

# A study of the reactions of trifluoromethyl sulfur pentafluoride, $\text{SF}_5\text{CF}_3$ , with several positive ions of atmospheric interest

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An investigation of the bimolecular reactions of several positive ions of atmospheric interest,  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{O}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$ , with the greenhouse gas  $\text{SF}_5\text{CF}_3$  is reported. The thermal rate coefficients and ion product distributions have been determined at 300 K using a selected ion flow tube.  $\text{H}_3\text{O}^+$ ,  $\text{NO}_2^+$  and  $\text{NO}^+$  are found to be unreactive. The reaction with  $\text{O}_2^+$  proceeds with a rate coefficient significantly less than the capture value *via* chemical routes, in which bonds are broken and formed. The other reagent ions,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$  react with  $\text{SF}_5\text{CF}_3$  with reaction rate coefficients close to or at the capture values. With the exception of the reaction with  $\text{H}_2\text{O}^+$ , all these efficient reactions occur by dissociative charge transfer, with  $\text{CF}_3^+$  and  $\text{SF}_3^+$  being the dominant product ions.  $\text{CF}_3^+$  forms by direct cleavage of the S–C bond in  $\text{SF}_5\text{CF}_3^+$ , and  $\text{SF}_3^+$  probably from dissociation of  $(\text{SF}_4^+)^*$  following intramolecular rearrangement within the lifetime of  $(\text{SF}_5\text{CF}_3^+)^*$ . For  $\text{H}_2\text{O}^+$ , the observed ion branching ratios suggest that the reaction proceeds *via* a chemical pathway. The reactions of  $\text{SF}_5\text{CF}_3$  with cations will destroy this molecule in the upper atmosphere.

## 1. Introduction

The recent detection of a new atmospheric trace gas in the stratosphere with a very high global warming potential, trifluoromethyl sulfur pentafluoride ( $\text{SF}_5\text{CF}_3$ ),<sup>1</sup> has resulted in a number of studies investigating its photoionisation<sup>2</sup> and electron attachment properties.<sup>3</sup> From the results of the photoionisation study, it has been deduced that the  $\text{SF}_5\text{CF}_3$  bond dissociation energy is  $4.1 \pm 0.5$  eV. On the basis of this value, it has been asserted that  $\text{SF}_5\text{CF}_3$  will not be broken down by UV photodissociation in the stratosphere.<sup>2</sup> This conclusion is supported by the height profile of  $\text{SF}_5\text{CF}_3$  through the stratosphere.<sup>1</sup> This leads to the question as to whether there are any reaction processes in the stratosphere or the ionosphere which could provide an atmospheric loss mechanism for  $\text{SF}_5\text{CF}_3$ . The electron attachment study shows that the molecule will be destroyed in the regions of the ionosphere where free electrons exist, providing an upper limit to the atmospheric lifetime of  $\text{SF}_5\text{CF}_3$  of *ca.* 1000 years.<sup>3</sup> Other competitive routes in the ionosphere leading to the possible destruction of  $\text{SF}_5\text{CF}_3$  are reactions with ions. Here we report the first gas-phase study of the reactions of  $\text{SF}_5\text{CF}_3$  with several positive ions found in the ionosphere, specifically (in order of increasing recombination energy)  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{O}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$ . This information provides details on the atmospheric fate of  $\text{SF}_5\text{CF}_3$ .

Whilst the major stimulus for this study comes from its application to the atmospheric ion chemistry of  $\text{SF}_5\text{CF}_3$ , the ion chemistry of a derivative of  $\text{SF}_6$  is also of interest.  $\text{SF}_6$  is used in reactive plasmas.<sup>4</sup> The rates and products of reactions in plasmas containing  $\text{SF}_6$  are either not known or are poorly

understood. Studies of the reactions of ions with  $\text{SF}_6$  and its derivatives can contribute towards a better understanding of the complex chemistry occurring in plasmas used for industrial purposes.

