF_6,$$
$$\Delta H = EA(SF_6) - EA(SF_5Cl) \qquad (6)$$

The low rate coefficient measured for reaction (6) could be taken to indicate a small thermodynamic barrier to electron transfer, i.e., $EA(SF_5Cl)$ is slightly less than $EA(SF_6)$, so that $k_r = k_c \times \exp(-\Delta/k_B T)$, where k_c is the collisional rate constant and $\Delta \cong EA(SF_6) - EA(SF_5Cl)$, resulting in $EA(SF_5Cl) \sim 1.0$ eV. However, the reaction of OH^- with SF_5Cl rules this out, with the observation of SF_5Cl^- as a major product anion formed by non-dissociative electron transfer, with a branching ratio of 28%. This implies that $EA(SF_5Cl) > EA(OH) = 1.828$ eV. Thus, there must be a significant barrier to the reaction of SF_6^- with SF_5Cl, the reaction of which by electron transfer must be highly exothermic.

Given that the electron affinity of SF_5 is greater than that of F and Cl, the observation of the SF_5^- as the only product anion from reactions of F^- and Cl^- implies that ClF and Cl_2 must be the neutrals formed during the reactions, respectively, if the processes are to be exothermic:

$$F^- + SF_5Cl \rightarrow SF_5^- + ClF, \quad \Delta_r H^\circ_{298} = -91\,\mathrm{kJ\,mol^{-1}} \qquad (7)$$

$$Cl^- + SF_5Cl \rightarrow SF_5^- + Cl_2, \quad \Delta_r H^\circ_{298} = -63\,\mathrm{kJ\,mol^{-1}} \qquad (8)$$

That F^- and Cl^- anions react with SF_5Cl with reasonable efficiencies could be taken to explain why we did not observe Cl^- and F^- product anions resulting from electron attachment, i.e., these two product anions reacted with SF_5Cl to form the SF_5^- anion within our drift tube on a timescale shorter than their transit time taken for them to drift down the reaction chamber and be detected. However, as described above, care was taken to monitor product anions as a function of SF_5Cl concentration in the drift tube of the electron swarm mass spectrometer. Further beam and swarm studies are therefore planned to help explain the observation of the Cl^- product anion in the beam study.

5. Conclusions

Our study of electron capture to SF_5Cl shows that there is a strong resonance to electron attachment at ∼0.0 eV that leads predominantly to dissociative attachment anion products, SF_5^- and SF_5Cl^-, with only a small branching ratio being associated with the parent anion, SF_5Cl^- (∼10%).

Although the resonance behaviour is similar to that observed for SF_6, the ratio of dissociative/non-dissociative products observed is distinctly different.

Neither of the two electron beam studies [8,9] indicates the appearance of SF_4^- at low electron energies, a product anion we observed in our swarm study with a large branching ratio above about 0.2 eV mean electron energy. Furthermore, for one of the beam studies [9], Cl^- is an observed product anion, dominating the dissociative electron attachment channels of SF_5Cl. However, in our electron swarm study we observed no Cl^- product anion at any of the mean electron energies investigated. Whilst, collisional stabilisation in the swarm environment can account for differences in the branching ratios measured by beam and swarm studies, it is difficult to explain our observations on those grounds.

Acknowledgements

We wish to acknowledge the support of EPSRC for funding this project.

References

[1] C.L. Lugez, M.E. Jacox, R.A. King, H.F. Schaefer III, J. Chem. Phys. 108 (1998) 9639.

[2] E.R. Fisher, B.L. Kickel, P.B. Armentrout, J. Chem. Phys. 97 (1992) 4859.

[3] V. Tarnovsky, H. Deutsch, K.E. Martus, K. Becker, J. Chem. Phys. 109 (1998) 6596.

[4] L.G. Christophorou, J.K. Olthoff (Eds.), Proceedings of the VIII International Symposium on Gaseous Dielectrics, Plenum Press, New York, 1998.

[5] G.K. Jarvis, R.A. Kennedy, C.A. Mayhew, Int. J. Mass Spectrom. 205 (2001) 253.

[6] R.A. Kennedy, C.A. Mayhew, Int. J. Mass Spectrom. 206 (2001) i.

[7] W. Sailer, H. Drexel, A. Pelc, V. Gill, N.J. Mason, E. Illenberger, J.D. Skalny, T. Mikoviny, P. Scheier, T. Märk, Chem. Phys. Lett. 351 (2002) 71.

[8] P. Harland, J.C.J. Thynne, J. Phys. Chem. 73 (1969) 4031.

[9] M. Fenzlaff, R. Gerhard, E. Illenberger, J. Chem. Phys. 88 (1988) 149.

[10] L.G. Christophorou (Ed.), Atomic and Molecular Radiation Physics, Wiley-Interscience, New York, 1971.

[11] S.R. Hunter, L.G. Christophorou, D.L. McCorkle, I. Sauers, H.W. Ellis, D.R. James, J. Phys. D: Appl. Phys. 16 (1983) 573.

[12] Y. Liu, C.A. Mayhew, R.P. Peverall, Int. J. Mass Spectrom. Ion Process. 152 (1996) 225.

[13] G.K. Jarvis, C.A. Mayhew, L. Singleton, S. Spyrou, Int. J. Mass Spectrom. Ion Process. 164 (1997) 207.

[14] S.R. Hunter, J.G. Carter, L.G. Christophorou, J. Chem. Phys. 90 (1989) 4879.

[15] J.K. Olthoff, J.A. Tossell, J.H. Moore, J. Chem. Phys. 83 (1985) 5627.

[16] C. Atterbury, A.D.J. Critchley, R.A. Kennedy, C.A. Mayhew, R.P. Tuckett, Phys. Chem. Chem. Phys. 4 (2002) 2206.

[17] W.G. Mallard, P.J. Linstrom (Eds.), NIST Chemistry Webbook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD 20899, February 2000 (http://webbook.nist.gov).

[18] T.M. Miller, A.E. Stevens Miller, J.F. Paulson, X. Liu, J. Chem. Phys. 100 (1994) 8841.

[19] N.G. Adams, D. Smith, in: J.M. Farrar, W.H. Saunders (Eds.), Techniques for the Study of Ion-Molecule Reactions, Wiley, New York, 1988, p. 165.

[20] D. Smith, N.G. Adams, Adv. At. Mol. Phys. 24 (1988) 1.

[21] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.