

A study of the gas phase reactions of various cations with two derivatives of SF₆; SF₅CF₃ and SF₅Cl

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A selected ion flow tube apparatus was used to investigate the positive ion chemistry of two derivatives of SF₆; SF₅CF₃ and SF₅Cl. This represents the first investigation of the positive ion chemistry of SF₅Cl, and much of the data on SF₅CF₃ is being presented here for the first time. Rate coefficients and ion product branching ratios have been determined at room temperature (300 K) for reactions with the following twenty-two cations; Ne⁺, F⁺, Ar⁺, N₂⁺, N⁺, CO⁺, CO₂⁺, O⁺, N₂O⁺, H₂O⁺, O₂⁺, SF₄⁺, CF₂⁺, SF⁺, SF₂⁺, NO₂⁺, SF₅⁺, NO⁺, CF⁺, CF₃⁺, SF₃⁺, and H₃O⁺ (listed in order of decreasing recombination energy). Comparisons are made in the text for the reactions of these ions with SF₆. SF₂⁺, NO₂⁺, NO⁺, SF₃⁺, and H₃O⁺ are found to be unreactive with both of the derivatives. The majority of the other reactions proceed with rate coefficients which are close to the capture value. The exceptions are the reactions of O₂⁺, SF⁺, SF₅⁺, and CF₃⁺ with SF₅CF₃, and SF₄⁺ and SF₅⁺ with SF₅Cl, all of which have rate coefficients significantly less than the capture mechanism value. Several distinct processes are observed among the large number of reactions studied, including dissociative charge transfer and various abstraction channels. Non-dissociative charge transfer is not observed, implying that any parent ions formed dissociate rapidly to the fragment ions and associated neutrals.

1. Introduction

There have been a number of investigations dealing with the positive ion chemistry of the important molecule sulfur hexafluoride, SF₆.^{1–8} These have been mostly associated with studies of the fundamental ion-molecule chemistry. Recent interest in this chemistry has come from the use of SF₆ in reactive plasmas for the etching of insulating and semiconductor layers.⁷ Studies of the reactions of ions with SF₆ and related molecules enhance our understanding of the complex ion chemistry and kinetics involved in SF₆ containing plasmas. For example, the data obtained could be used to help model plasmas in order to ascertain which physical and chemical parameters will need to be varied in order to optimise the plasma environment for a particular application. In this paper we present a study of the reactions of a series of positive ions with two derivatives of SF₆; trifluoromethyl sulfur pentafluoride, SF₅CF₃, and sulfur chloropentafluoride, SF₅Cl, and compare them with the corresponding reactions for SF₆.

Whilst the major stimulus for this investigation comes from its application to plasma ion chemistry, the recent detection of SF₅CF₃ in the stratosphere provides additional motivation to this study.⁹ As found for SF₆, SF₅CF₃ is not broken down by UV photodissociation in the stratosphere.¹⁰ This leads naturally to the question as to whether there are any other atmospheric loss mechanisms. A recent electron attachment study shows that the molecule will be destroyed in the regions of the ionosphere where free electrons exist.¹¹ This provides an upper limit to the atmospheric lifetime of SF₅CF₃ of ca. 1000 years. Other competitive routes in the ionosphere leading to the possible destruction of SF₅CF₃ are reactions with ions. These may play a major role in the atmospheric lifetime of SF₅CF₃ and hence have an impact on its global warming potential, which is currently estimated to be 18 000 times that of CO₂.⁹ A preliminary communication by us reported the first

gas-phase study of the reactions of SF₅CF₃ with several positive ions of atmospheric interest.¹² A more detailed investigation of the reactions of a larger number of positive ions with this molecule is presented here. This includes cations of importance to industrial plasmas, *e.g.* F⁺, Ar⁺, SF₅⁺, CF⁺, CF₃⁺, and SF₃⁺. In addition, this paper presents the first reported ion-molecule chemistry of SF₅Cl.

Rate coefficients and product ion branching ratios for thermal (300 K) reactions of SF₅CF₃ and SF₅Cl with the following cations of fundamental, atmospheric and/or plasma processing interest are reported: Ne⁺, F⁺, Ar⁺, N₂⁺, N⁺, CO⁺, CO₂⁺, O⁺, N₂O⁺, H₂O⁺, O₂⁺, SF₄⁺, CF₂⁺, SF⁺, SF₂⁺, NO₂⁺, SF₅⁺, NO⁺, CF⁺, CF₃⁺, SF₃⁺, and H₃O⁺. These ions cover a large range of recombination energies, from 21.56 eV (Ne⁺ + e[−] → Ne) to 6.27 eV (H₃O⁺ + e[−] → H₂O + H). (1 eV = 96.4845 kJ mol^{−1}.) Owing to this large range of available energies, several distinct reaction processes are observed amongst the large number of reactions studied, including dissociative charge transfer and various abstraction processes. For completeness, and ease of comparison, the results of the reactions of the above ions with SF₆ collected from various published papers are also presented here. Where results for SF₆ are unavailable in the literature, additional experiments have been performed as part of this investigation, the data from which are presented here.

2. Experimental

The selected ion flow tube (SIFT) apparatus used to obtain the reaction rate coefficients and product ion branching ratios has been described in detail elsewhere,^{13,14} so only a brief overview of the salient points of the experimental technique is included here. The reagent ions were generated in an electron impact high-pressure ion source containing an appropriate gas

(Ne for Ne^+ , CF_4 for F^+ and CF_m^+ ($m = 1-3$), Ar for Ar^+ , N_2 for N_2^+ and N^+ , CO for CO^+ , CO_2 for CO_2^+ , N_2O for O^+ , NO^+ and N_2O^+ , H_2O for H_2O^+ and H_3O^+ , O_2 for O_2^+ , SF_6 for SF_n^+ ($n = 1-5$), and NO_2 for NO_2^+). The reagent ions were mass selected using a quadrupole mass filter, before being injected into a 300 K helium carrier gas at a pressure of *ca.* 0.5 Torr. The helium gas (high-purity grade (99.997%)) was passed through a liquid nitrogen cooled zeolite trap before use. The reagent ions were transported along the flow tube and detected by a downstream quadrupole mass spectrometer detection system. Neutral reactant gas was added in controlled amounts to the ion swarm/carrier gas.

The loss of the reagent ions and the appearance of product ions were monitored by the detection system. Relaxed resolution on the quadrupole mass spectrometer, in order to minimize mass discrimination effects, was used in the determination of the branching ratios. The reaction rate coefficients and ion product distributions were then determined in the usual way.¹³⁻¹⁵ Reaction rate coefficients, which were extracted from linear least-squares fits of the plot of the logarithm of the reagent ion signal *versus* reactant neutral concentration, are considered to be accurate to $\pm 20\%$. The percentage product ion branching ratios, determined from the product ion counts as a function of reactant neutral concentration and extrapolated to zero flow conditions to allow for secondary reactions, are only used to provide a qualitative indication of the relative importance of different channels, and therefore accurate values are not important in our discussions. However, a statistical analysis on the branching ratios indicates a fractional accuracy of better than 20% for the reaction channels with branching ratios greater than 10%. For ion channels with branching ratios less than this value, the accuracy is reduced. For the ion channels with branching ratios of only 1%, the uncertainty is as high as $\pm 100\%$.

The high pressure of the gases used in the ionisation source, *ca.* several Torr, should help to quench electronically and/or vibrationally excited states of molecular ions prior to their injection into the flow tube. However, quenching of vibrational states is not assured, as confirmed by studies on the O_2^+ reagent ion. Whilst the majority of the O_2^+ ions were found to be in the $v = 0$ level, approximately 30% were found to be in the $v = 1$ and 2 vibrational levels. This was established from observed reactions with Xe and SO_2 . The lack of a reaction of the reagent ion O_2^+ with H_2O showed that the $v \geq 3$ vibrational levels of O_2^+ were not populated. Similarly, for the N_2^+ reagent ions, reaction with Ar indicated that approximately 40% of the N_2^+ ions were in the $v = 1$ vibrational level. It is possible that other reagent molecular ions had internal energies above the thermal value. However, no curvature was observed in any of the pseudo-first-order kinetic plots, indicating that rate coefficients are the same for reactions involving the ground and any vibrationally excited states. This does not rule out reagent ion vibrational excitation influencing the ion product distributions for those reactions which produce more than one ion product.

Atomic ions are expected to be in their ground electronic states prior to reaction with a neutral molecule. Thus Ar^+ and Ne^+ should emerge from the high-pressure ion source in their lowest energy, $^2\text{P}_{3/2}$ states. Even if this were not the case, the energy separation between the $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ states is only 0.18 eV for Ar^+ and 0.10 eV for Ne^+ , and therefore differences in reactivities between the two spin-orbit states are not expected. No evidence was found for differences in the reaction rate coefficients of the $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ states. Whether differences in branching ratios result from reactions involving these two spin-orbit states is more difficult to assess, but given the small differences in energy, none are expected. The ground state of F^+ is a closely-spaced triplet with recombination energies of 17.42 eV ($^3\text{P}_2$), 17.47 eV ($^3\text{P}_1$) and 17.48 eV ($^3\text{P}_0$). Thus, for this ion, there will be significant population in all three

states. As for Ar^+ and Ne^+ , no differences in the reactivity of the F^+ ion in its various spin-orbit states are to be expected. For the other two atomic ions used in this investigation, electronically excited states of N^+ and O^+ have previously been shown not to be present.¹⁶

Water contamination in the flow tube and He buffer gas flow resulted in electron transfer from H_2O to those injected ions whose recombination energies are greater than the ionisation potential of H_2O , 12.62 eV. This resulted in an H_2O^+ signal, which was usually less than 5% of the parent ion signal. Product ion branching ratios have been corrected for the contribution to the signals resulting from the reaction with H_2O^+ . Some of the H_2O^+ was converted to H_3O^+ in the flow tube ($\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$). This caused no problem in the determination of the product ion branching ratios, because H_3O^+ is unreactive with SF_5CF_3 , SF_5Cl , and SF_6 . Experiments with H_2O^+ as the reagent ion presented a separate problem, for it was found that OH^+ and H_3O^+ ions were being injected into the flow tube together with H_2O^+ . Again, because the H_3O^+ ions are unreactive with both SF_5CF_3 and SF_5Cl , their presence in the flow tube could be ignored. However, it was observed from the decrease in the OH^+ signal as a function of neutral concentration that this ion reacts efficiently with SF_5CF_3 and SF_5Cl . Reduction of the injection ion energy, which insured that the OH^+ was not produced by collision-induced dissociation, did not remove the problem. Attempts to eliminate the OH^+ signal by increasing the resolution of the injection mass spectrometer drastically reduced the H_2O^+ signal. The best compromise between OH^+ rejection and H_2O^+ signal gave a reagent ion flux comprised of 5% OH^+ and 95% H_2O^+ . No allowances have been made for the (small) contributions due to the OH^+ reaction to the branching ratios for the reaction of H_2O^+ with either SF_5CF_3 or SF_5Cl . Reaction rate coefficients and product ions for the reaction with OH^+ were not obtained. OH^+ was also produced in the flow tube when Ne^+ was used as the reagent ion. Again, the OH^+ signal was small (approximately 5% of that of Ne^+) and was ignored in the determination of product ion branching ratios. Ne^+ also resulted in the formation of HeNe^+ cations in the flow tube from termolecular association, which led to a HeNe^+ signal of about 2%–3% of the Ne^+ signal. Given the low percentage of this impurity ion in the flow tube, its contributions to the yields of the product ions for Ne^+ were reasonably neglected.

The samples of the reactant neutrals, SF_5CF_3 and SF_5Cl , were commercially purchased (Apollo Scientific Limited, Whaley Bridge, Derbyshire, UK) with stated purities of 99% and 97%, respectively. They were used in the experiments without further purification. The SF_6 was purchased from Fluorochem Limited, Old Glossop, Derbyshire, UK with a stated purity of >99%. This sample was also used directly without additional purification.

3. Results and discussion

The experimental rate coefficients, k_{exp} , the observed product ions, and their branching ratios for the reactions of SF_5CF_3 , SF_5Cl and SF_6 with 22 different reagent ions are given in Tables 1–3, respectively. The reagent ions are listed (top to bottom) in order of decreasing recombination energy (RE). Where no reaction was observed, this implies that the experimental rate coefficient, $k_{\text{exp}} < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The majority of the SF_6 data presented in Table 3 has been collected from the literature,¹⁻⁸ and are given here to aid comparison. In the cases of the reactions with SF_6 for which no published data exist, we have made the appropriate measurements to complete Table 3.

To assess the efficiency of the reactions, the experimental rate coefficients are compared in the tables with the predictions

Table 1 The measured 300 K reaction rate coefficients (in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), cation product ions, their branching ratios (percentages), suggested neutral products and 0 K enthalpies for the reactions of Ne^+ , F^+ , Ar^+ , N_2^+ , N^+ , CO^+ , CO_2^+ , O^+ , N_2O^+ , H_2O^+ , O_2^+ , SF_4^+ , CF_2^+ , SF^+ , SF_2^+ , NO_2^+ , SF_5^+ , NO^+ , CF^+ , CF_3^+ , SF_3^+ and H_3O^+ with SF_5CF_3 are presented. The recombination energies of the reagent cations are listed in eV in round brackets under the cations. The value in square brackets is the fluoride affinity of the reagent cation. The capture rate coefficients, calculated using parametrized fits to results from trajectory calculations,¹⁸ are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to $\pm 20\%$. When dissociative charge transfer is exothermic, only this channel is represented in the table, with the neutrals assembled to give the lowest reaction enthalpy. The trace given for the SF_4^+ product ion for a number of reactions and for SF_4CF_3^+ from the reaction with CF_2^+ represents a detectable signal with our apparatus, but whose branching ratio is less than 1%. 0 K enthalpies of formation for CF_m^+ , CF_m ,²⁴ and for SF_n , SF_n ⁺²⁵ are taken from recent high level *ab initio* calculations. $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673 \text{ kJ mol}^{-1}$ (see text). Other 0 K enthalpy data are taken from the JANAF tabulations,²⁷ information available at the NIST website,⁵¹ and additional sources of data as identified in the table footnotes. The major source of uncertainty in the values is $\pm 40 \text{ kJ mol}^{-1}$ in $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3)$