## 2. Experimental

A selected ion flow tube (SIFT) was used to measure rate coefficients and product ion branching ratios of the reactions. The SIFT apparatus and its mode of operation have been described in detail previously.<sup>5,6</sup> In brief, the reagent ions were generated in an electron impact high-pressure ion source containing an appropriate gas ( $\text{N}_2$  for  $\text{N}_2^+$  and  $\text{N}^+$ ,  $\text{CO}$  for  $\text{CO}^+$ ,  $\text{CO}_2$  for  $\text{CO}_2^+$ ,  $\text{N}_2\text{O}$  for  $\text{N}_2\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}^+$ ,  $\text{H}_2\text{O}$  for  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$ ,  $\text{O}_2$  for  $\text{O}_2^+$ , and  $\text{NO}_2$  for  $\text{NO}_2^+$ ). The reagent ions were mass selected using a quadrupole mass filter, injected into a 300 K helium carrier gas at a pressure of *ca.* 0.5 Torr, transported along the flow tube and detected by a downstream quadrupole mass spectrometer detection system.  $\text{SF}_5\text{CF}_3$  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. Owing to uncertainties in the flow dynamics the reaction rate coefficients are considered to have an uncertainty of  $\pm 20\%$ . Relaxed resolution on the quadrupole mass spectrometer was used to determine the branching ratios in order to minimize mass discrimination effects. Ion product distributions were then determined by extrapolating ion production distributions to zero neutral reactant flow rate.<sup>5–7</sup> The branching ratios are only used to provide a qualitative indication of the important ion 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 difficult, as confirmed by studies on the  $\text{O}_2^+$  reagent ion. Whilst the majority of these ions were found to be in the  $v = 0$  level, approximately 30% were found to be in the  $v = 1$  and 2 vibrational levels. Similarly, for the  $\text{N}_2^+$  reagent ions  $\sim 40\%$  were found to be in the  $v = 1$  vibrational level. It is possible that other reagent molecular ions may have internal energies above thermal. That no curvature was observed in any of the pseudo-first-order kinetic plots, indicates that rate coefficients are the same for reactions involving the ground and any vibrationally excited states. However, note that the product ion branching ratios may be affected by the presence of internally excited ions. For the two atomic ions

used in this investigation,  $\text{N}^+$  and  $\text{O}^+$ , electronically excited states have previously been shown not to be present.<sup>8</sup>

Water contamination in the flow tube and He buffer gas flow resulted in electron transfer from  $\text{H}_2\text{O}$  to those injected ions whose recombination energies are greater than the ionisation potential of  $\text{H}_2\text{O}$ , 12.61 eV. This resulted in an  $\text{H}_2\text{O}^+$  signal, which was usually less than 10% of the parent ion signal. Product ion branching ratios have been corrected for the contribution to the signals resulting from the reaction of  $\text{SF}_5\text{CF}_3$  with  $\text{H}_2\text{O}^+$ . Some of the  $\text{H}_2\text{O}^+$  was converted to  $\text{H}_3\text{O}^+$  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  $\text{H}_3\text{O}^+$  is unreactive with  $\text{SF}_5\text{CF}_3$ . A separate problem encountered during experiments with  $\text{H}_2\text{O}^+$  as the reagent ion was that  $\text{OH}^+$  and  $\text{H}_3\text{O}^+$  were being injected into the flow tube together with  $\text{H}_2\text{O}^+$ . Again, because the  $\text{H}_3\text{O}^+$  ions are unreactive with  $\text{SF}_5\text{CF}_3$ , their presence in the flow tube could be ignored. However,  $\text{OH}^+$  was found to react efficiently with  $\text{SF}_5\text{CF}_3$ . Reduction of the injection ion energy, which insured that the  $\text{OH}^+$  was not produced by collision-induced dissociation, did not remove the problem. Attempts to eliminate the  $\text{OH}^+$  signal by increasing the resolution of the injection mass spectrometer drastically reduced the  $\text{H}_2\text{O}^+$  signal. The best compromise

between  $\text{OH}^+$  rejection and  $\text{H}_2\text{O}^+$  signal gave a reactant ion flux comprising 95%  $\text{H}_2\text{O}^+$  and 5%  $\text{OH}^+$ . No allowances have been made for the (small) contributions due to the  $\text{OH}^+$  reaction to the branching ratios for the reaction of  $\text{H}_2\text{O}^+$  with  $\text{SF}_5\text{CF}_3$ .

The sample of  $\text{SF}_5\text{CF}_3$  was purchased (Apollo Scientific Limited) with a stated purity of 99%, and was used without further purification.

### 3. Results and discussion

The experimental reaction rate coefficients,  $k_{\text{exp}}$ , the product ions, and their branching ratios are given in Table 1.  $\text{NO}_2^+$ ,  $\text{NO}^+$  and  $\text{H}_3\text{O}^+$ , whose recombination energies are 9.75 eV, 9.26 eV and 6.37 eV, respectively, do not react with  $\text{SF}_5\text{CF}_3$ , and hence are not included in Table 1. In order to assess the efficiency of the reactions, the experimental rate coefficients are compared with the predictions of capture theory. Essential information for capture theory are the polarisability and the dipole moment of  $\text{SF}_5\text{CF}_3$ . Neither of these quantities are available in the literature. The polarisability is estimated to be  $8.4 \times 10^{-30} \text{ m}^3$  using the empirical approach of Miller and Savchik.<sup>9</sup> Assuming that the dipole moment is zero, the