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ/\text{kJ mol}^{-1}$
Ne^+ (21.56) [1753]	1.5 [1.8]	CF_3^+ (47) SF_2^+ (5) SF_3^+ (37) SF_4^+ (1) SF_5^+ (10)	$\text{SF}_5 + \text{Ne}$ $\text{CF}_4 + \text{F}_2 + \text{Ne}$ $\text{CF}_4 + \text{F} + \text{Ne}$ $\text{CF}_4 + \text{Ne}$ $\text{CF}_3 + \text{Ne}$	-836 -645 -898 -946 -786
F^+ (17.42) [1508]	1.6 [1.9]	CF_3^+ (73) SF_3^+ (24) SF_4^+ (trace) SF_5^+ (3)	$\text{SF}_5 + \text{F}$ $\text{CF}_4 + \text{F} + \text{F}$ $\text{CF}_4 + \text{F}$ $\text{CF}_3 + \text{F}$	-436 -498 -546 -386
Ar^+ (15.76) [1193]	1.4 [1.3]	CF_3^+ (65) SF_3^+ (30) SF_5^+ (4) SF_4CF_3^+ (1)	$\text{SF}_5 + \text{Ar}$ $\text{CF}_4 + \text{F} + \text{Ar}$ $\text{CF}_3 + \text{Ar}$ $\text{F} + \text{Ar}$	-276 -338 -226 $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) + 230$
N_2^+ (15.58) [1175]	1.6 [1.6]	CF_3^+ (65) SF_3^+ (28) SF_4^+ (trace) SF_5^+ (5) SF_4CF_3^+ (2)	$\text{SF}_5 + \text{N}_2$ $\text{CF}_4 + \text{F} + \text{N}_2$ $\text{CF}_4 + \text{N}_2$ $\text{CF}_3 + \text{N}_2$ $\text{F} + \text{N}_2$	-259 -321 -368 -209 $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) + 247$
N^+ (14.53) [1374]	2.2 [2.1]	CF_3^+ (80) SF_3^+ (17) SF_4^+ (trace) SF_5^+ (3)	$\text{SF}_5 + \text{N}$ $\text{CF}_4 + \text{F} + \text{N}$ $\text{CF}_4 + \text{N}$ $\text{CF}_3 + \text{N}$	-158 -220 -267 -108
CO^+ (14.01) [1173] ^a	1.6 [1.6]	CF_3^+ (75) SF_3^+ (22) SF_4^+ (trace) SF_5^+ (3)	$\text{SF}_5 + \text{CO}$ $\text{CF}_4 + \text{F} + \text{CO}$ $\text{CF}_4 + \text{CO}$ $\text{CF}_3 + \text{CO}$	-107 -169 -217 -57
CO_2^+ (13.78) [1049] ^b	1.2 [1.3]	CF_3^+ (76) SF_3^+ (14) SF_4^+ (8) SF_5^+ (2)	$\text{SF}_5 + \text{CO}_2$ $\text{CF}_4 + \text{F} + \text{CO}_2$ $\text{CF}_4 + \text{CO}_2$ $\text{CF}_3 + \text{CO}_2$	-85 -147 -194 -35
O^+ (13.62) [1202]	1.9 [2.0]	CF_3^+ (83) SF_3^+ (16) SF_4^+ (trace) SF_5^+ (1)	$\text{SF}_5 + \text{O}$ $\text{CF}_4 + \text{F} + \text{O}$ $\text{CF}_4 + \text{O}$ $\text{CF}_3 + \text{O}$	-69 -131 -179 -19
N_2O^+ (12.89) [971]	1.1 [1.3]	CF_3^+ (75) SF_3^+ (19) SF_4^+ (5) SF_5^+ (1)	$\text{SF}_5 + \text{N}_2\text{O}$ $\text{CF}_4 + \text{F} + \text{N}_2\text{O}$ $\text{CF}_4 + \text{N}_2\text{O}$ $\text{CF}_3\text{O} + \text{N}_2$	+1 -61 -109 -203 ^c
H_2O^+ (12.62) [962]	1.6 [1.9]	CF_3^+ (8) SF_3^+ (92) SF_4^+ (trace) CF_3^+ (63)	$\text{CF}_2\text{O} + \text{N}_2 + \text{F}$ $\text{SF}_5 + \text{H}_2\text{O}$ $\text{CF}_4 + \text{F} + \text{H}_2\text{O}$ $\text{CF}_4 + \text{HF} + \text{OH}$ $\text{CF}_4 + \text{H}_2\text{O}$	-98 ^d +27 -35 -108 -83
O_2^+ (12.07) [887]	0.01 [1.5]	SF_3^+ (31) SF_4^+ (2) SF_5^+ (4)	$\text{SF}_5 + \text{O}_2$ SF_5O_2 $\text{CF}_4 + \text{F} + \text{O}_2$ $\text{CF}_4 + \text{FO}_2$ $\text{CF}_4 + \text{O}_2$ $\text{CF}_3 + \text{O}_2$	+80, +58, +36 ^e 29 ^f 18 -32 -29 130
SF_4^+ (11.92) [976]	0.17 [0.92]	SF_3^+ (100%)	CF_3O_2 $\text{CF}_4 + \text{SF}_5$	-33 ^g -121
CF_2^+ (11.43) [1122]	1.1 [1.2]	CF_3^+ (38) SF_3^+ (60) SF_5^+ (2) SF_4CF_3^+ (trace)	$\text{SF}_4 + \text{CF}_3$ $\text{SF}_3 + \text{CF}_4$ $\text{CF}_3 + \text{CF}_4$ C_2F_5 CF_3	-52 -193 -267 -49 ^h $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) + 301$

Table 1 (continued)

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_r H_0^\circ / \text{kJ mol}^{-1}$
SF ⁺ (10.25) [1034]	0.03 [1.2]	CF ₃ ⁺ (44) SF ₃ ⁺ (56)	SF ₂ + SF ₄ CF ₄ + SF ₂	+36 −179
SF ₂ ⁺ (10.17) [876]	no reaction			
NO ₂ ⁺ (9.59) [607]	no reaction			
SF ₅ ⁺ (9.55) [1040]	0.14 [0.88]	CF ₃ ⁺ (13) SF ₃ ⁺ (87)	SF ₄ + SF ₆ SF ₆ + CF ₄	+30 −185
NO ⁺ (9.26) [797]	no reaction			
CF ⁺ (9.10) [1066]	1.2 [1.5]	CF ₃ ⁺ (47) SF ₃ ⁺ (51)	CF ₄ + SF ₂ CF ₂ + SF ₄ CF ₂ + CF ₄ C ₂ F ₆	−261 +4 −211 −431 ⁱ
CF ₃ ⁺ (9.03) [1085]	0.48 [1.1]	SF ₅ ⁺ (2) SF ₃ ⁺ (98) SF ₅ ⁺ (2)	C ₂ F ₄ CF ₄ + CF ₄ C ₂ F ₆	−40 ^j −230 +8 ⁱ
SF ₃ ⁺ (8.26) [870]	no reaction			
H ₃ O ⁺ (6.27) [843]	no reaction			

^a $\Delta_r H_0^\circ(\text{FCO}) = -185 \text{ kJ mol}^{-1}$ from Dixon and Feller.⁵² ^b $D_0(\text{F-CO}_2) = 48 \text{ kJ mol}^{-1}$ from Arnold *et al.*³⁹ ^c $\Delta_r H_0^\circ(\text{CF}_3\text{O}) = -630 \text{ kJ mol}^{-1}$ from Louis *et al.*⁵³ ^d $\Delta_r H_0^\circ(\text{CF}_2\text{O}) = -603 \text{ kJ mol}^{-1}$ from Louis *et al.*⁵³ ^e The values given are for the $v = 0, 1$ and 2 vibrational levels of O_2^+ , respectively. Energy levels calculated using O_2^+ ground state vibrational spectroscopic constants from Huber and Herzberg.⁵⁴ ^f $D_0(\text{SF}_5\text{-O}_2) = 51 \text{ kJ mol}^{-1}$ estimated from $\Delta_r H_{295}^\circ(\text{SF}_5\text{O}_2 \rightarrow \text{SF}_5 + \text{O}_2) = 57.3 \text{ kJ mol}^{-1}$ obtained by Sehested *et al.*⁵⁵ ^g $D_0(\text{CF}_3\text{-O}_2) = 163 \text{ kJ mol}^{-1}$ from Louis *et al.*⁵³ ^h $\Delta_r H_0^\circ(\text{CF}_3\text{CF}_2) = -896 \text{ kJ mol}^{-1}$ from Bauschlicher and Ricca.⁴⁷ ⁱ $\Delta_r H_0^\circ(\text{CF}_3\text{CF}_3) = -1341 \text{ kJ mol}^{-1}$ from Bauschlicher and Ricca.⁴⁷ ^j $\Delta_r H_0^\circ(\text{CF}_2\text{CF}_2) = -673 \text{ kJ mol}^{-1}$ from Bauschlicher and Ricca.⁴⁷

of capture theory, k_c . Essential pieces of information for making capture theory calculations of k_c are the polarisability and the dipole moment of the neutral reactant molecule. Neither of these quantities are available in the literature for SF₅CF₃ and SF₅Cl. The polarisabilities of SF₅CF₃ and SF₅Cl have been estimated to be $8.44 \times 10^{-30} \text{ m}^3$ and $8.38 \times 10^{-30} \text{ m}^3$, respectively, using Miller and Savchik's empirical approach.¹⁷ At the Hartree-Fock level, the dipole moments for SF₅CF₃ and SF₅Cl have been calculated to be 0.95 and 0.93 D, respectively. Given these values the capture rate coefficients can be estimated using the results of parameterised fits to trajectory calculations,¹⁸ and these k_c values appear in square brackets in Tables 1 and 2. A comparison of the experimental rate coefficients with the capture values provides a good indication of whether a reaction is efficient, with most captures leading to reaction, or inefficient. The capture rate coefficients are readily determined for the centrosymmetric molecule SF₆ using the Langevin equation,¹⁹ and a value for the polarisability of SF₆ ($= 6.54 \times 10^{-30} \text{ m}^3$ ²⁰). These k_c values are presented in Table 3.

The determination of reaction pathways requires knowledge of the ion and neutral products. In our experiments, only the masses and relative yields of the ion products are determined, so the neutral products can only be inferred from mass balance and thermochemical arguments. The thermochemical analysis is restricted to considerations of enthalpy at 0 K (*i.e.* $\Delta_r H_0^\circ < 0$ for an observable reaction), and we have ignored any entropic effects. In the tables we have generally listed the neutrals which give the most exothermic pathway to a particular

observed ion product, so that the maximum energy is available for partitioning between the internal and translational degrees of freedom. In many cases there is sufficient energy to break chemical bonds in the neutral products.

3.1 SF₅CF₃ reactions

An investigation of the reactions of a number of positive ions of atmospheric interest (N₂⁺, N⁺, CO⁺, CO₂⁺, O⁺, N₂O⁺, H₂O⁺, O₂⁺, NO₂⁺, NO⁺, and H₃O⁺) with SF₅CF₃ has recently been reported by us.¹² A more extensive study, which includes many additional ions, *i.e.* Ne⁺, F⁺, Ar⁺, SF₄⁺, CF₂⁺, SF⁺, SF₂⁺, SF₅⁺, CF⁺, CF₃⁺, and SF₃⁺, is presented here. The experimental reaction rate coefficients, the observed product ions, and their percentage branching ratios are given in Table 1.

Dissociative charge transfer is almost certainly the dominant reaction mechanism for reagent ions whose recombination energies are greater than about 12.5 eV. The overall process can be viewed as a two step mechanism, transfer of an electron from the reactant neutral to the reagent ion (often described as occurring at long range), followed by fragmentation of the unstable intermediate ion, here (SF₅CF₃⁺)^{*}, with the newly formed neutral acting as a spectator. Simple dissociations such as:

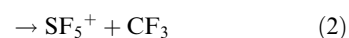
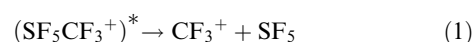


Table 2 The measured 300 K reaction rate coefficients (in units of 10^{-9} cm³ molecule⁻¹ s⁻¹), cation product ions, their branching ratios (percentages), suggested neutral products and 0 K enthalpies for the reactions of Ne⁺, F⁺, Ar⁺, N₂⁺, N⁺, CO⁺, CO₂⁺, O⁺, N₂O⁺, H₂O⁺, O₂⁺, SF₄⁺, CF₂⁺, SF⁺, SF₂⁺, NO₂⁺, SF₅⁺, NO⁺, CF⁺, CF₃⁺, SF₃⁺ and H₃O⁺ with SF₅Cl are presented. The recombination energies of the reagent cations are listed in eV in brackets under the cations. The value in square brackets is the fluoride affinity of the reagent cation. The capture rate coefficients, calculated using parametrized fits to results from trajectory calculations,¹⁸ are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to $\pm 20\%$. It is assumed that ClF₂ and ClF₃ are not formed in dissociative charge-transfer reactions. When dissociative charge transfer is exothermic, only this channel is represented in the table, with the neutrals assembled to give the lowest reaction enthalpy. The trace given for the SF₃⁺ and SF₂Cl⁺ product ions resulting from the reaction with CO₂⁺ represents a detectable signal with our apparatus, but whose branching ratio is less than 1%. 0 K enthalpies of formation for CF_m⁺, CF_m,²⁴ and for SF_n, SF_n⁺²⁵ are taken from recent high level *ab initio* calculations. $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -985$ kJ mol⁻¹ (see text). Other 0 K enthalpy data are taken from the JANAF tabulations,²⁷ information available at the NIST website,⁵¹ and additional sources of data as identified in the table footnotes

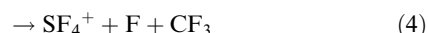
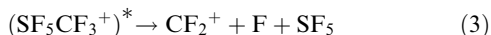
Reagent ion	Rate coefficient/ 10^{-9} cm ³ molecule ⁻¹ s ⁻¹	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ/\text{kJ mol}^{-1}$ ^a
Ne ⁺ (21.56) [1753]	1.7 [1.8]	Cl ⁺ (4) SF ₂ ⁺ (trace) SF ₃ ⁺ (86) SF ₄ ⁺ (1) SF ₅ ⁺ (5) SF ₄ Cl ⁺ (4)	SF ₅ + Ne ClF + F ₂ + Ne ClF + F + Ne ClF + Ne Cl + Ne F + Ne	-562 -457 -709 -757 -892 -868 ^a
F ⁺ (17.42) [1508]	1.9 [1.9]	SF ₃ ⁺ (19) SF ₄ ⁺ (30) SF ₅ ⁺ (19) SF ₄ Cl ⁺ (32)	ClF + F + F ClF + F Cl + F F + F	-309 -357 -492 -623 ^a
Ar ⁺ (15.76) [1193]	1.3 [1.4]	SF ₅ ⁺ (47) SF ₄ Cl ⁺ (53)	Cl + Ar F + Ar	-332 -308 ^a
N ₂ ⁺ (15.58) [1175]	1.6 [1.6]	SF ₅ ⁺ (52) SF ₄ Cl ⁺ (48)	Cl + N ₂ F + N ₂	-315 -291 ^a
N ⁺ (14.53) [1374]	1.9 [2.1]	SF ₃ ⁺ (3) SF ₅ ⁺ (77) SF ₄ Cl ⁺ (20)	ClF + F + N Cl + N F + N	-31 -214 -190 ^a
CO ⁺ (14.01) [1173]	1.6 [1.6]	SF ₅ ⁺ (50) SF ₄ Cl ⁺ (50)	Cl + CO F + CO	-163 -140 ^a
CO ₂ ⁺ (13.78) [1049] ^b	1.2 [1.3]	SFCl ⁺ (5) SF ₃ ⁺ (trace) SF ₂ Cl ⁺ (trace)	CF ₄ + O ₂ ClF ₂ + CO ₂ CF ₂ O + FO	$\Delta_f H_0^\circ(\text{SFCl}^+)^c - 878$ -90 ^d $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+)^e - 446^f$
		SF ₅ ⁺ (93) SF ₄ Cl ⁺ (2)	CF ₃ O ₂ Cl + CO ₂ F + CO ₂	$\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+)^e - 591^g$ -141 -117 ^a
O ⁺ (13.62) [1202]	2.0 [2.0]	SF ₅ ⁺ (84) SF ₄ Cl ⁺ (16)	Cl + O F + O	-125 -102 ^a
N ₂ O ⁺ (12.89) [971]	1.2 [1.3]	SF ₅ ⁺ (98) SF ₄ Cl ⁺ (2)	Cl + N ₂ O F + N ₂ O	-55 -31
H ₂ O ⁺ (12.62) [962]	1.7 [1.9]	SF ₂ OH ⁺ (4) SF ₃ ⁺ (2) SF ₂ Cl ⁺ (6) SF ₅ ⁺ (35) SF ₄ Cl ⁺ (53)	ClF ₂ + FH 2 HF + ClO 2 HF + FO Cl + H ₂ O FH + OH	$\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+)^h - 331^d$ -78 $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+)^e - 431$ -29 -78 ^a
O ₂ ⁺ (12.07) [887]	1.2 [1.5]	SF ₅ ⁺ (97) SF ₄ Cl ⁺ (3)	ClO ₂ FO ₂	3 -3 ^a
SF ₄ ⁺ (11.92) [976]	0.3 [1.0]	SF ₄ Cl ⁺ (100)	SF ₅	-91 ^a
CF ₂ ⁺ (11.43) [1122]	1.2 [1.2]	CF ₂ Cl ⁺ (17) SF ₅ ⁺ (14) SF ₄ Cl ⁺ (69)	SF ₅ CF ₂ Cl CF ₃	-206 -116 -237 ^a
SF ⁺ (10.25) [1034]	0.8 [1.2]	SF ₅ ⁺ (93) SF ₄ Cl ⁺ (7)	ClSF SF ₂	-77 ⁱ -149 ^a
SF ₂ ⁺ (10.17) [876]	no reaction			
NO ₂ ⁺ (9.59) [607]	no reaction			
SF ₅ ⁺ (9.55)	0.08 [0.9]	SF ₄ Cl ⁺ (100)	SF ₆	-156 ^a