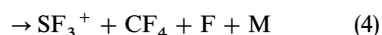
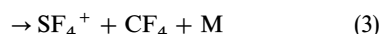
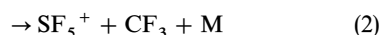
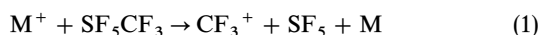
**Table 1** The measured 300 K reaction rate coefficients (in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ),  $k_{\text{exp}}$ , and cation product ions and their branching ratios (percentage) for the reactions of  $\text{O}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$  with  $\text{SF}_5\text{CF}_3$ . The recombination energies of the reagent cations are listed in eV in brackets under the cations. The capture rate coefficients, calculated using Langevin theory,<sup>10</sup> are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to  $\pm 20\%$ . The trace given for the  $\text{SF}_4^+$  product ion represents a detectable signal with our apparatus, but whose branching ratio is less than 1%. The reaction channel is assumed to be dissociative charge transfer, and the 0 K enthalpies of reaction for these channels are presented. Alternative chemical routes are discussed in the text for those dissociative charge transfer pathways which are endothermic. For the formation of the ions products  $\text{SF}_3^+$  and  $\text{SF}_4^+$ , two values for the 0 K enthalpy of reaction are given. The first value is calculated using the data set of Fisher *et al.*<sup>12</sup> whereas the second corresponds to that of Irikura.<sup>13</sup> The two values given for the 0 K enthalpy of reaction for the formation of  $\text{SF}_5^+$  by dissociative charge transfer result from taking the adiabatic ionisation potential of  $\text{SF}_5$  to be either 9.60 eV (Fisher *et al.*<sup>12</sup>) or 9.71 eV (Irikura<sup>13</sup>)

Reagent ion	Rate coefficient / $10^{-9} \text{ cm}^3 \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_r H_0^\circ$ /kJ mol <sup>-1</sup>
$\text{N}_2^+$ (15.58)	1.6 [1.4]	$\text{CF}_3^+$ (65) $\text{SF}_3^+$ (28) $\text{SF}_4^+$ (trace) $\text{SF}_4^+\text{CF}_3$ (2) $\text{SF}_5^+$ (5)	$\text{SF}_5 + \text{N}_2$ $\text{CF}_4 + \text{F} + \text{N}_2$ $\text{CF}_4 + \text{N}_2$ $\text{F} + \text{N}_2$ $\text{CF}_3 + \text{N}_2$	-258 -248, -289 -283, -345 — <sup>a</sup> -185, -175
$\text{N}^+$ (14.53)	2.2 [1.9]	$\text{CF}_3^+$ (80) $\text{SF}_3^+$ (17) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (3)	$\text{SF}_5 + \text{N}$ $\text{CF}_4 + \text{F} + \text{N}$ $\text{CF}_4 + \text{N}$ $\text{CF}_3 + \text{N}$	-157 -147, -187 -181, -243 -84, -73
$\text{CO}^+$ (14.01)	1.6 [1.4]	$\text{CF}_3^+$ (75) $\text{SF}_3^+$ (22) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (3)	$\text{SF}_5 + \text{CO}$ $\text{CF}_4 + \text{F} + \text{CO}$ $\text{CF}_4 + \text{CO}$ $\text{CF}_3 + \text{CO}$	-107 -96, -137 -131, -193 -34(±43), -23(±46)
$\text{CO}_2^+$ (13.77)	1.2 [1.1]	$\text{CF}_3^+$ (76) $\text{SF}_3^+$ (14) $\text{SF}_4^+$ (8) $\text{SF}_5^+$ (2)	$\text{SF}_5 + \text{CO}_2$ $\text{CF}_4 + \text{F} + \text{CO}_2$ $\text{CF}_4 + \text{CO}_2$ $\text{CF}_3 + \text{CO}_2$	-84 -73, -114 -108, -170 -11(±43), 0(±46)
$\text{O}^+$ (13.62)	1.9 [1.8]	$\text{CF}_3^+$ (83) $\text{SF}_3^+$ (16) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (1)	$\text{SF}_5 + \text{O}$ $\text{CF}_4 + \text{F} + \text{O}$ $\text{CF}_4 + \text{O}$ $\text{CF}_3 + \text{O}$	-69 -59, -100 -93, -156 4(±43), 14(±46)
$\text{N}_2\text{O}^+$ (12.89)	1.1 [1.1]	$\text{CF}_3^+$ (75) $\text{SF}_3^+$ (19) $\text{SF}_4^+$ (5) $\text{SF}_5^+$ (1)	$\text{SF}_5 + \text{N}_2\text{O}$ $\text{CF}_4 + \text{F} + \text{N}_2\text{O}$ $\text{CF}_4 + \text{N}_2\text{O}$ $\text{CF}_3 + \text{N}_2\text{O}$	1(±39) 12(±45), -29(±47) -23(±45), -85 74, 84
$\text{H}_2\text{O}^+$ (12.61)	1.6 [1.7]	$\text{CF}_3^+$ (8) $\text{SF}_3^+$ (92) $\text{SF}_4^+$ (trace)	$\text{SF}_5 + \text{H}_2\text{O}$ $\text{CF}_4 + \text{F} + \text{H}_2\text{O}$ $\text{CF}_4 + \text{H}_2\text{O}$	28(±39) 39(±45), -2(±47) 4(±45), -58
$\text{O}_2^+$ (12.07)	0.01 [1.3]	$\text{CF}_3^+$ (63) $\text{SF}_3^+$ (31) $\text{SF}_4^+$ (2) $\text{SF}_5^+$ (4)	$\text{SF}_5 + \text{O}_2$ $\text{CF}_4 + \text{F} + \text{O}_2$ $\text{CF}_4 + \text{O}_2$ $\text{CF}_3 + \text{O}_2$	80, 62, 43(±39) <sup>b</sup> 91, 50(±47) 56, -6(±46) 153, 164