Table 2 (continued)

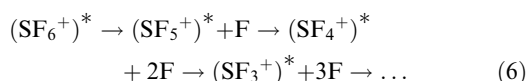
Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}{}^a$
[1040] NO ⁺ (9.26)	no reaction			
[797] CF ⁺ (9.10)	1.5 [1.5]	CF ₂ Cl ⁺ (3) SF ₃ ⁺ (3)	SF ₄ CClF ₃	−343 −482
[1066]		SF ₅ ⁺ (27) SF ₄ Cl ⁺ (67)	ClF + CF ₂ CClF	−22 −74
CF ₃ ⁺ (9.03)	0.7 [1.1]	SF ₅ ⁺ (39) SF ₄ Cl ⁺ (61)	CF ₂ CClF ₃	−181 ^a −43
[1085] SF ₃ ⁺ (8.26)	no reaction		CF ₄	−201 ^a
[870] H ₃ O ⁺ (6.27)	no reaction			
[843]				

^a $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}^+) = 150 \text{ kJ mol}^{-1}$, see text. ^b $D_0(\text{F}-\text{CO}_2) = 48 \text{ kJ mol}^{-1}$ from Arnold *et al.*³⁹ ^c $\Delta_f H_0^\circ(\text{SFCI}^+) \sim 782 \text{ kJ mol}^{-1}$, estimate, see text. ^d $\Delta_f H_0^\circ(\text{ClF}_2) = -105 \text{ kJ mol}^{-1}$, from Lias *et al.*⁵⁶ ^e $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+) \sim 453 \text{ kJ mol}^{-1}$, estimate, see text. ^f $\Delta_f H_0^\circ(\text{CF}_2\text{O}) = -603 \text{ kJ mol}^{-1}$ from Louis *et al.*⁵³ ^g $\Delta_f H_0^\circ(\text{CF}_3\text{O}_2) = -640 \text{ kJ mol}^{-1}$ from Haworth *et al.*⁵⁷ ^h $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+) \sim 321 \text{ kJ mol}^{-1}$, estimate, see text. ⁱ Assuming bond additivity, $\Delta_f H_0^\circ(\text{ClSF}) = [\Delta_f H_0^\circ(\text{SF}_2) + \Delta_f H_0^\circ(\text{SCl}_2)]/2 = -154 \text{ kJ mol}^{-1}$.

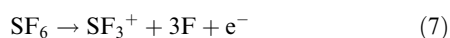
can occur, with smaller product ions possibly resulting from more extensive fragmentation, for example:



Experimental observations of the fragmentation of $(\text{SF}_6^+)^{*21}$ favour a mechanism with sequential loss of F atoms:²²



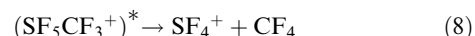
Indeed, the observed threshold for the production of SF_3^+ from SF_6^{23} corresponds closely to the energy needed to access the dissociative ionisation limit:



The dissociation of isolated energy-selected $(\text{SF}_5\text{CF}_3^+)^*$ ions has been investigated using the TPEPICO (Threshold Photo-Electron PhotoIon COincidence) technique.¹⁰ Making the assumption that the pathway to CF_3^+ is reaction (1), the experimentally established adiabatic energy for the production of CF_3^+ ($12.9 \pm 0.4 \text{ eV}^{10}$) can be used as the starting point to build up the adiabatic energies for the production of other ions from SF_5CF_3 by dissociative ionisation. The results are displayed in Fig. 1, which was constructed using recently published 0 K enthalpies of formation for CF_m and CF_m^+ ,²⁴ and for SF_n and SF_n^+ ,²⁵ obtained from high level *ab initio* calculations.

The predicted lower bounds on the appearance energies for the formation of SF_5^+ , SF_4^+ , SF_3^+ , and CF_2^+ from the pathways (reactions (2) to (5)) listed above are collected in Table 4. These ions have been detected following both photoionisation¹⁰ and electron impact ionisation²⁶ of SF_5CF_3 , and the experimental appearance energies (at 298 K) are presented in Table 4. The appearance energy for SF_5^+ is entirely consistent with the suggestion that this ion is formed by simple scission of the S–C bond (reaction (2)). However, SF_4^+ , SF_3^+ , and CF_2^+ all appear at energies well below the predicted thresholds. In order to find energetically accessible pathways

to these fragment ions at their observed appearance energies, it is necessary to postulate more complicated dissociation mechanisms, which involve bond making as well as bond breaking. The lowest energy pathways to SF_4^+ , SF_3^+ , and CF_2^+ are:



In each case the breaking of the S–C bond is accompanied by migration of F across this bond. One view of the overall process is that reaction (8) corresponds to dissociation (1) followed by F[−] abstraction from SF_5 by CF_3^+ , similarly (10) commences with (2). Reactions (8) and (9) may be connected, with excited $(\text{SF}_4^+)^*$ formed by (8) subsequently fragmenting to produce SF_3^+ ; the $\text{SF}_3^+ - \text{F}$ bond is quite weak ($D_0(\text{SF}_3^+ - \text{F}) = 48 \text{ kJ mol}^{-1}$). The predicted threshold energies for SF_4^+ , SF_3^+ , and CF_2^+ produced through pathways (8), (9), and (10) are given in Table 4. In each case the prediction lies below the experimentally observed appearance energies for these ions. At threshold it is concluded that production of SF_4^+ , SF_3^+ , and CF_2^+ requires migration of an F atom across the S–C bond. Fig. 1 includes these predicted threshold energies. Also shown are the lowest energy channels to SF_2^+ , SF^+ , S^+ , CF^+ , F_2^+ , and F^+ , most of these channels involve migration of an F atom across the S–C bond. Many other dissociative ionisation pathways do exist.

When information on the energetics of the dissociative ionisation pathways is combined with the recombination energies of the reagent ions, Fig. 1 provides a visual summary of which product ions are accessible through exothermic charge-transfer pathways for the various reagent ions. The calculated 0 K enthalpy changes of the lowest energy charge-transfer reactions to the observed product ions are given in Table 1. For reagent ions with recombination energies of 12.5 eV or greater, charge transfer provides an exothermic or close to thermoneutral pathway to each of the observed product ions.

It is frequently instructive to compare the product ion branching ratios observed for a reagent ion of recombination

Table 3 The measured 300 K reaction rate coefficients (in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), cation product ions, their branching ratios (percentages), suggested neutral products and 0 K enthalpies for the reactions of Ne^+ , F^+ , Ar^+ , N_2^+ , N^+ , CO^+ , CO_2^+ , O^+ , N_2O^+ , H_2O^+ , O_2^+ , SF_4^+ , CF_2^+ , SF^+ , SF_2^+ , NO_2^+ , SF_5^+ , NO^+ , CF^+ , CF_3^+ , SF_3^+ and H_3O^+ with SF_6 are presented. The recombination energies of the reagent cations are listed in eV in brackets under the cations. The value in square brackets is the fluoride affinity of the reagent cation. The capture rate coefficients, calculated using Langevin theory,¹⁹ are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to $\pm 20\%$. When dissociative charge transfer is exothermic, only this channel is represented in the table, with the neutrals assembled to give the lowest reaction enthalpy. 0 K enthalpies of formation for CF_m^+ , CF_m ,²⁴ and for SF_n , SF_n^{+25} are taken from recent high level *ab initio* calculations. Other 0 K enthalpy data are taken from the JANAF tabulations,²⁷ information available at the NIST website,⁵¹ and additional sources of data as identified in the table footnotes

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$
Ne^+ (21.56) [1753]	0.69, ^a 0.8 ^b [1.5]	SF_3^+ (91) ^b SF_4^+ (3) ^b	$\text{F}_2 + \text{F} + \text{Ne}$ $\text{F}_2 + \text{Ne}$	−437 −485
F^+ (17.42) [1508]	1.1 ^a [1.5]	SF_5^+ (6) ^b SF_3^+ (10) ^a SF_5^+ (90) ^a	$\text{F} + \text{Ne}$ $\text{F}_2 + \text{F} + \text{F}$ $\text{F} + \text{F}$	−713 −38 −313
Ar^+ (15.76) [1193]	0.91, ^a 0.93, ^c 1.2 ^d [1.1]	SF_5^+ (100)	$\text{F} + \text{Ar}$	−153
N_2^+ (15.58) [1175]	1.0, ^a 1.2, ^b 1.3 ^{d,e} [1.3]	SF_5^+ (100)	$\text{F} + \text{N}_2$	−135
N^+ (14.53) [1374]	1.8, ^b 1.4 ^{d,e} [1.7]	SF_3^+ (2) ^b SF_5^+ (98) ^b	$\text{F}_2 + \text{FN}$ $\text{F} + \text{N}$	−58 −34
CO^+ (14.01) [1173]	0.92, ^a 1.3, ^d 0.98 ^f [1.3]	SF_5^+ (100)	$\text{CO} + \text{F}$ FCO	+16 −133 ^g
CO_2^+ (13.77) [1049]	0.009, ^a 0.014 ^e [1.1]	SF_5^+ (100)	$\text{F} + \text{CO}_2$ FCO_2	+39 −10 ^h
O^+ (13.62) [971]	1.5, ^d 2.4 ⁱ [1.6]	SF_5^+ (100)	$\text{F} + \text{O}$ FO	+54 −162
N_2O^+ (12.89) [971]	0.003 ^a [1.1]	SF_5^+ (100)	$\text{F} + \text{N}_2\text{O}$ $\text{FO} + \text{N}_2$	+124 +69
H_2O^+ (12.6) [962]	0.19 ^b [1.5]	OSF_4^+ OHSF_5^+ H_2OSF_6^+	2 HF HF	$\Delta_f H_0^\circ(\text{OSF}_4^+) - 317$ $\Delta_f H_0^\circ(\text{OHSF}_5^+) - 45$ $\Delta_f H_0^\circ(\text{H}_2\text{OSF}_6^+) + 228$
O_2^+ (12.07) [887]	no reaction ^d			
SF_4^+ (11.92) [976]	no reaction ^j			
CF_2^+ (11.43) [1122]	0.79 ^a [1.0]	SF_5^+ (100)	CF_3	−82
SF^+ (10.25) [1034]	no reaction ^j			
SF_2^+ (10.17) [876]	no reaction ^j			
NO_2^+ (9.59) [607]	no reaction ^e			
SF_5^+ (9.55) [1040]	no reaction ^j			
NO^+ (9.26) [797]	no reaction ^{d,e}			
CF^+ (9.10) [1066]	0.88 ^a [1.2]	CF_3^+ (5) ^a SF_5^+ (95) ^a	SF_4 CF_2	−269 −26
CF_3^+ (9.03) [1085]	0.22, ^a 0.25 ^e [0.9]	SF_5^+ (100)	CF_4	−45
SF_3^+ (8.26)	no reaction ^j			

Table 3 (continued)

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$
[870] H_3O^+ (6.27) [843]	no reaction ^a			
^a Jarvis <i>et al.</i> ^{8 b} Williams <i>et al.</i> ^{7 c} Shul <i>et al.</i> ^{4 d} Fehsenfeld. ^{1 e} Babcock and Streit. ^{3 f} Bowers <i>et al.</i> ^{2 g} $\Delta_f H_0^\circ(\text{FCO}) = -185 \text{ kJ mol}^{-1}$ from Dixon and Feller. ^{52 h} $D_0(\text{F}-\text{CO}_2) = 48 \text{ kJ mol}^{-1}$, experimental value from Arnold <i>et al.</i> ^{39 i} Morris <i>et al.</i> ^{6 j} This study.				

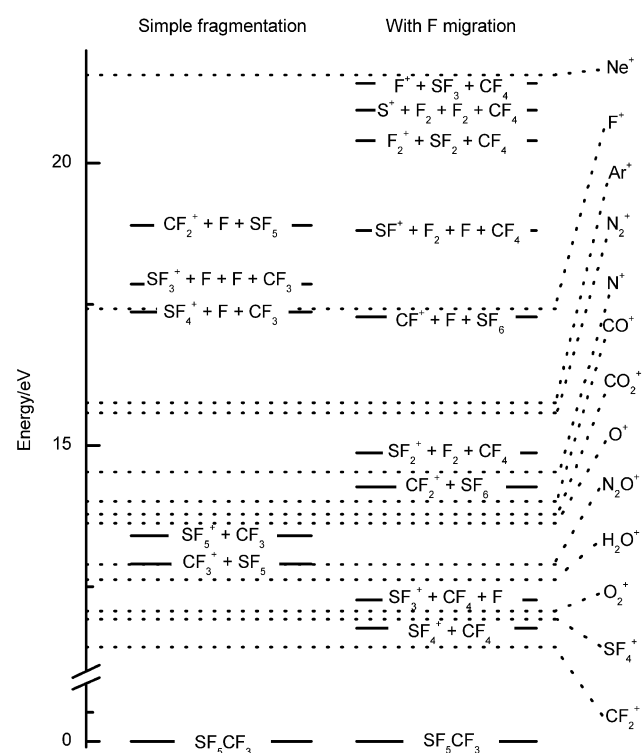


Fig. 1 Adiabatic dissociative ionisation limits below 22 eV for SF_5CF_3 . The limits are divided into those attained by simple fragmentation, and those involving the migration of an F atom across the S–C bond. The recombination energies of the reagent ions with $\text{RE} > 11 \text{ eV}$ are also presented in the figure. The electrons have been omitted from the labelling of the various limits.

energy RE with the TPEPICO ion product branching ratios obtained with photons of energy RE . Similar values and trends for branching ratios are regarded as an indicator that the charge-transfer reaction proceeds *via* a long-range mechanism. TPEPICO experiments¹⁰ have shown that the