<sup>a</sup>  $\Delta_r H_0^\circ(\text{SF}_4^+\text{CF}_3)$  is unknown. <sup>b</sup> The values given are for the  $v = 0, 1$  and 2 vibrational levels of  $\text{O}_2^+$ , respectively.

capture rate coefficient can be calculated using the Langevin equation.<sup>10</sup> The results of these calculations are the values for  $k_L$  presented in Table 1. The presence of a dipole moment will increase the capture rate coefficient. The effect can be estimated by using the results of parametrized fits to trajectory calculations.<sup>11</sup> For example, for the reaction of  $N^+$  with  $SF_5CF_3$ , a value for the dipole moment of 1 Debye would increase the capture rate coefficient from  $1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  to  $2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .† A comparison of the experimental rate coefficients with the Langevin values will nevertheless provide a good indication of whether a reaction is efficient, with most captures leading to reaction, or inefficient.

The determination of reaction pathways requires knowledge of the ion and neutral products. In our experiments, only the masses and relative intensities of the ion products are determined, so the neutral product(s) can only be inferred from mass balance and thermochemical arguments. The thermochemical analysis is restricted to considerations of enthalpy, and we have ignored any entropic effects. As discussed below, the majority of the reactions are presumed to proceed through dissociative charge transfer, and Table 1 contains the 0 K enthalpies for this reaction channel for all the product ions. The 0 K enthalpies of the dissociative charge transfer routes have been calculated using the dissociative ionisation energy (DIE) for  $SF_5CF_3 \rightarrow CF_3^+ + SF_5 + e^-$  of  $12.9 \pm 0.4 \text{ eV}$  determined from the TPEPICO study,<sup>2</sup> the adiabatic ionisation potentials (IP) for  $SF_5$  and  $CF_3$ , and the bond dissociation energies (BDE) for  $(SF_4^+ - F)$ ,  $(SF_3^+ - F)$  and  $(CF_3 - F)$ . Thus, if  $RE(M^+)$  represents the recombination energy of the reagent ion  $M^+$ , the enthalpies of reaction for the various dissociative charge transfer channels are determined as follows:



The enthalpies of these reactions are, respectively, given by

$$\Delta_r H_0^\circ(1) = \text{DIE} - RE(M^+)$$

$$\Delta_r H_0^\circ(2) = \Delta_r H_0^\circ(1) + IP(SF_5) - IP(CF_3),$$

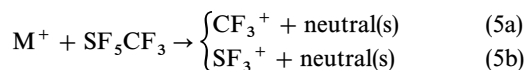
$$\Delta_r H_0^\circ(3) = \Delta_r H_0^\circ(2) + BDE(SF_4^+ - F) - BDE(CF_3 - F)$$