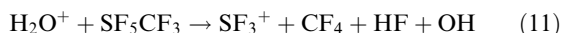
major product ions from photoionisation of SF_5CF_3 are CF_3^+ and SF_3^+ , accompanied by small amounts of SF_4^+ , SF_5^+ , and CF_2^+ . Over the photon energy range 15 to 20 eV, the TPEPICO branching ratios to CF_3^+ and SF_3^+ are approximately constant, 70% CF_3^+ and 20% SF_3^+ . The product branching ratios for the reactions of SF_5CF_3 with N_2^+ , Ar^+ , and F^+ , presented in Table 1, mirror this behaviour. Above about 20 eV, the TPEPICO branching ratio to CF_3^+ starts to fall, whilst that to SF_3^+ rises. The product branching ratios for the reaction of Ne^+ , compared to N_2^+ , Ar^+ , and F^+ , with SF_5CF_3 display the same trend. The TPEPICO data show two interesting features within the photon energy range 12.7 to 15.5 eV. At about 14.9 eV, there is a rapid increase in the SF_3^+ branching ratio, from 2% ($h\nu < 14.8 \text{ eV}$) to 20% ($h\nu > 15 \text{ eV}$). This change in dissociation behaviour occurs at the onset of photoionisation into the first excited state of SF_5CF_3^+ . In contrast, the product branching ratios show no evidence of a significant change in the yield of SF_3^+ , which remains at close to 20% as the recombination energy of the reagent ion increases from 12.9 eV to more than 16 eV. Below 13 eV the TPEPICO branching ratio for SF_3^+ shows a rapid rise, with a matching fall for CF_3^+ . These observations at around 12.9 eV, the observed thermodynamic limit for the formation of CF_3^+ by (1), reflect the competition between (1) and (9). Reaction (1) is a simple dissociation, through a loose transition state, while the more complicated mechanism envisaged for (9), requiring intramolecular F^- abstraction as well as dissociation, will have a tight transition state. Once (1) opens, the yield of SF_3^+ (calculated threshold 12.26 eV) rapidly decreases, and CF_3^+ is the dominant product ion. This may account for the very high SF_3^+ branching ratio (92%) from the reaction of H_2O^+ ($\text{RE} = 12.61 \text{ eV}$) with SF_5CF_3 , compared to 19% from the reaction of N_2O^+ ($\text{RE} = 12.89 \text{ eV}$). An alternative view¹² is that there is a change in reaction mechanism between N_2O^+ and H_2O^+ . It is postulated that N_2O^+ reacts by charge transfer, leading to CF_3^+ as the major product. Since the recombination energy of H_2O^+ (12.62 eV) is below the observed onset of photoionisation of SF_5CF_3 ($12.9 + 0.2 \text{ eV}^{10}$), H_2O^+ is unlikely

Table 4 Calculated and observed appearance energies for the dissociative ionisation of SF_5CF_3

Fragment ion	Neutral fragment(s)	Reaction	Predicted appearance energy/eV	Observed appearance energy/eV	
				Photoionisation (TPEPICO) ¹⁰	Electron impact ionisation ²⁶
CF_3^+	SF_5	(1)	12.9 ^a	12.9 ± 0.4	12.9 ± 0.1
SF_5^+	CF_3	(2)	13.40	13.9 ± 1.5	13.2 ± 0.6
CF_2^+	$\text{F} + \text{SF}_5$	(3)	18.90		
	SF_6	(10)	14.27	16.0 ± 2.0	17.8 ± 0.5
SF_4^+	$\text{F} + \text{CF}_3$	(4)	17.37		
	CF_4	(8)	11.76	13.5 ± 1.5	12.1 ± 0.3
SF_3^+	$\text{F} + \text{F} + \text{CF}_3$	(5)	17.86		
	$\text{F} + \text{CF}_4$	(9)	12.26	14.94 ± 0.13	14.5 ± 0.1

^a Obtained from the TPEPICO study.¹⁰

to react efficiently by charge transfer, and instead a chemical pathway in which bonds are broken and formed leads to the major product:



It is difficult to discern trends in the small TPEPICO branching ratios to SF_5^+ , SF_4^+ , and CF_2^+ , but it does appear that the yield of SF_5^+ increases with photon energy. The charge-transfer data show that the reactions produce an increasing proportion of SF_5^+ as the recombination energy of the reagent ion increases. This can be viewed as a consequence of competition between channels (1) and (2). As the available energy increases, the dissociation of $(\text{SF}_5\text{CF}_3)^+$ produces a greater proportion of SF_5^+ (thermodynamic threshold 13.40 eV) compared to CF_3^+ (12.90 eV).

In addition to product ion branching ratios, the reaction rate coefficient can be a useful diagnostic of the mechanism. For long-range charge-transfer to be efficient, identified by $k_{\text{exp}}/k_{\text{c}} \sim 1$, it is necessary that there is good vibrational overlap between the neutral reactant M and the ion $(\text{M}^+)^*$ initially formed by charge transfer:

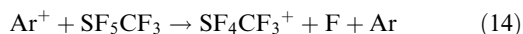


This can be judged by inspecting the photoelectron spectrum of M. For the generic charge-transfer reaction (12), energy balance requires that:

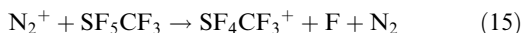
$$E[(\text{M}^+)^*] - E(\text{M}) = \text{RE}(\text{A}^+) \quad (13)$$

so if there is a strong signal in the photoelectron spectrum of M at an ionisation energy equal to $\text{RE}(\text{A}^+)$, efficient charge-transfer (reaction (12)) can be anticipated. The photoelectron spectrum of SF_5CF_3 has not been reported. However, a TPES (Threshold PhotoElectron Spectrum) of SF_5CF_3 is available.¹⁰ It shows a significant yield of electrons for all photon energies from 12.5 eV to greater than 23 eV. This suggests that if the mechanism of reaction for all reagent ions with recombination energies greater than 12.5 eV is long-range charge-transfer, then the reactions should all be efficient. This is confirmed by the data in Table 1. The combination of reaction rate coefficients equal to the capture estimates, and product ion yields matching TPEPICO results confirms that the reactions of SF_5CF_3 with reagent ions possessing recombination energies greater than 12.5 eV can be viewed as long-range charge transfer reactions.

The reactions with Ar^+ and N_2^+ resulted in one product ion not observed from other charge-transfer reactions. This product ion has a mass of 177 u, and could be either SF_4CF_3^+ or SF_5CF_2^+ (or both). Since the bond dissociation energy of S–F in SF_6 is less than that of C–F in CF_4 , we propose that SF_4CF_3^+ is the product ion. SF_4CF_3^+ (and/or SF_5CF_2^+) was not a reported product of either the electron impact ionisation²⁶ or the photoionisation of SF_5CF_3 .¹⁰ The observation of the charge-transfer reactions:



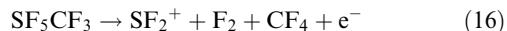
and



can be used to estimate an upper bound for the enthalpy of formation of SF_4CF_3^+ , $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+)$. However, the possibility that the Ar^+ ($^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$) and N_2^+ ($v = 1$ and 0) reagent ions may not be fully thermalised increases the uncertainty in the estimate. If the SF_4CF_3^+ , for which the branching ratio is only 1 or 2%, is formed from the reactions of Ar^+ ($^2\text{P}_{1/2}$) and N_2^+ ($v = 1$), then the bound obtained is $< -221 \text{ kJ mol}^{-1}$, while if this ion can be formed from Ar^+ ($^2\text{P}_{3/2}$) and N_2^+ ($v = 0$), then the bound is $< -247 \text{ kJ mol}^{-1}$. These limits use a value for $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673 \text{ kJ mol}^{-1}$, obtained by

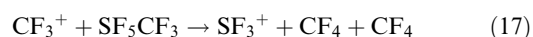
combining the TPEPICO determination of the dissociative ionisation limit for reaction (1), with the enthalpies of formation for CF_3^{+24} and SF_5^{25} obtained from recent *ab initio* calculations. The failure to observe SF_4CF_3^+ as a product of the reaction of N^+ with SF_5CF_3 provides a tentative lower bound $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) > -348 \text{ kJ mol}^{-1}$.

The product ion mass spectra were carefully inspected for the presence of SF_2^+ , which has a mass only 1 u greater than that of CF_3^+ . The lowest energy dissociative ionisation pathway to SF_2^+ is:

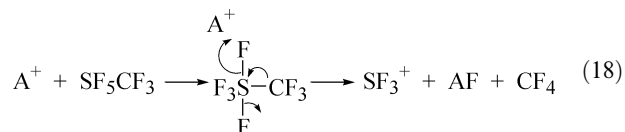


for which the thermodynamic limit is 14.87 eV. SF_2^+ was only observed as a product of the reaction of SF_5CF_3 with Ne^+ . It was not seen in the TPEPICO spectra of SF_5CF_3 .

Inspection of Table 1 shows that there are reactions between SF_5CF_3 and certain reagent ions whose recombination energies are below the calculated adiabatic threshold for the lowest energy dissociative ionisation channel of SF_5CF_3 ($\rightarrow \text{SF}_4^+ + \text{CF}_4 + \text{e}^-$, 11.76 eV). An example is the reaction between CF_3^+ and SF_5CF_3 :



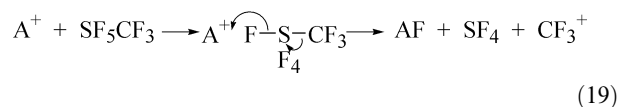
(this is the most exothermic pathway to SF_3^+ from these reactants). In contrast to the charge-transfer reactions (12), where there is no exchange of atoms between A and M, and A is a spectator to the dissociation of $(\text{M}^+)^*$, the pathway to these proposed products involves the formation of a new chemical bond between the reagent ion (CF_3^+) and a fragment abstracted from SF_5CF_3 (F^-). For the reaction above this is coupled with fragmentation of SF_4CF_3^+ to release the observed ion product SF_3^+ . Since SF_4CF_3^+ is not observed as a product of the reaction (which is consistent with the proposed bounds on $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+)$), the overall reaction may well be concerted:



(CF_3^+ has been replaced by the generic reagent ion A^+ , because we believe the several other reactions in which SF_3^+ is formed proceed *via* this mechanism, see below)

The reactions of SF_5CF_3 do not furnish any examples of detected ion products which contain new bonds between units from SF_5CF_3 and the reagent ion. The existence of pathways such as (18) is inferred from the requirement that the overall proposed reaction must be close to thermoneutral or exothermic, in order for it to proceed at an observable rate. The reactions of SF_5CF_3 with SF_4^+ , CF_2^+ , SF^+ , SF_5^+ , CF^+ , and CF_3^+ provide further examples of reactions proceeding *via* chemical rather than charge-transfer pathways. Table 1 indicates the likely neutral products, identified from the exothermicity criterion. For all of the reactions, SF_3^+ is one of the major product ions, and the inferred product neutrals point to reaction *via* mechanism (18). A more exothermic pathway exists for the reaction with CF^+ , with C_2F_6 as the neutral product, rather than $\text{CF}_2 + \text{CF}_4$ as anticipated for reaction (18).

The other major product ion seen from the reactions of CF_2^+ , SF^+ , SF_5^+ , and CF^+ is CF_3^+ , and reaction (19) shows a possible mechanism:



As Table 1 shows, for both CF_2^+ and CF^+ there is a more exothermic route to CF_3^+ , with CF_4 as one of the neutral products. The lowest energy pathways to CF_3^+ from the reactions of SF_4^+ , SF_2^+ , and SF_3^+ have substantial endothermicities,

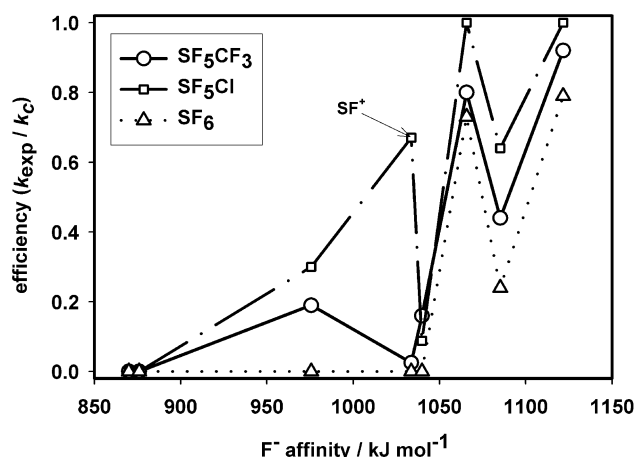


Fig. 2 Plot of reaction efficiencies (k_{exp}/k_c) against fluoride ion affinity for the reactions of the CF_m^+ ($m = 1-3$) and SF_n^+ ($n = 1-5$) reagent ions with SF_5CF_3 , SF_5Cl , and SF_6 .

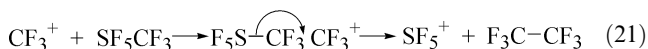
which accounts for the non-observation of CF_3^+ as a product of any of these reactions.

Reaction schemes (18) and (19) involve the abstraction of F^- from SF_5CF_3 by the reagent ion, so some correlation of the reaction efficiencies with the F^- affinities of the reagent ions can be anticipated. The fluoride affinities of the reagent ions, expressed as minus the 0 K enthalpy change for the reaction:



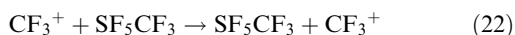
are given in Table 1. The reaction efficiencies are plotted against fluoride affinities in Fig. 2. Comparing the CF_m^+ ($m = 1-3$) and SF_n^+ ($n = 1-5$) reagent ions, the CF_m^+ ions have higher fluoride affinities, and react more efficiently. For CF_2^+ , which has the highest fluoride affinity, F^- abstraction is directly observed, through the identification of SF_4CF_3^+ as one of the product ions.

SF_5^+ was identified as a product of the reactions of CF_2^+ , CF^+ , and CF_3^+ with SF_5CF_3 . For CF_2^+ and CF_3^+ , the most likely reaction pathway is CF_3^- abstraction:



However, a more complicated pathway is required for CF^+ , because in order to satisfy the exothermicity criterion, the neutral product must be $\text{CF}_2=\text{CF}_2$, and not $\text{CF}-\text{CF}_3$. Despite this, the SF_5^+ branching ratio from $\text{CF}^+ + \text{SF}_5\text{CF}_3$ is about the same (2%) as for the reactions of CF_2^+ and CF_3^+ .

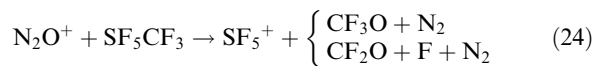
Some confirmation of the proposed mechanisms for the reactions of CF_m^+ and SF_n^+ could be obtained by studying the reactions of the isotopically labelled reagent ions, $^{13}\text{CF}_m^+$ and $^{34}\text{SF}_n^+$. Thus reaction scheme (19) predicts that the CF_3^+ product will not incorporate the ^{13}C present in labelled $^{13}\text{CF}_m^+$ reagent ions, and according to scheme (18) the use of labelled $^{34}\text{SF}_n^+$ will not lead to the production of $^{34}\text{SF}_3^+$. CF_3^+ may undergo two reactions, which are not listed in Table 1, because they do not consume CF_3^+ :



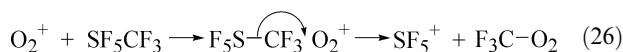
The occurrence of these reactions would be revealed through the use of labelled $^{13}\text{CF}_3^+$ as the reagent ion.

In accord with the observation that NO^+ and NO_2^+ do not react with SF_5CF_3 , a search of the possible ion-molecule reactions failed to identify any exothermic reactions. Since H_3O^+ does not react with SF_5CF_3 , it is concluded that the proton affinity of SF_5CF_3 is less than that of H_2O .

For reagent ions with recombination energies greater than 12.5 eV, there is only one case where it is necessary to invoke a chemical pathway to obtain an exothermic reaction to one of the observed ion products. This is:



For O_2^+ , given the large uncertainty in the dissociative ionisation energy of SF_5CF_3 , it is not possible to be certain as to which pathways are exothermic. The situation is further complicated by the likely presence of vibrationally excited O_2^+ . However, plots of $\ln(\text{O}_2^+ \text{ counts})$ against SF_5CF_3 concentration show no curvature, indicating that the rate coefficient is the same for O_2^+ in $v = 0, 1$, and 2. For O_2^+ the production of CF_3^+ and SF_5^+ is likely to be *via* chemical routes:



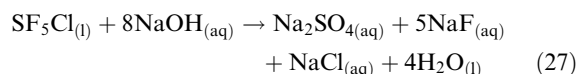
(reaction (26) is CF_3^- abstraction, analogous to (21)), with SF_4^+ coming from a dissociative charge-transfer reaction (8).