$$\Delta_r H_0^\circ(4) = \Delta_r H_0^\circ(3) + BDE(SF_3^+ - F)$$

There has been some controversy in the literature with regard to the values of  $IP(SF_5)$  and  $IP(CF_3)$ . The value we have adopted for  $IP(CF_3)$ ,  $8.84 \pm 0.20 \text{ eV}$ , comes from the recent TPEPICO study.<sup>2</sup> For  $IP(SF_5)$ ,  $BDE(SF_4^+ - F)$  and  $BDE(SF_3^+ - F)$ , two sets of values have been used. One set is from the experimental guided ion beam study of Fisher *et al.* who report  $IP(SF_5) = 9.60 \pm 0.05 \text{ eV}$ ,  $BDE(SF_4^+ - F) = 444 \pm 10 \text{ kJ mol}^{-1}$  and  $BDE(SF_3^+ - F) = 35 \pm 5 \text{ kJ mol}^{-1}$ .<sup>12</sup> The other set is from the theoretical study reported by Irikura, with values of  $IP(SF_5) = 9.71 \pm 0.16 \text{ eV}$ ,  $BDE(SF_4^+ - F) = 371 \pm 6 \text{ kJ mol}^{-1}$  and  $BDE(SF_3^+ - F) = 56 \pm 6 \text{ kJ mol}^{-1}$ .<sup>13</sup> The bond dissociation energy of  $CF_3 - F$  is taken to be  $541 \pm 4 \text{ kJ mol}^{-1}$ .<sup>14</sup> We note that the error in the values of  $\Delta_r H_0^\circ$  for the four product channels (1)–(4) is dominated by the uncertainty in the value of the DIE of  $SF_5CF_3$  to  $CF_3^+ + SF_5 + e^-$ , namely  $0.4 \text{ eV}$  or  $39 \text{ kJ mol}^{-1}$ .

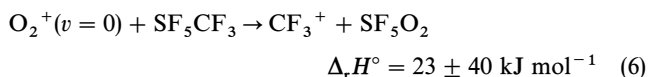
Dissociative charge transfer is endothermic for a number of reaction channels presented in Table 1. When this is the case, alternative chemical routes, in which bonds are broken and formed, are suggested and discussed below. For these chemical routes, enthalpies of formation at 0 K ( $\Delta_f H_0^\circ$ ) for the neutral fragments are generally well-established.<sup>15</sup> In the few cases where values were not available from the JANAF tables, we have made use of the enthalpies of formation at 298 K from the compilation by Lias *et al.*,<sup>16</sup> supplemented by thermochemical information from various other sources, as noted below.

As mentioned above, of the reagent ions used in this study,  $H_3O^+$ ,  $NO^+$  and  $NO_2^+$  are found to be unreactive with  $SF_5CF_3$ . The reactions of the other ions with  $SF_5CF_3$  are similar; namely, the reactions are efficient ( $k_{\text{exp}} \approx k_L$ ) and  $CF_3^+$  and  $SF_3^+$  are the dominant product ions:



With the exception of  $H_2O^+$ ,  $SF_4^+$  and  $SF_5^+$  product ions are also observed for all the reactions. No  $SF_2^+$ , whose mass is only 1 u greater than that of  $CF_3^+$ , and which energetically is an allowed product ion for a number of reagent ions, was observed.

Dissociative charge transfer is an exothermic mechanism for reactions (5a), for  $M = O$ ,  $CO_2$ ,  $CO$ ,  $N$  or  $N_2$  (see Table 1). For reactions with  $M = H_2O$  and  $N_2O$ , the errors on the enthalpies of the reactions are sufficiently large that dissociative charge transfer leading to  $CF_3^+$  could be either endothermic or exothermic. Chemical pathways leading to the observed  $CF_3^+$  product ion cannot be ruled out for these two reactions. However, as discussed below, the  $CF_3^+$  and  $SF_3^+$  branching ratios associated with the  $N_2O^+$  reaction, 75% and 19% respectively, imply that long-range dissociative charge transfer has taken place.  $CF_3^+$  is also an observed product for the reaction with  $O_2^+$ , with a high branching ratio (63%). This indicates that  $CF_3^+$  can be produced from a reaction of  $SF_5CF_3$  with  $O_2^+$  in any of its vibrational states ( $v = 0, 1$  or  $2$ ). In agreement with this, the pseudo-first-order plots of  $\ln(O_2^+ \text{ counts})$  vs.  $SF_5CF_3$  concentration show no curvature. For the reaction with  $O_2^+$ , the reaction enthalpies for the dissociative charge transfer channel leading to  $CF_3^+$  ( $+SF_5 + O_2$ ) are  $\Delta_r H_0^\circ = 80, 62$  and  $43 \text{ kJ mol}^{-1}$ , for  $O_2^+ v = 0, 1$  and  $2$ , respectively, with an associated error of  $\pm 39 \text{ kJ mol}^{-1}$  in each value. Thus dissociative charge transfer is endothermic for this reaction. We conclude that the  $CF_3^+$  channel is the result of a chemical interaction in which bonds are broken and formed. The only possible route is one in which  $SF_5$  binds with  $O_2$ :

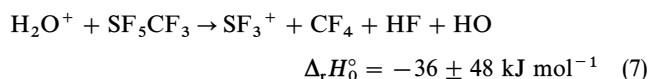


The enthalpy of this reaction was determined using a value for the 295 K  $BDE(SF_5 - O_2)$  of  $57 \pm 8 \text{ kJ mol}^{-1}$ .<sup>17</sup>

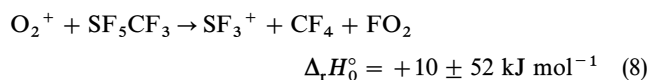
Dissociative charge transfer is exothermic for the reactions (5b), providing the neutral products are  $M$ ,  $CF_4$  and  $F$  for  $M = H_2O$ ,  $N_2O$ ,  $O$ ,  $CO_2$ ,  $CO$ ,  $N$  or  $N_2$ , respectively. There are other possible exothermic pathways leading to the formation of the ion products in reactions (5a) and (5b) which require the breaking and formation of bonds, many of which are more exothermic than those for dissociative charge transfer. For the reactant ions whose recombination energies are greater than  $12.8 \text{ eV}$ , the branching ratios are in excellent agreement with those obtained in the recent TPEPICO experiment.<sup>2</sup> This suggests that long-range dissociative charge transfer is the dominant mechanism for these reactions.<sup>18,19</sup> For  $H_2O^+$ , dissociative charge transfer leading to  $SF_3^+$  cannot be ruled out on energetic grounds, because of the substantial uncertainty in the dissociative ionisation energy of  $SF_5CF_3$  ( $\rightarrow SF_5 + CF_3^+ + e^-$ ). There is a dramatic change in the pattern of the product ion branching ratios for  $N_2O^+$  ( $RE = 12.89 \text{ eV}$ ) compared to  $H_2O^+$  ( $RE = 12.61 \text{ eV}$ ). For  $N_2O^+$  the major product ion is  $CF_3^+$  (75%), while the reaction with  $H_2O^+$  mainly generates  $SF_3^+$  (92%). This change in the reaction pathway correlates well with the observed (weak) onset of photoionisation of  $SF_5CF_3$  at  $12.9 \text{ eV}$ .<sup>2</sup> Reagent ions with recombination energies close to or greater than  $12.9 \text{ eV}$  are probably reacting efficiently by a (long-range) dissociative charge transfer mechanism. Ions whose recombination energies are less than  $12.9 \text{ eV}$  can only react with  $SF_5CF_3$  through a short-range mechanism, either by charge transfer (if energetically allowed) or by chemical reaction channels in which bonds are broken and formed. In particular,  $H_2O^+$  reacts

†  $1 \text{ D} \approx 3.33564 \times 10^{-30} \text{ C m}$ .

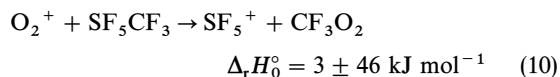
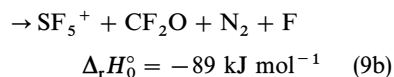
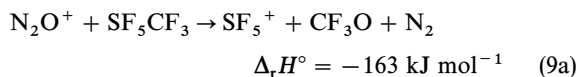
with  $\text{SF}_5\text{CF}_3$  via a close-range interaction in which a chemical pathway is likely to dominate. The only possibility is:



For  $\text{O}_2^+$  ( $v=0$ ) the production of  $\text{SF}_3^+$  by dissociative charge transfer is endothermic. The high branching ratio associated with  $\text{SF}_3^+$  (31%) indicates that all  $\text{O}_2^+$  ions ( $v=0$ , 1 and 2) can proceed down the pathway leading to this product ion. Hence we propose that an inefficient chemical pathway produces  $\text{SF}_3^+$ , with  $\text{CF}_4$  and  $\text{FO}_2$  as the neutral products:



The  $\text{SF}_4^+$  ion observed as a minor product for the reactions with  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$  probably results from dissociative charge transfer (see below).  $\text{SF}_4^+$  is also observed in the reaction with  $\text{O}_2^+$ . This appears not to be consistent with the experimental thermochemical data set of Fisher *et al.*<sup>12</sup> (unless  $\text{SF}_4^+$  is formed from vibrationally excited  $\text{O}_2^+$ ) and suggests that the theoretical data set of Irikura<sup>13</sup> may be the better set. However,  $\text{SF}_4^+$  is a minor product, so the observation of this ion does not provide a strong comparison of the two data sets. Chemical pathways are the only exothermic routes leading to  $\text{SF}_5^+$  for the reactions with  $\text{N}_2\text{O}^+$  and  $\text{O}_2^+$ :