Surveying the thermochemistry in Table 1, for which the major source of uncertainty is ± 0.4 eV (± 39 kJ mol $^{-1}$) in the dissociative ionisation energy of SF_5CF_3 (reaction (1)), shows that all of the observed products can be formed in reactions which are close to thermoneutral or exothermic. Thus application of the exothermicity criterion indicates that there are no obvious inconsistencies in the thermochemical data used in the construction of Table 1. By combining the dissociative ionisation energy of SF_5CF_3 ¹⁰ with the *ab initio* values for $\Delta_f H_0^\circ(\text{CF}_3^+)$, $\Delta_f H_0^\circ(\text{CF}_3)$,²⁴ and $\Delta_f H_0^\circ(\text{SF}_5^+)$,²⁵ the following thermochemical data for SF_5CF_3 are obtained: $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673$ kJ mol $^{-1}$ and $D_0(\text{SF}_5-\text{CF}_3) = 374$ kJ mol $^{-1}$.

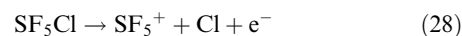
3.2 SF_5Cl reactions

The experimental reaction rate coefficients for the reactions of SF_5Cl with Ne^+ , F^+ , Ar^+ , N_2^+ , N^+ , CO^+ , CO_2^+ , O^+ , N_2O^+ , H_2O^+ , O_2^+ , SF_4^+ , CF_2^+ , SF^+ , SF_2^+ , NO_2^+ , SF_5^+ , NO^+ , CF^+ , CF_3^+ , SF_3^+ , and H_3O^+ , together with the observed product ions, and their branching ratios are given in Table 2. Before discussing these results, some basic thermochemistry needs to be evaluated.

The JANAF tables²⁷ provide a value for the enthalpy of formation of SF_5Cl ($\Delta_f H_0^\circ(\text{SF}_5\text{Cl}) = -1026$ kJ mol $^{-1}$) derived from a thermochemical study of the reaction:²⁸



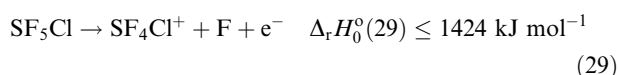
When this is combined with the enthalpy of formation of SF_5^+ obtained from the high level *ab initio* calculations of Bauschlicher and Ricca,²⁵ the 0 K adiabatic energy for the lowest dissociative ionisation limit of SF_5Cl :



is predicted to be 1230 kJ mol $^{-1}$ or 12.75 eV. This is not consistent with the reported photoionisation data for SF_5Cl . The photoelectron spectrum of SF_5Cl ²⁹ places an upper bound on the adiabatic ionisation energy of SF_5Cl of 12.33 eV. Further, the photoionisation mass spectrum (PIMS) of SF_5Cl ³⁰ shows an onset for the formation of SF_5^+ of 12.32 eV, with other fragment ions appearing at higher energies. It seems that either $\Delta_f H_0^\circ(\text{SF}_5\text{Cl})$ or $\Delta_f H_0^\circ(\text{SF}_5^+)$ must be wrong. Recent years have seen considerable efforts, both experimental and theoretical, to establish a reliable value for $\Delta_f H_0^\circ(\text{SF}_5^+)$. A recommended experimental value due to Fisher *et al.*³¹ of 11 kJ mol $^{-1}$ would

place the dissociative ionisation limit (28) at 11.99 eV, and give consistency with the observed upper bound to this limit of 12.32 eV. However, theoretical calculations^{25,32,33} consistently give rather larger values, for example $\Delta_f H_0^0(\text{SF}_5^+) = 84 \text{ kJ mol}^{-1}$,²⁵ and some potential problems in the experimental determination of $\Delta_f H_0^0(\text{SF}_5^+)$ have been identified.³⁴ In the absence of an independent test of $\Delta_f H_0^0(\text{SF}_5\text{Cl})$, and the need to use a consistent set of thermochemistry for SF_5Cl , SF_n and SF_n^+ , we have chosen to use the observed onset for the dissociative ionisation (28) combined with $\Delta_f H_0^0(\text{SF}_5^+) = 84 \text{ kJ mol}^{-1}$,²⁵ to determine a lower limit to $\Delta_f H_0^0(\text{SF}_5\text{Cl}) \geq -985 \text{ kJ mol}^{-1}$. With the exception that this value is a lower limit, the procedure matches that adopted to determine $\Delta_f H_0^0(\text{SF}_5\text{CF}_3)$. In Table 2 and the remainder of the text, we have used $\Delta_f H_0^0(\text{SF}_5\text{Cl}) = -985 \text{ kJ mol}^{-1}$. Calculated reaction enthalpies are thus upper bounds. When the revised value for $\Delta_f H_0^0(\text{SF}_5\text{Cl})$ is combined with thermochemistry for SF_n and SF_n^+ from the *ab initio* calculations of Bauschlicher and Ricca,²⁵ and for other neutrals and ions from the JANAF tables,²⁷ Fig. 3, showing the relative energies of many of the lower dissociative ionisation limits of SF_5Cl , can be constructed.

SF_4Cl^+ is a product of many of the ion-molecule reactions of SF_5Cl , so in analysing the reactions it would be useful to have a value for $\Delta_f H_0^0(\text{SF}_4\text{Cl}^+)$. SF_4Cl^+ is seen in the electron impact mass spectrum of SF_5Cl ,³⁵ with an appearance energy of 15.9 eV, and is known to be a product of the dissociative photoionisation of SF_5Cl ,^{30,36} the ion is first observed at a photon energy of 14.76 eV. This places an upper bound on the energy for:



The exothermicity criterion ($\Delta_f H_0^0 < 0$ for an observed reaction) can be applied to refine the upper bound to $\Delta_f H_0^0(29)$. In particular, the observation of SF_4Cl^+ from the reaction of O_2^+ with SF_5Cl produces the lowest upper bound. If the pathway to SF_4Cl^+ is through dissociative charge transfer:

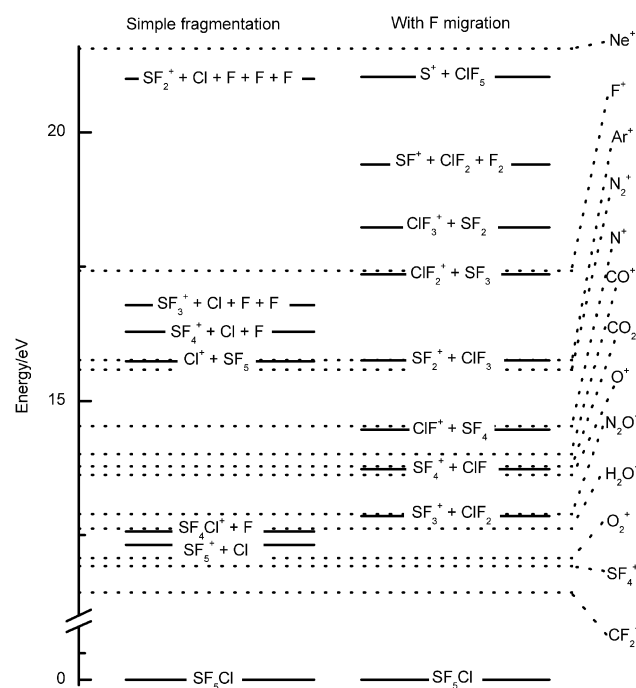
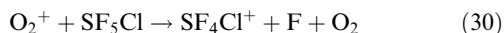
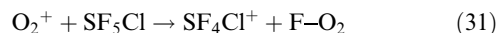


Fig. 3 Adiabatic dissociative ionisation limits below 22 eV for SF_5Cl . The limits are divided into those attained by simple fragmentation, and those involving the migration of an F atom across the S–Cl bond. The recombination energies of the reagent ions with $\text{RE} > 12 \text{ eV}$ are also presented in the figure. The electrons have been omitted from the labelling of the various limits.

then $\Delta_f H_0^0(29) < 1165 \text{ kJ mol}^{-1}$. The other possible route is F[•] abstraction by O_2^+ :

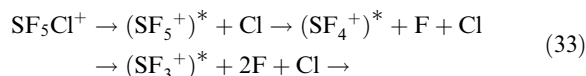


taking $D_0(\text{F} - \text{O}_2) = 50 \text{ kJ mol}^{-1}$ ²⁷ leads to $\Delta_f H_0^0(29) < 1215 \text{ kJ mol}^{-1}$. These bounds assume that SF_4Cl^+ can be formed from $\text{O}_2^+(v=0)$. The neutral products, $\text{F} + \text{O}_2$ or FO_2 , are unknown, so other data must be used to choose between these two bounds. The bond dissociation energy $D_0(\text{SF}_4^+ - \text{F})$ is 383 kJ mol^{-1} ,²⁵ it is expected that $D_0(\text{SF}_4^+ - \text{Cl})$ will be lower. Adopting $\Delta_f H_0^0(29) < 1215 \text{ kJ mol}^{-1}$ gives $D_0(\text{SF}_4^+ - \text{Cl}) > 356 \text{ kJ mol}^{-1}$, which is reasonable, while $\Delta_f H_0^0(29) < 1165 \text{ kJ mol}^{-1}$ leads to $D_0(\text{SF}_4^+ - \text{Cl}) > 406 \text{ kJ mol}^{-1}$. At the onset of photoionisation (12.32 eV) the only observed ion product is SF_5^{+30} (reaction 28), a value for $\Delta_f H_0^0(29)$ below 1189 kJ mol^{-1} is then unlikely to be correct. The recommended bound is thus $\Delta_f H_0^0(29) < 1215 \text{ kJ mol}^{-1}$, and the value is expected to be quite close to this upper bound. The calculation of the 0 K enthalpy changes for ion-molecule reactions is facilitated by combining $\Delta_f H_0^0(29)$ with $\Delta_f H_0^0(\text{SF}_5\text{Cl}) = -985 \text{ kJ mol}^{-1}$, to give $\Delta_f H_0^0(\text{SF}_4\text{Cl}^+) < 152 \text{ kJ mol}^{-1}$; the calculations shown in Table 2 used $\Delta_f H_0^0(\text{SF}_4\text{Cl}^+) = 150 \text{ kJ mol}^{-1}$. Since SF_4Cl^+ is a minor product of the reaction between O_2^+ and SF_5Cl , it could be formed exclusively from the vibrationally excited O_2^+ known to be present. For example, if all the SF_4Cl^+ is produced by the reaction of $\text{O}_2^+(v=2)$ with SF_5Cl :

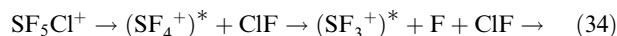


then $\Delta_f H_0^0(29) < 1259 \text{ kJ mol}^{-1}$, $D_0(\text{SF}_4^+ - \text{Cl}) > 312 \text{ kJ mol}^{-1}$, and $\Delta_f H_0^0(\text{SF}_4\text{Cl}^+) < 197 \text{ kJ mol}^{-1}$. This rather higher upper bound for $\Delta_f H_0^0(29)$ is not ruled out by application of the exothermicity criterion to any of the other reactions observed to form SF_4Cl^+ .

SF_4^+ and SF_3^+ are observed as products of the photoionisation of SF_5Cl ,³⁰ with appearance energies of 15.87 and 16.2 eV, respectively. Some preliminary work on the TPEPICO spectrum of SF_5Cl ³⁶ gives slightly higher values (at 298 K) of 16.2 ± 0.3 and $16.8 \pm 0.3 \text{ eV}$, respectively. SF_4^+ and SF_3^+ are observed in the electron impact mass spectrum of SF_5Cl ,³⁵ but their appearance energies have not been reported. The fragmentation of SF_5Cl^+ may occur by step-wise loss of Cl and F atoms:



in which case the adiabatic limits to SF_4^+ and SF_3^+ will be 16.28 and 16.78 eV, respectively. The other possibility is a concerted fragmentation leading to the formation of ClF :



the predicted limits are now 13.72 eV (SF_4^+) and 14.22 eV (SF_3^+). The limit for SF_3^+ could be even lower, if ClF_2^+ is formed as the neutral product. The fragment ions SF_4^+ and SF_3^+ are not observed at energies well below the limits for their formation by step-wise loss of Cl and F from SF_5Cl^+ (reaction scheme (33)). Indeed the preliminary TPEPICO data suggest that their appearance may coincide with the adiabatic energies for simple fragmentation.

Ion product branching ratio comparisons between the ion-molecule reactions (Table 2) and preliminary results from a TPEPICO study of energy selected $\text{SF}_5\text{Cl}^{+36} provide strong evidence that the reactions of SF_5Cl with Ne^+ , F^+ , Ar^+ , and N_2^+ all occur *via* long-range charge transfer.³⁸ Fig. 4 shows the mass spectrum obtained for the reaction of Ne^+ with SF_5Cl . A large amount of energy (9.25 eV, relative to the lowest dissociative ionisation limit to $\text{SF}_5^+ + \text{Cl}$) is available to dissociate $(\text{SF}_5\text{Cl}^+)^*$, and this is reflected in the range of pro-$

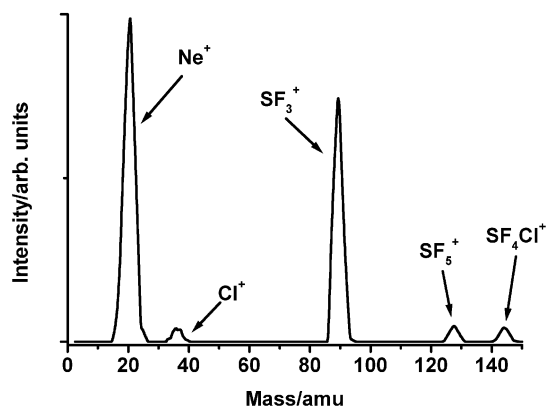
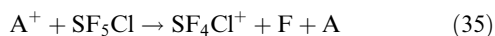


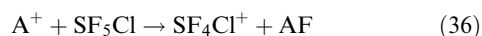
Fig. 4 A typical mass spectrum obtained from the charge-transfer reaction of Ne^+ with SF_5Cl , illustrating the considerable degree of fragmentation, that results from the high recombination energy of Ne^+ (21.56 eV) compared to the other reagent ions used in this study. Four product ions are identified in the figure; Cl^+ , SF_3^+ (dominant), SF_5^+ and SF_4Cl^+ . SF_2^+ and SF_4^+ are also observed products of the reaction, but their branching ratios are very small, resulting in product ion intensities which are too small to be discernible on the figure.

duct fragment ions seen in the mass spectrum. Indeed, Cl^+ and SF_2^+ are only observed from the reaction of SF_5Cl with Ne^+ .

For photon energies below 14.8 eV, the only product ion observed in the TPEPICO experiments is SF_5^+ . The results in Table 2 show that the reactions of SF_5Cl with ions having recombination energies in the range 12.3 to 14.8 eV are efficient, but yield various ion products in addition to SF_5^+ . SF_4Cl^+ is a product of all these reactions. It could be the product of charge transfer and fragmentation, induced by short-range interactions:

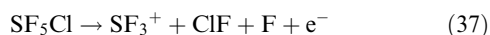


and/or the formation of SF_4Cl^+ may be linked to chemical reaction between F and A, such as:

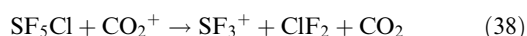


Either (or both) of reactions (35) and (36) may occur when $\text{RE}(\text{A}^+) > \Delta_f H_0^\circ(29)$, schemes of the type shown in reaction (36) will be necessary when $\text{RE}(\text{A}^+) < \Delta_f H_0^\circ(29)$. The relative branching ratios for SF_5^+ and SF_4Cl^+ vary widely with the reagent ion. There is no correlation of the $\text{SF}_5^+/\text{SF}_4\text{Cl}^+$ ratio with either the recombination energies of the reagent ions, or with the enthalpies of reactions in which bonds are formed and broken. Specific short-range interactions within the initially formed ion-molecule complex are evidently important to the outcome of the reactions. Without further information, particularly the identification of the neutral products, the mechanisms of the reactions must remain uncertain.

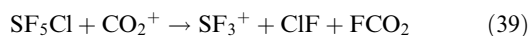
The reaction of CO_2^+ with SF_5Cl produces a number of interesting products. The recombination energy of CO_2^+ (13.77 eV) is well below the minimum energy (14.22 eV) required for the dissociative ionisation:



$\Delta_f H_0^\circ(37) - \text{RE}(\text{CO}_2^+) = 43 \text{ kJ mol}^{-1}$, but SF_3^+ is an observed (trace) product from the reaction of CO_2^+ . Two possible routes to SF_3^+ are dissociative charge transfer with ClF_2 as the neutral product:



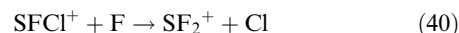
and F^- abstraction by CO_2^+ coupled with fragmentation of the intermediate SF_4Cl^+ :



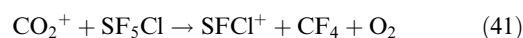
ClF_2 is a stable species, with $D_0(\text{FCl}-\text{F})$ calculated to lie

between 75 and 133 kJ mol^{-1} .³⁷ An experimental determination of $D_0(\text{F}-\text{CO}_2)$ has yielded a value of 48 kJ mol^{-1} ,³⁹ with calculations providing a slightly higher value of 61 kJ mol^{-1} .^{40–42} Thus (38) and (39) are both exothermic routes to SF_3^+ , and both involve the formation of a relatively weakly bound product neutral.

The CO_2^+ reaction generates two ion products, in addition to SF_4Cl^+ , for which enthalpies of formation have not been reported. They are SFCl^+ and SF_2Cl^+ , but it should be noted that only traces of SF_2Cl^+ were observed. Estimates of their enthalpies of formation can be obtained, starting from the calculated thermochemistry²⁵ of SF_2^+ and SF_3^+ , and the knowledge that S–Cl bonds are weaker than S–F bonds (for example $D_0(\text{SF}_5-\text{F}) > D_0(\text{SF}_5-\text{Cl})$, and $D_0(\text{S}-\text{F}) > D_0(\text{S}-\text{Cl})$). Assuming that for the exchange reaction:



$\Delta_f H_0^\circ = -50 \text{ kJ mol}^{-1}$, we obtain $\Delta_f H_0^\circ(\text{SFCl}^+) = 782 \text{ kJ mol}^{-1}$, which is compatible with the bound of $\Delta_f H_0^\circ(\text{SFCl}^+) < 878 \text{ kJ mol}^{-1}$, implied by the observation of the reaction:



(other neutral products can be excluded, for pathways leading to them cannot satisfy the exothermicity criterion). Adopting the procedure described above to generate an estimate for the enthalpy of formation of SF_2Cl^+ yields $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+) = 453 \text{ kJ mol}^{-1}$. Even with the aid of this estimate it is not possible to identify conclusively the pathway that leads to the production of SF_2Cl^+ from the reaction of CO_2^+ with SF_5Cl , and two possible sets of neutral products are listed in Table 2. Dissociative charge transfer is not the route to SF_2Cl^+ . SF_2Cl^+ is also an observed product of the reaction with H_2O^+ , and a chemical pathway such as:



is required to satisfy the exothermicity criterion. The reaction with H_2O^+ also produces SF_2OH^+ , providing direct confirmation that reactions involving the making as well as breaking of bonds do occur. An estimate for $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+)$ can be obtained by assuming that $D_0(\text{SF}_2^+-\text{OH}) \approx D_0(\text{SF}_2^+-\text{F})$, which leads to $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+) \approx 321 \text{ kJ mol}^{-1}$. This is compatible with the formation of SF_2OH^+ in the reaction of H_2O^+ with SF_5Cl :



For the CF_m^+ and SF_n^+ reagent ions, which all have recombination energies less than 12.0 eV, *i.e.* well below the energy needed for dissociative ionisation of SF_5Cl , the majority of

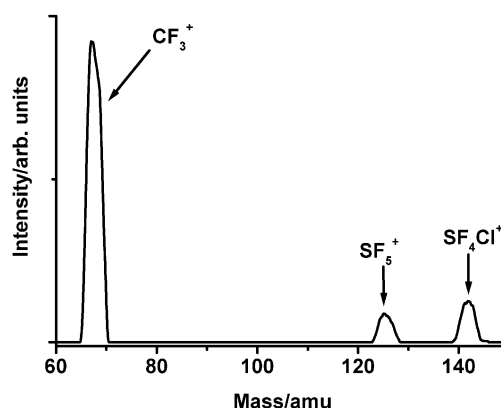


Fig. 5 A typical mass spectrum obtained from the chemical reaction of CF_3^+ with SF_5Cl . Two product ions are observed; SF_5^+ and SF_4Cl^+ .

the observed ion products are the result of F^- and Cl^- abstraction:

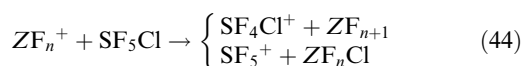
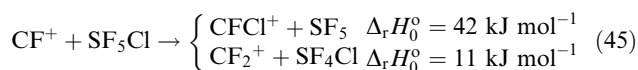


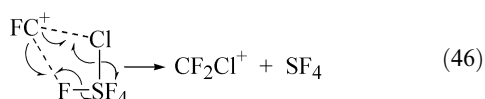
Fig. 5 shows a mass spectrum from the reaction of CF_3^+ with SF_5Cl , both SF_4Cl^+ and SF_5^+ are seen, together with unreacted CF_3^+ . There are wide variations in both the efficiencies of the reactions, and in the relative yields of SF_4Cl^+ (F^- abstraction) and SF_5^+ (Cl^- abstraction). Fig. 2 shows how the reaction efficiencies vary with the fluoride affinities of the reagent ions. SF^+ reacts with a much higher efficiency than the other SF_n^+ reagent ions. The major ion product for the reactions of each of the CF_m^+ and SF_n^+ reagent ions is SF_4Cl^+ , but for SF^+ it is SF_5^+ (Cl^- abstraction). The overall reactions can be viewed as two linked steps - formation of an ion pair from SF_5Cl , $\text{SF}_5^+ + \text{Cl}^-$ for Cl^- abstraction and $\text{SF}_4\text{Cl}^+ + \text{F}^-$ for F^- abstraction, coupled with combining the released anion with the reagent ion. $\text{SF}_4\text{Cl}^+ + \text{F}^-$ lies 45 kJ mol^{-1} higher in energy than $\text{SF}_5^+ + \text{Cl}^-$. This may be expected to favour the production of SF_5^+ over SF_4Cl^+ . However, bond formation between the reagent ion and Cl^-/F^- is occurring simultaneously. The reagent ions all have higher affinities for F^- than for Cl^- , which will tend to lead to the formation of SF_4Cl^+ in preference to SF_5^+ . The overall outcome is a balance between these two competing factors. The difference between the F^- and Cl^- affinities is smallest for SF^+ , and this is reflected in the product branching ratios, for the reaction with SF^+ gives the highest yield of SF_5^+ . Indeed in the case of SF^+ , the branching ratio for SF_5^+ is greater than for SF_4Cl^+ , even though the F^- abstraction pathway has a higher overall exothermicity.

In addition to Cl^- and F^- abstraction, leading to SF_5^+ and SF_4Cl^+ , respectively, CF_2^+ reacts to produce CF_2Cl^+ , by transfer of a Cl atom from SF_5Cl to CF_2^+ . It is perhaps surprising that CF_3^+ , arising from F atom transfer was not one of the observed products. It is unlikely that the F abstraction pathway is endothermic. To show this a value for $\Delta_f H_0^\circ(\text{SF}_4\text{Cl})$ is required. $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}) = \Delta_f H_0^\circ(\text{SF}_4) + \Delta_f H_0^\circ(\text{Cl}) - D_0(\text{SF}_4\text{—Cl})$, assuming that $D_0(\text{SF}_4\text{—Cl}) = 120 \text{ kJ mol}^{-1}$ (a little less than $D_0(\text{SF}_4\text{—F}) = 153 \text{ kJ mol}^{-125}$) leads to $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}) = -761 \text{ kJ mol}^{-1}$, from which $\Delta_f H_0^\circ(\text{CF}_2^+ + \text{SF}_5\text{Cl} \rightarrow \text{CF}_3^+ + \text{SF}_4\text{Cl}) = -277 \text{ kJ mol}^{-1}$. Based on overall exothermicity, F abstraction should be favoured over Cl abstraction. The atom abstraction reactions begin with stretching an S—F or S—Cl bond, the greater strength of the S—F bond compared to the S—Cl bond may account for the formation of CF_2Cl^+ rather than CF_3^+ .

The reaction with CF^+ produces an ion product, CF_2Cl^+ , corresponding to the transfer of two neutral atoms to the reagent ion. Transfer of a single Cl or F atom to CF^+ is not observed. This is consistent with estimates of $\Delta_r H_0^\circ$ for:

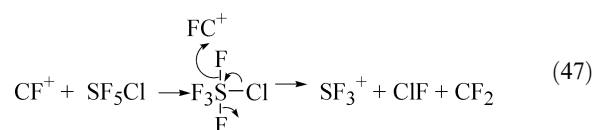


which suggest that both these reactions are endothermic. The endothermicities are not large ($<50 \text{ kJ mol}^{-1}$), but they do imply that CF_2Cl^+ will not be formed by the sequential transfer of two atoms, but rather by a concerted mechanism:



CF_3^+ could also be produced by a mechanism of this type. The estimated exothermicity (-349 kJ mol^{-1} , using $\Delta_f H_0^\circ(\text{SF}_3\text{Cl}) = -619 \text{ kJ mol}^{-1}$) is similar to that calculated for the production of CF_2Cl^+ , but CF_3^+ was not observed. This parallels the reaction of CF_2^+ , where CF_3^+ was not one of the observed products, and may be explained by the relative

strengths of the S–Cl and S–F bonds in SF₅Cl. SF₃⁺ (+CClF₃) may be the result of CF₂Cl⁺ abstracting F[−] from SF₄ before the ion-molecule complex breaks up following reaction. An alternative pathway to SF₃⁺ is:



This route to SF_3^+ from the reaction of CF^+ with SF_5Cl is much less exothermic (see Table 2), but without identification of the neutral products, a conclusive identification of the pathway cannot be established.

SF_2^+ was observed not to react with SF_5Cl , but it appears likely that F atom transfer ($\rightarrow\text{SF}_3^+ + \text{SF}_4\text{Cl}$) and Cl atom transfer ($\rightarrow\text{SF}_2\text{Cl}^+ + \text{SF}_5$) are exothermic pathways. These neutral atom transfer pathways are also predicted to be exothermic for SF^+ , but SFCl^+ and SF_2^+ were not formed. For SF_3^+ , NO^+ , and NO_2^+ , an exploration of the possible reaction pathways, including transfer of F^- , Cl^- , F, and Cl, did not identify any overall exothermic reactions, which accounts for the failure of these ions to react with SF_5Cl . H_3O^+ also did not react, showing that the proton affinity of SF_5Cl is less than that of H_2O .

3.3 SF₆ reactions

There have been several past studies of the gas-phase reactions under thermal conditions of SF_6 with positive ions.^{1-4,6-8} The results are summarised in Table 3. We have extended the previous studies by investigating the reactions, under thermal conditions, of SF_n^+ ($n = 1$ to 5) with SF_6 . In each case we observed no depletion of the reagent ion signals over the full range of SF_6 concentrations accessible to us. This implies that for each of these reactions the rate coefficient is less than $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As for Tables 1 and 2, the thermochemis-

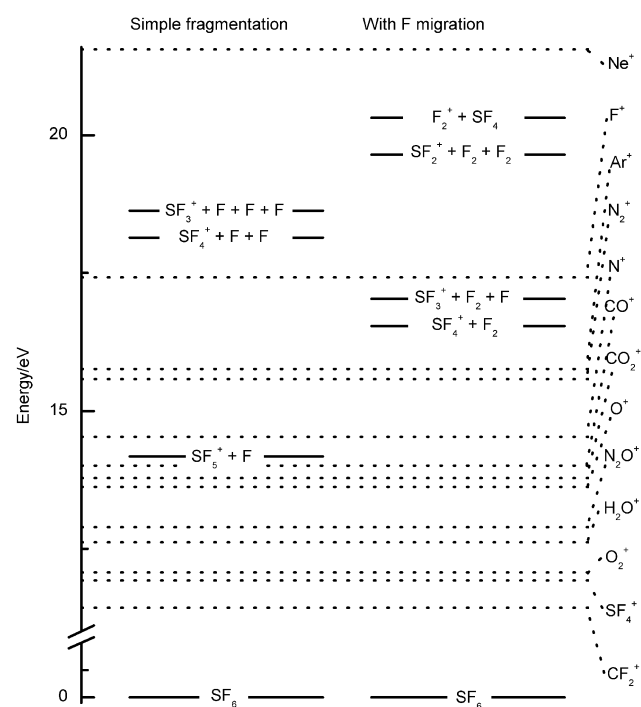
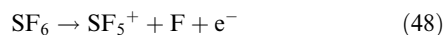


Fig. 6 Adiabatic dissociative ionisation limits below 22 eV for SF₆. The limits are divided into those attained by simple fragmentation, and those involving the migration of an F atom across an S-F bond. The recombination energies of the reagent ions with RE > 14 eV are also presented in the figure. The electrons have been omitted from the labelling of the various limits.

try has been constructed using enthalpies of formation for CF_m , CF_m^{+24} and SF_n , SF_n^{+25} from recent high level *ab initio* calculations. These *ab initio* values place the dissociative ionisation energy for:



at 14.18 eV. The dissociative ionisation limits of SF_6 that lie below 22 eV are shown in Fig. 6. The high energies of the limits mean that only Ne^+ , F^+ , Ar^+ , N_2^+ , and N^+ may react with SF_6 by dissociative charge transfer. All other reactions must occur by chemical pathways, for example:

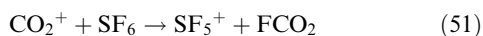


Williams *et al.*⁷ have demonstrated that the reactions of SF_6 with positive ions possessing recombination energies greater than 14.2 eV conform well to the expectations of models of long-range charge-transfer reactions. They also found evidence to indicate that the reaction of SF_6 with Ne^+ is mediated by short-range interactions. On thermochemical evidence they concluded that the minor SF_3^+ product from the reaction of N^+ with SF_6 is the result of a chemical pathway leading to the formation of NF as one of the neutral products.