To determine the  $\Delta_r H_{298}^\circ$  for reaction (9a) we have used a value of  $\Delta_r H_{298}^\circ(\text{CF}_3\text{O}) = -672 \text{ kJ mol}^{-1}$ , obtained from a G3 calculation by Haworth *et al.*<sup>20</sup> The enthalpy for reaction (10) has been determined using Fisher *et al.*'s value<sup>12</sup> for  $\text{IP}(\text{SF}_5)$  and a  $\text{BDE}(\text{CF}_3\text{--O}_2)$  of  $150 \pm 15 \text{ kJ mol}^{-1}$  presented in the study by Danis *et al.*<sup>21</sup> from a reinterpretation of the results of Antonik.<sup>22</sup> If Irikura's value<sup>13</sup> for  $\text{IP}(\text{SF}_5)$  is used, a value of  $\Delta_r H_0^\circ = 14 \pm 48 \text{ kJ mol}^{-1}$  for reaction (10) is obtained. For the other reagent ions ( $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$  and  $\text{N}_2^+$ ) with higher recombination energies, dissociative charge transfer leading to  $\text{SF}_5^+$  is exothermic.

Only the reaction with  $\text{N}_2^+$ , the ion with highest recombination energy in this study, resulted in a product ion not observed in any other reaction. This product ion has a mass of 177 u, and could be either  $\text{SF}_4\text{CF}_3^+$  or  $\text{SF}_5\text{CF}_2^+$  (or both). However, the S–F bond strength in  $\text{SF}_6$  is less than that of C–F in  $\text{CF}_4$ , and hence we propose that  $\text{SF}_4\text{CF}_3^+$  is the product ion. The enthalpy of formation of  $\text{SF}_4\text{CF}_3^+$  is not available in the literature, but its observation from the reaction:

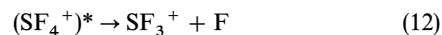


can be combined with  $\Delta_r H_0^\circ(\text{SF}_5\text{CF}_3) = -1770 \text{ kJ mol}^{-1}$  from the TPEPICO study,<sup>2</sup> to provide an upper limit;  $\Delta_r H_0^\circ(\text{SF}_4\text{CF}_3^+) < -318 \text{ kJ mol}^{-1}$ .

The formation of  $\text{CF}_3^+$  results from the cleavage of the S–C bond following charge transfer to  $\text{SF}_5\text{CF}_3$ . The minor product  $\text{SF}_5^+$  can also be formed by cleavage of the S–C bond. The energy difference between the lowest energy states of these two channels is equal to the difference in the ionisation potentials of  $\text{SF}_5$  and  $\text{CF}_3$ ,  $\text{IP}(\text{SF}_5) - \text{IP}(\text{CF}_3) = 0.76 \text{ eV}$ , Fisher *et al.*<sup>12</sup> or  $0.87 \text{ eV}$ , Irikura.<sup>13</sup> The relative ion product branching ratios for  $\text{CF}_3^+$  and  $\text{SF}_5^+$  are then seen to reflect the relative energies of the two channels. Nevertheless,

the small branching ratio associated with the  $\text{SF}_5^+$  ion for reactions of  $\text{SF}_5\text{CF}_3$  with the higher recombination energy ions (*e.g.*  $\text{N}_2^+$  and  $\text{N}^+$ ), is surprising and cannot readily be explained.

The route to  $\text{SF}_3^+$  is uncertain. Intramolecular rearrangement may occur within the lifetime of  $(\text{SF}_5\text{CF}_3^+)^*$ , involving  $\text{F}^-$  migration from  $\text{SF}_5$  to  $\text{CF}_3^+$  to form  $\text{SF}_4^+$  in an excited state and neutral  $\text{CF}_4$ . The decay of the excited  $\text{SF}_4^+$  is the suggested channel for the formation of  $\text{SF}_3^+$ :



## 4. Conclusions

This communication presents the first gas-phase study describing the reactions of small cations with  $\text{SF}_5\text{CF}_3$ . For reagent cations ( $\text{M}^+$ ) whose recombination energies are greater than or equal to  $12.9 \text{ eV}$ , the major ion product,  $\text{CF}_3^+$ , is a result of dissociative charge transfer leading to the cleavage of the S–C bond. The neutral products are inferred to be  $\text{SF}_5 + \text{M}$ . We propose that the other major ion product,  $\text{SF}_3^+$ , results from an intramolecular transfer, with  $\text{F}^-$  migrating to  $\text{CF}_3^+$  within the lifetime of the ion–molecule complex, forming  $\text{SF}_4^+$  in an excited state which has a high probability of decaying to  $\text{SF}_3^+$  and  $\text{F}$ . The neutral products of the reactions are then  $\text{CF}_4 + \text{F} + \text{M}$ .  $\text{H}_2\text{O}^+$  and  $\text{O}_2^+$  have recombination energies below  $12.9 \text{ eV}$ . Their reactions with  $\text{SF}_5\text{CF}_3$ , as revealed by the ion product branching ratios and thermochemical analysis, are different, and have been shown to involve chemical pathways.