The slow reaction with CO_2^+ is interesting. The obvious pathway to the observed SF_5^+ product is dissociative charge transfer:



but this pathway is so endothermic ($\Delta_r H_0^\circ(50) = 39 \text{ kJ mol}^{-1}$) that this reaction should not be observable with our SIFT apparatus at 300 K. It seems improbable that even a small fraction of the CO_2^+ reagent ions possess sufficient internal energy to surmount the endothermicity. Instead, following the suggestion of Babcock and Streit,³ the proposed pathway for the formation of SF_5^+ is F^- transfer:



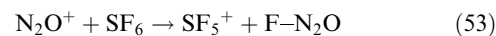
to form the weakly bound molecule FCO_2 , providing a pathway to SF_5^+ with a lower overall enthalpy change:

$$\Delta_r H_0^\circ(50) = \Delta_r H_0^\circ(49) - D_0(\text{F-CO}_2) \quad (52)$$

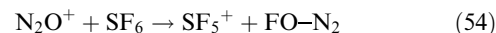
FC(O)O has been characterised experimentally by a variety of spectroscopic methods.^{39,43,44} The measurement of the electron affinity of FCO_2 has led to the determination of $D_0(\text{F-C(O)O}) = 48 \pm 13 \text{ kJ mol}^{-1}$.³⁹ Theoretical calculations at the G2 level have given $\Delta_r H_0^\circ(\text{FC(O)O}) = -378 \pm 8 \text{ kJ mol}^{-1}$.^{40,41} A very similar value ($\Delta_r H_0^\circ(\text{FC(O)O}) = -376 \pm 13 \text{ kJ mol}^{-1}$) has resulted from the use of density functional theory to calculate the enthalpy changes for a number of isodesmic reactions involving FC(O)O .⁴² Combining these theoretical values with $\Delta_r H_0^\circ(\text{CO}_2)$ and $\Delta_r H_0^\circ(\text{F})$ from the JANAF tables²⁷ gives $D_0(\text{F-C(O)O}) = 61 \pm 15 \text{ kJ mol}^{-1}$. Either value for $D_0(\text{F-C(O)O})$ leads to the conclusion that reaction (51) is exothermic. The observed low rate coefficient for the reaction of CO_2^+ with SF_6 ($k_{\text{exp}}/k_c = 0.008$) may reflect a barrier associated with F^- abstraction from SF_6 , which is not fully removed by the small overall exothermicity of the reaction. Several other reactions in which F^- is abstracted from SF_6 also have rate constants less than predicted by capture theory (see below).

The slow reaction of N_2O^+ with SF_6 to form SF_5^+ provides another example of a reaction where it is necessary to postulate the formation of a weakly bound product in order to provide a pathway with a sufficiently low overall endothermicity to be

consistent with an observable rate coefficient. Two possibilities are:



and



with 0 K enthalpy changes given by:

$$[\Delta_r H_0^\circ(52)/\text{kJ mol}^{-1}] = 124 - [D_0(\text{F-N}_2\text{O})/\text{kJ mol}^{-1}] \quad (55)$$

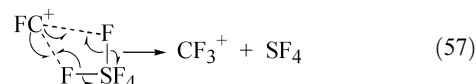
and

$$[\Delta_r H_0^\circ(53)/\text{kJ mol}^{-1}] = 69 - [D_0(\text{FO-N}_2)/\text{kJ mol}^{-1}] \quad (56)$$

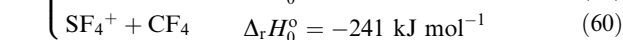
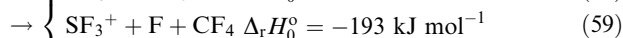
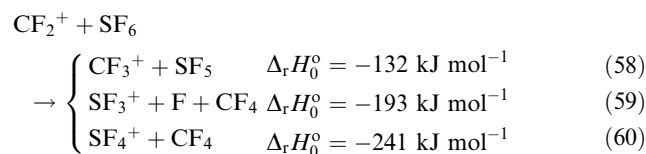
There appears to be no independent evidence for the existence of any isomer of FN_2O , and $D_0(\text{F-N}_2\text{O})$ and $D_0(\text{FO-N}_2)$ are unknown.

F^- abstraction from SF_6 to form SF_5^+ is exothermic for CF^+ , CF_2^+ , and CF_3^+ , but for each of these reactions the experimental rate coefficient (k_{exp}) is less than the calculated value from Langevin capture theory (k_c), and for CF_3^+ $k_{\text{exp}} \approx 0.25 \times k_c$. The efficiencies of the reactions, defined as k_{exp}/k_c , are plotted in Fig. 2 against the fluoride affinities of the reagent ions, to show the correlation between reaction efficiency and reagent ion fluoride affinity.

A minor product from the reaction of CF^+ is CF_3^+ . Sequential transfer of two F atoms is unlikely to be the mechanism for the first step (to form $\text{CF}_2^+ + \text{SF}_5$) is highly endothermic ($\Delta_r H_0^\circ = 156 \text{ kJ mol}^{-1}$). Instead the transfer must be concerted:

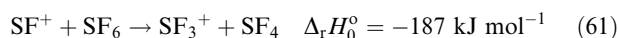


The greater complexity of this scheme, compared to the much less exothermic F^- abstraction leading to SF_5^+ , provides an explanation for the higher branching ratio to form SF_5^+ compared to CF_3^+ . With CF_2^+ as the reagent ion, there are several pathways of greater exothermicity than F^- abstraction:

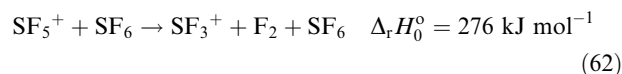


yet the ion products of these reactions were not observed.

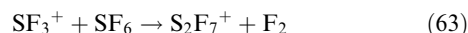
For the SF_n^+ reagent ions, only one exothermic pathway was identified:



but this reaction, involving the transfer of two F atoms, was not observed. In experiments using non-thermal reagent ions,^{5,45} evidence has been presented for the occurrence of the endothermic reaction:



and for:

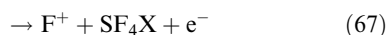
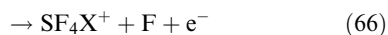
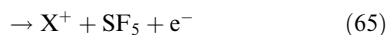
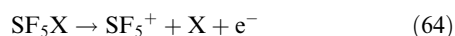


The reaction products are only accessible for reagent ions which are translationally and/or internally excited, and the reactions are not observed in SIFT experiments, where the ions have been thermalised before they can react.

F^- abstraction is calculated to be highly endothermic for NO^+ and NO_2^+ , and SF_6 does not react with either of these reagent ions. SF_6 has a much lower proton affinity than H_2O ,⁴⁶ and as a consequence there is no reaction between H_3O^+ and SF_6 .

3.4 Comparisons

The parent cation SF_5X^+ ($X = CF_3, Cl, F$) was not observed as a product from any of the reactions. When it is formed by charge transfer, it immediately dissociates. The most obvious pathways for dissociative ionisation involve scission of one bond:

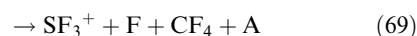
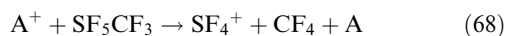


with smaller SF_p^+ ($p < 5$) and SF_qX^+ ($q < 4$) ions resulting from stepwise fragmentation of SF_5^+ and SF_4X^+ . F^+ was not observed among the ion products for any of the reactions. Even with Ne^+ , the reagent ion with the highest recombination energy, the products of pathway (67) are energetically inaccessible for SF_6 , and barely accessible for SF_5CF_3 and SF_5Cl . Dissociative channels (64) and (65) differ only in the location of the positive charge. For $X = Cl$ and F , channel (65) lies higher in energy than (64), by 3.42 eV (330 kJ mol⁻¹) for $X = Cl$, and by 7.88 eV (760 kJ mol⁻¹) for $X = F$, but for $X = CF_3$ channel (65) is below (64) by 0.50 eV (48 kJ mol⁻¹). For channel (64) the S–X bond is broken, channel (66) corresponds to breaking an S–F bond. The energy differences between (64) and (66) can be obtained using our estimates of $\Delta_f H_0^0(SF_4CF_3^+)$ ($= -221$ to -348 kJ mol⁻¹) and $\Delta_f H_0^0(SF_4Cl^+)$ (~ 150 kJ mol⁻¹). For SF_5CF_3 the products of (60) lie considerably below those of (66), the difference is between 1.13 and 2.45 eV (109 and 236 kJ mol⁻¹). In the case of SF_5Cl , the difference between (64) and (66) is small, 0.24 eV (23 kJ mol⁻¹), with (66) being the lower energy channel.

These energy differences play a significant role in determining the products observed from the charge-transfer reactions of the SF_5X molecules. In the case of SF_5CF_3 , for reagent ions with recombination energies in excess of 12.9 eV, the experimentally determined limit for (65),¹⁰ CF_3^+ is the dominant product ion. The ratio of SF_5^+ to CF_3^+ increases with the recombination energy of the reagent ion, reflecting the higher energy of (64) compared to (65). The energy difference between (66) and (65) is quite large, and $SF_4CF_3^+$ was observed as a trace product from only a few of the reactions. The pattern of the energies of the channels is quite different for SF_5Cl (compare Figs. 1 and 3), (64) is the lowest (12.32 eV^{30,36}), (66) is only slightly higher (12.56 eV), with (65) much higher (15.74 eV). The relative branching ratios for SF_5^+ and SF_4Cl^+ vary greatly, and there is no obvious correlation with the recombination energy of the reagent ion. The TPEPICO experiments on the fragmentation of energy-selected SF_5Cl^+ ions³⁶ do not show these variations. The results thus show a deviation from the predictions of long-range charge-transfer theory. This suggests that when the energy difference between two channels is small, short-range interactions within the ion-molecule complex between formation by capture and break-up leading to the release of the products can have a large effect on the relative yields of different product ions. For SF_6 the only energetically accessible channel is (64), which is identical to (66). Available energy appears to be the most important factor in determining the outcome of the charge-transfer reactions.

Various SF_p^+ ($p < 5$) and SF_qX^+ ($q < 4$) ions were observed from the charge-transfer reactions. In many cases these can be formed by fragmentation of SF_5^+ and SF_4X^+ . However, con-

sideration of the energetics indicates that in some cases the appearance of certain fragment ions is only possible if new bonds are formed. The great majority of these cases occur for SF_5CF_3 , where exothermic charge-transfer routes to SF_3^+ and SF_4^+ in general require the formation of CF_4 as one of the neutral products:



Reactions of this type can be identified in Table 1. The high bond dissociation energy $D_0(CF_3-F)$ ($= 374$ kJ mol⁻¹) is a strong thermochemical driving force for these reactions of SF_5CF_3 . For SF_5Cl and SF_6 , the fragment ions SF_4^+ and SF_3^+ are not observed at energies well below the limits for their formation by stepwise loss of atoms from SF_5Cl^+ and SF_6^+ (reaction scheme (33)). $D_0(Cl-F)$ ($= 247$ kJ mol⁻¹) and $D_0(F-F)$ ($= 154$ kJ mol⁻¹) are much lower than $D_0(CF_3-F)$, and there are few examples of reactions requiring the formation of ClF or F_2 . In addition, the XF forming pathways to SF_4^+ and SF_3^+ can be viewed as dissociation of SF_5X^+ ($\rightarrow SF_5 + X^+$) coupled with abstraction of F^- from SF_5 by X^+ . This will be a much higher energy pathway for SF_5Cl and SF_6 than for SF_5CF_3 , because of the higher ionisation energy of Cl (12.97 eV) and F (17.42 eV) compared to CF_3 (9.04 eV). The formation of SF_3^+ from the reactions of N^+ , CO_2^+ , and H_2O^+ with SF_5Cl probably involves the formation of ClF or ClF_2 . In the case of SF_6 , the formation of SF_3^+ from the reaction with F^+ requires the formation of F_2 . Other charge-transfer reactions of each of the molecules may occur with the formation of new bonds, but without identification of the neutral products this cannot be demonstrated.

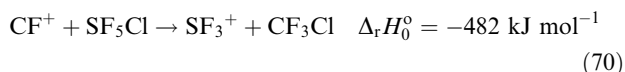
Almost all of the (presumed) charge-transfer reactions proceed with rate constants close to the values calculated by capture theories. The only clear exception is the reaction of Ne^+ with SF_6 . According to the long-range charge-transfer model $k_{exp} \approx k_c$ implies that there is a match between the recombination energy of the reagent ion (RE) and a band in the photoelectron spectrum of the molecule. A photoelectron spectrum is not available for SF_5CF_3 . For SF_5Cl there is a good match between a band in the photoelectron spectrum²⁹ and the recombination energy of each of the reagent ions, including Ne^+ , for which charge-transfer reactions are energetically possible (*i.e.* $RE > 12.3$ eV). In the case of SF_6 , the match for Ne^+ is poor, which provides an explanation for the low rate coefficient for the reaction, compared to the capture theory prediction.⁷

Since the product neutrals from the reactions cannot be detected, the identification of charge-transfer reactions is based on a combination of knowledge of the product ions and basic energetic data. Without energetic data on the dissociative ionisation limits of the molecules, obtained from various photoionisation experiments^{10,30,36} and theoretical calculations,^{24,25} it would be impossible to discern when the reaction mechanism must change from charge transfer to a chemical pathway.

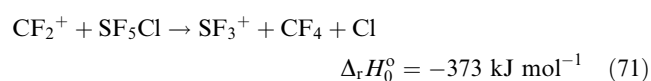
The reagent ions CF_m^+ ($m = 1-3$) and SF_n^+ ($n = 1-5$) all have recombination energies below 12.0 eV, so their reactions with SF_5CF_3 , SF_5Cl , and SF_6 must occur *via* chemical pathways. The observed ion products of the reactions of these ions with SF_5CF_3 (mainly SF_3^+ and CF_3^+) show that they are mechanistically quite different from their reactions with SF_5Cl (SF_4Cl^+ and SF_5^+ are the major products) and SF_6 (primarily yield SF_5^+). While the major reaction pathways for SF_5Cl and SF_6 are simple Cl^- and F^- abstractions, for SF_5CF_3 transfer of F^- to the reagent ion is combined with breaking the S–C bond (see reaction schemes (18) and (19)). In large part the differences between SF_5CF_3 and the other two reactants appear to follow the thermochemistry of the reaction pathways.

Mechanism (18) is the proposed pathway to SF_3^+ , which is an observed product from the reactions of SF_5CF_3 with each of the CF_m^+ and SF_n^+ reagent ions, except SF_3^+ and SF_2^+ . For SF_3^+

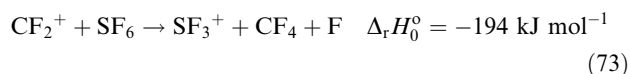
it is not possible to distinguish product SF_3^+ from the reagent ions. For SF_2^+ , the calculated enthalpy change for the production of SF_3^+ ($\Delta_r H_0^\circ = -21 \text{ kJ mol}^{-1}$) reveals that pathway (18) is less exothermic than for the reactions of other reagent ions with SF_5CF_3 in which SF_3^+ is an observed product (see Table 1). This must be an important factor in making the reaction of SF_2^+ too slow to be detected. As the group X of SF_5X changes from CF_3 to Cl and then F pathway (18) becomes increasingly less exothermic, due mainly to the decreasing strength of the new X–F bond. In the case of SF_5Cl , pathway (18) is only calculated to be exothermic for the CF_m^+ reagent ions. The SF_3^+ product ion was only observed from the reaction of CF^+ . With CF^+ as the reagent ion, the calculated exothermicity (-23 kJ mol^{-1}) is less than for CF_3^+ (-41 kJ mol^{-1}) and CF_2^+ (-80 kJ mol^{-1}) which suggests that the CF^+ reaction may proceed by a different, more exothermic pathway:



There is a highly exothermic pathway to SF_3^+ for CF_2^+ :



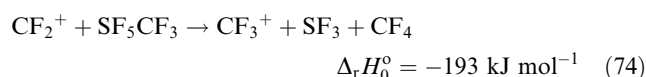
but SF_3^+ was not one of the detected ion products from the reaction of CF_2^+ with SF_5Cl . For SF_6 , pathway (18) to SF_3^+ is in every case endothermic. There are exothermic pathways, analogous to (70) and (71) above, when the reagent ion is CF^+ and CF_2^+ :



but SF_3^+ was not one of the detected product ions from the reactions of CF^+ and CF_2^+ with SF_6 . Exothermicity alone is not sufficient to predict the outcome of these ‘chemical’ ion-molecule reactions.

Most of the reactions of SF_5CF_3 lead to the formation of CF_3^+ as one of the ion products. Reaction scheme (19) is the most likely pathway. Whenever (19) is exothermic or close to thermoneutral, CF_3^+ is detected. Cl^+ and F^+ were not observed from the reactions of SF_5Cl and SF_6 with CF_m^+ and SF_n^+ . This is due to the high ionisation energies of Cl and F, compared to CF_3 , making all pathways to Cl^+ and F^+ endothermic.

The transfer of F^- to the reagent ion to form SF_4X^+ was observed whenever this pathway is exothermic. The occurrence of this reaction for particular reagent ion/neutral reactant combinations then depends on the difference between the fluoride affinity of the reagent ion and of SF_4X^+ . Using our bounds for $\Delta_r H_0^\circ(\text{SF}_4\text{CF}_3^+)$, the fluoride affinity of SF_4CF_3^+ lies between 1074 and 1201 kJ mol^{-1} , which is greater than for SF_5^+ (1040 kJ mol^{-1}) and SF_4Cl^+ (884 kJ mol^{-1}). This is reflected in the observation that the ion product of F^- transfer is seen for many of the reactions of SF_5Cl , and for the reactions of SF_6 with each of the CF_n^+ reagent ions. In contrast, SF_4CF_3^+ was seen only as a trace product from the reaction of SF_5CF_3 with CF_2^+ . F atom transfer may occur in the reaction of CF_2^+ with SF_5CF_3 , but the observed CF_3^+ product may result from a number of other pathways, including (19) and:



For SF_5CF_3 and SF_5Cl there is the possibility of transferring CF_3^- (Cl^-) and CF_3 (Cl) in addition to F^- and F. Compared

to the other CF_m^+ and SF_n^+ reagent ions, CF_2^+ is expected to have the highest affinity for CF_3 and Cl. The only example of transfer of a Cl atom is the reaction of CF_2^+ with SF_5Cl , where it is highly exothermic (see Table 2). The reaction is facilitated by the relatively low $\text{SF}_5\text{--Cl}$ bond strength ($D_0(\text{SF}_5\text{--Cl}) = 268 \text{ kJ mol}^{-1}$, compared to $D_0(\text{SF}_5\text{--CF}_3) = 374 \text{ kJ mol}^{-1}$, and $D_0(\text{SF}_5\text{--F}) = 447 \text{ kJ mol}^{-1}$). Using $\Delta_r H_0^\circ(\text{CF}_3\text{CF}_2^+) = 14 \text{ kJ mol}^{-1}$,⁴⁷ the transfer of CF_3 from SF_5CF_3 to CF_2^+ is calculated to be exothermic ($\Delta_r H_0^\circ = -60 \text{ kJ mol}^{-1}$), but CF_3CF_2^+ was not observed. Transfer of CF_3^- (Cl^-) leads to the formation of SF_5^+ . SF_5^+ was detected as an ion product from a number of reactions, and in each case the CF_3^- (Cl^-) transfer pathway is calculated to be exothermic (for CF^+ reacting with SF_5CF_3 a rearrangement of the neutral product is required).

The only reactions which do not fall into the above categories are those of CF^+ with SF_5Cl ($\rightarrow \text{CF}_2\text{Cl}^+$), and SF_6 ($\rightarrow \text{CF}_3^+$). For SF_5CF_3 , the CF_3^+ product can result from reaction scheme (19), but a very different mechanism must operate for SF_5Cl and SF_6 . An exothermic route to CF_2Cl^+ and CF_3^+ , respectively, is obtained by transferring Cl + F and F + F, respectively, (mechanism (46) for SF_5Cl , and (57) for SF_6) to the reagent CF^+ . This mechanism might also be operative for SF_5CF_3 , in which case the neutral product would be $\text{SF}_3\text{--CF}_3$. The suggestion that the production of CF_3^+ from SF_5CF_3 occurs by a different mechanism from the formation of CF_2Cl^+ from SF_5Cl , and CF_3^+ from SF_6 , is supported by the very different product ion yields (47% CF_3^+ (SF_5CF_3), 3% CF_2Cl^+ (SF_5Cl), and 5% CF_3^+ (SF_6)).

The major ion products of the reactions with CF_m^+ and SF_n^+ are formed through mechanisms that commence with the abstraction of F^- (Cl^- in the case of the reactions of SF_5Cl which form SF_5^+). Fig. 2 shows how the efficiencies of the reactions vary with the F^- affinity of the reagent ion. In addition to the anticipated general increase in overall efficiency with F^- affinity, it is observed that for each of the reagent ions the efficiencies are in the sequence $\text{SF}_5\text{Cl} > \text{SF}_5\text{CF}_3 > \text{SF}_6$. This does not follow the order of the energies needed for F^- abstraction from the molecules ($\text{SF}_5\text{Cl} < \text{SF}_6 < \text{SF}_5\text{CF}_3$), which provides further evidence of mechanistic differences for the reactions of SF_5CF_3 compared to those of SF_5Cl and SF_6 . The reaction of SF^+ with SF_5Cl has an unexpectedly high efficiency (0.67 for SF_5Cl , compared to 0.025 for SF_5CF_3). As discussed earlier, on the basis of the observed ion products, this reaction proceeds primarily by Cl^- rather than F^- abstraction. The trends between CF^+ , CF_2^+ , and CF_3^+ are the same for each of the reactant molecules, with CF_3^+ in each case having a significantly lower reaction efficiency than both CF^+ and CF_2^+ , even though the F^- affinity of CF_3^+ is greater than that of CF^+ . This is suggestive of some steric factor impeding the reaction of the relatively bulky CF_3^+ to a greater extent than for CF^+ and CF_2^+ .

4. Conclusions

Rate coefficients and product ion distributions are reported for the reactions of twenty-two atomic and molecular reagent cations with two derivatives of SF_6 ; SF_5CF_3 and SF_5Cl . The reagent ions have a wide range of recombination energies, so that both charge transfer and chemical ion-molecule reactions are observed. Most of the reactions proceed with rate coefficients close to the predictions of capture theories. There are notable exceptions to this, as can be seen by inspecting the data in Tables 1 to 3. A variety of reaction processes are evident, including dissociative charge transfer and various abstraction routes. SF_5X^+ ($\text{X} = \text{F}, \text{Cl}, \text{CF}_3$) ions were not observed as products of any of the reactions. Although there may well be bound regions on the potential energy surfaces of the parent ions, these are not accessed in charge-transfer reactions. Instead, as seen in studies of the photoionisation of SF_5X ,

the initially formed SF_5X^+ ions dissociate very rapidly over repulsive energy surfaces.

The observed ion products show that the reactions of SF_5CF_3 are quite different from those of SF_5Cl and SF_6 . The major products from the charge-transfer reactions of reagent ions A^+ with SF_5CF_3 are SF_3^+ ($+\text{CF}_4 + \text{F} + \text{A}$) and CF_3^+ ($+\text{SF}_5 + \text{A}$), while SF_5^+ ($+\text{Cl} + \text{A}$) and SF_4Cl^+ ($+\text{F} + \text{A}$) are formed from SF_5Cl , and SF_5^+ ($+\text{F} + \text{A}$) from SF_6 . These differences can be traced to the thermochemistry of the reactions, the energies of the dissociative ionisation pathways are shown in Figs. 1, 3, and 6. The high dissociation energy of $\text{CF}_3\text{--F}$ (374 kJ mol^{-1}) compared to F--Cl (247 kJ mol^{-1}) and F--F (154 kJ mol^{-1}) accounts for the appearance of SF_3^+ from SF_5CF_3 . The low ionisation energy of CF_3 (9.04 eV) compared to SF_5 (9.52 eV), Cl (12.97 eV), and F (17.42 eV) is responsible for the formation of CF_3^+ and little SF_5^+ from SF_5CF_3 , while the ion products from SF_5Cl are SF_5^+ and SF_4Cl^+ , and SF_5^+ from SF_6 . These energetic factors also influence the products of chemical ion-molecule reactions of the molecules. Thus the major ion products from SF_5CF_3 are again SF_3^+ and CF_3^+ , SF_5Cl produces mainly SF_5^+ and SF_4Cl^+ , and SF_6 yields SF_5^+ .

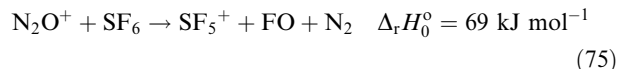
The charge-transfer reactions generally conform well to the expectations of models of long-range charge-transfer processes. However, it was noted that some of the reactions of SF_5CF_3 , specifically those with N^+ , CO^+ , CO_2^+ , O^+ , and N_2O^+ , produced more SF_3^+ than expected on the basis of TPEPICO experiments on the fragmentation of isolated energy selected (SF_5CF_3^+)*. Also the wide variations in the $\text{SF}_4\text{Cl}^+/\text{SF}_5^+$ ratio with the recombination energy of the reagent ion are not compatible with other data on the ionisation of SF_5Cl . There is thus evidence that short-range interactions can influence the outcome of fast charge-transfer reactions.

F^- abstraction and processes in which F^- abstraction is coupled to other chemical transformations dominate the reactions of ions such as CF_m^+ and SF_n^+ , which have recombination energies below the lowest dissociative ionisation limits of SF_5CF_3 , SF_5Cl , and SF_6 . Many of these reactions have rate coefficients below those predicted by capture theories, the efficiencies generally do correlate with the fluoride affinity of the reagent ion. Lower than expected efficiencies for the reactions of CF_3^+ , when compared against CF^+ and CF_2^+ , may be indicative of steric factors associated with the relatively bulky CF_3^+ reagent ion. As for the charge-transfer reactions, the ion products show that SF_5CF_3 reacts by pathways that are mechanistically distinct from the routes followed by SF_5Cl and SF_6 . For SF_5CF_3 the major products from the chemical reaction with A^+ are CF_3^+ ($+\text{SF}_4 + \text{AF}$) and SF_3^+ ($+\text{CF}_4 + \text{AF}$), SF_5Cl forms SF_5^+ ($+\text{Cl}$) and SF_4Cl^+ ($+\text{F}$), and SF_6 yields SF_5^+ ($+\text{F}$). These differences are again attributed to the energetics - the low ionisation potential of CF_3 , and the high $\text{CF}_3\text{--F}$ bond dissociation energy are major factors.

We have chosen to base our thermochemical analysis of the reactions on enthalpies of formation for CF_m^+ and SF_n^+ taken from recent *ab initio* calculations.^{24,25} This immediately impacts on the enthalpies of formation of SF_5CF_3 and SF_5Cl , which can be derived from appearance energies of $\text{SF}_5 + \text{CF}_3^+$ and $\text{SF}_5^+ + \text{Cl}$, respectively, obtained from photoionisation experiments.^{10,30} We have adopted $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673 \text{ kJ mol}^{-1}$ and $\Delta_f H_0^\circ(\text{SF}_5\text{Cl}) \geq -985 \text{ kJ mol}^{-1}$.

Central to our analysis of the results is the exothermicity criterion, that for a particular ion product to be observed in a SIFT study of a reaction, there must be a pathway that is exothermic, or at least close to thermoneutral. Use of this criterion has allowed us to propose values for the enthalpies of formation of some of the product ions, these include: $-348 \text{ kJ mol}^{-1} < \Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) < -221 \text{ kJ mol}^{-1}$, and $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}^+) = 150 \text{ kJ mol}^{-1}$. Values for a number of SF_pCl^+ ions were suggested by comparisons with SF_{p+1}^+ ions,

and shown to be consistent with the observation of SF_pCl^+ from some of the reactions of SF_5Cl . These include: $\Delta_f H_0^\circ(\text{SFCl}^+) = 782 \text{ kJ mol}^{-1}$, and $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+) = 453 \text{ kJ mol}^{-1}$. Other estimated values are $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+) = 321 \text{ kJ mol}^{-1}$, and $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}) = -761 \text{ kJ mol}^{-1}$. With one exception there are no observed reactions for which, allowing for uncertainties in the values of the enthalpies of formation, the enthalpy of reaction is greater than $+20 \text{ kJ mol}^{-1}$. The one exception is the slow reaction between N_2O^+ and SF_6 , to form SF_5^+ . The least endothermic pathway to SF_5^+ is:



but, as calculated, this is too endothermic to account for the formation of SF_5^+ . It is unlikely that the weak binding between FO--N_2 can be sufficiently strong to make the reactions proceed with a high enough rate coefficient to be observable by the SIFT technique at 300 K . Thus the observation of SF_5^+ from the reaction of SF_6 with N_2O^+ suggests that $\Delta_f H_0^\circ(\text{SF}_5^+) = 84 \text{ kJ mol}^{-125}$ is too high. The experimental data on SF_5Cl may also point to a problem with $\Delta_f H_0^\circ(\text{SF}_5^+)$. If the observed appearance energy of 12.32 eV for the dissociative photoionisation (28)³⁰ is combined with $\Delta_f H_0^\circ(\text{SF}_5\text{Cl}) = -1026 \text{ kJ mol}^{-1,27}$ obtained from calorimetric measurements,²⁸ then $\Delta_f H_0^\circ(\text{SF}_5^+) \leq 43 \text{ kJ mol}^{-1}$. Chim *et al.*¹⁰ have sought to determine the dissociative ionisation energy of SF_6 ($\rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$) by extrapolation of TPEPICO data to zero kinetic energy release. From a rather long extrapolation they determined the dissociative ionisation energy to be $13.6 (\pm 0.1) \text{ eV}$, when combined with standard literature values for $\Delta_f H_0^\circ(\text{SF}_6)$ and $\Delta_f H_0^\circ(\text{F})$ ²⁷ this result gives $\Delta_f H_0^\circ(\text{SF}_5^+) = 28 \text{ kJ mol}^{-1}$. $\Delta_f H_0^\circ(\text{SF}_5^+) = 84 \text{ kJ mol}^{-125}$ is strongly supported by other theoretical calculations.^{48,49} Irikura⁵⁰ has proposed that $\Delta G^\circ (= \Delta H^\circ - T\Delta S^\circ)$ rather than ΔH_0° might be used to predict the spontaneity (observation) of gas-phase ion-molecule reactions. This introduces entropic factors, which we have ignored in our analysis of the thermodynamics of the reactions. For reactions in which there is an increase in the number of molecules (*e.g.* (75)), $\Delta S^\circ > 0$, making $\Delta G^\circ < \Delta H^\circ$, so that if $\Delta G^\circ < 0$ is the criterion, then endothermic reactions may become observable. For the two reactions $\Delta S_{298}^\circ(75) = 180.76 \text{ J K}^{-1} \text{ mol}^{-1,27}$ neglecting the small temperature dependence of ΔH° , $\Delta G_{298}^\circ(75) = 15 \text{ kJ mol}^{-1}$, suggesting that SF_5^+ might be produced by reaction (75), and that the reaction would have a low efficiency. However, for reactions in which there is a change in the number of molecules, both ΔS and ΔG change with the partial pressures of the reactants and products. It is then not clear that ΔG_{298}° will be the correct quantity from which to predict whether a particular ion-molecule reaction will be observable using the SIFT technique.

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