The results presented demonstrate that ionospheric cations will react with and destroy  $\text{SF}_5\text{CF}_3$ . Therefore, such reactions will have to be taken into account in any modelling used to determine the atmospheric lifetime of  $\text{SF}_5\text{CF}_3$ . A more detailed study of the reactions of a large number of other cations of importance to industrial plasmas (*e.g.*  $\text{Ar}^+$ ,  $\text{F}^+$ ,  $\text{CF}^+$ ,  $\text{CF}_3^+$ ,  $\text{SF}_3^+$  and  $\text{SF}_5^+$ ) with  $\text{SF}_5\text{CF}_3$  and another derivative of  $\text{SF}_6$ ,  $\text{SF}_5\text{Cl}$ , will be reported soon.<sup>23</sup> We are also studying the reactions of small anions with both  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$  in the SIFT apparatus.

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## References

- W. T. Sturges, T. J. Wallington, M. D. Hurley, K. P. Shine, K. Sihra, A. Engel, D. E. Oram, S. A. Penkett, R. Mulvaney and C. A. M. Brenninkmeijer, *Science*, 2000, **289**, 611.
- R. Y. L. Chim, R. A. Kennedy, R. P. Tuckett, W. Zhou, G. K. Jarvis, D. J. Collins and P. A. Hatherly, *J. Phys. Chem. A*, submitted.
- R. A. Kennedy and C. A. Mayhew, *Int. J. Mass. Spectrom.*, 2001, **206**, vii.
- T. L. Williams, L. M. Babcock and N. G. Adams, *Int. J. Mass Spectrom.*, 1999, **185–188**, 759.
- N. G. Adams and D. Smith, in *Techniques for the Study of Ion–Molecule Reactions*, ed. J. M. Farrar and W. H. Saunders, Wiley, New York, 1988, pp. 165–220.
- D. Smith and N. G. Adams, *Adv. At. Mol. Phys.*, 1988, **24**, 1.
- D. Smith and N. G. Adams, *Int. J. Mass Spectrom. Ion Phys.*, 1976, **21**, 349.
- G. K. Jarvis, C. A. Mayhew and R. P. Tuckett, *J. Phys. Chem.*, 1996, **100**, 17166.
- K. J. Miller and J. A. Savchik, *J. Am. Chem. Soc.*, 1979, **101**, 7206.
- G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, 1958, **29**, 294.
- T. Su and W. J. Chesnavich, *J. Chem. Phys.*, 1982, **76**, 5183.
- E. R. Fisher, B. L. Kickel and P. B. Armentrout, *J. Chem. Phys.*, 1992, **97**, 4859.
- K. K. Irikura, *J. Chem. Phys.*, 1995, **102**, 5357.

- 14 R. L. Asher and B. Ruscic, *J. Chem. Phys.*, 1997, **106**, 201.
- 15 M. W. Chase, Jr., NIST-JANAF Thermochemical Tables, 4th edn., *J. Phys. Chem. Ref. Data, Monograph*, 2000, **9**.
- 16 S. J. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data Suppl.*, 1988, **1**, 17.
- 17 J. Sehested, T. Ellerman, O. J. Nielsen and T. J. Wallington, *Int. J. Chem. Kinet.*, 1994, **26**, 615.
- 18 G. K. Jarvis, R. A. Kennedy, C. A. Mayhew and R. P. Tuckett, *Int. J. Mass Spectrom. Ion Processes*, 2000, **202**, 323.
- 19 G. K. Jarvis, R. A. Kennedy, C. A. Mayhew and R. P. Tuckett, *J. Phys. Chem. A*, 2000, **104**, 10766.
- 20 N. L. Haworth, M. H. Smith, G. B. Bacskay and J. C. Mackie, *J. Phys. Chem. A*, 2000, **104**, 7600.
- 21 F. Danis, F. Caralp, M. T. Rayez and R. Lesclaux, *J. Phys. Chem.*, 1991, **95**, 7300.
- 22 S. Antonik, *Bull. Soc. Chim. Fr.*, 1983, **15**, 605.
- 23 C. Atterbury, A. Critchley, R. A. Kennedy, C. A. Mayhew and R. P. Tuckett, *Phys. Chem. Chem. Phys.*, in preparation.