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A study of low energy electron attachment to trifluoromethyl sulphur pentafluoride, SF₅CF₃: atmospheric implications

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Abstract

An investigation of electron attachment to the potent greenhouse gas SF₅CF₃ has been carried out in atmospheric pressure nitrogen and argon buffer gases at 300 K. The experiments were conducted under nonthermal electron-swarm conditions, using an instrument that combines a drift tube with a quadrupole mass spectrometer. Electron attachment rate constants, k_a , have been determined as a function of mean electron energy ($\bar{\epsilon} = 0.04\text{--}1.9$ eV). k_a decreases as $\bar{\epsilon}$ increases. The estimated thermal electron attachment rate constant is $k_{th}(\text{SF}_5\text{CF}_3) \approx (7.7 \pm 0.6) \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The only observed anion product is SF₅⁻. Free electron attachment destroys SF₅CF₃. This places an upper limit on the atmospheric lifetime of SF₅CF₃ of the order of 1000 years. (Int J Mass Spectrom 206 (2001) i–iv) © 2001 Elsevier Science B.V.

Keywords: Electron attachment; SF₅CF₃; Rate constants

1. Introduction

Trifluoromethyl sulphur pentafluoride (SF₅CF₃) has recently been discovered in samples of stratospheric air at about 0.12 ppt [1]. This small atmospheric concentration is growing at approximately 6% per year. SF₅CF₃ has the strongest radiative forcing, on a per molecule basis, of any molecule found in the atmosphere to date. By assuming that SF₅CF₃ has the same atmospheric lifetime as SF₆, Sturges et al. [1] estimate its global warming potential (GWP) to be

18 000 times that of CO₂. Confidence in this value requires confirmation of the atmospheric lifetime of SF₅CF₃. Toward this goal, we are conducting studies of the reactions of ions and electrons with SF₅CF₃. Here we report a swarm study of electron attachment to SF₅CF₃, covering mean electron energies, $\bar{\epsilon}$, from just above thermal to 1.9 eV.

To our knowledge, there have been no studies of electron attachment to SF₅CF₃. There have been numerous investigations of electron attachment to the closely related molecule SF₆ [2–10]. SF₆ has a large rate constant for low energy electron attachment. The thermal electron attachment rate constant at 300 K is $(3.1 \pm 0.5) \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is

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close to the theoretical maximum [4]. This large electron attachment rate constant, and the inertness of SF₆ have led to its use as a high voltage insulator. It is speculated [1] that SF₅CF₃, which has no natural sources, originates when SF₅, formed as a breakdown product of SF₆ within high-voltage equipment, reacts with CF₃ groups on the surface of fluoropolymers. SF₆ is also used in plasma-etching applications in industry [11–17]. A thorough understanding of the electron attaching properties of SF₆ and its reactions with ions is important for modeling and characterising such plasmas [18]. Studies of electron attachment to and ion reactions with related molecular species will shed light on the dynamics of the ion and electron chemistry occurring in SF₆-containing plasmas.

2. Experimental details

The electron-swarm technique and our apparatus have been described in the literature [19–22]. An electric potential is applied along a drift tube creating a uniform electric field, E , drawing electrons toward a Faraday plate detector. An electron energy distribution is established, determined by a dynamic balance between the kinetic energy gained from the electric field and energy loss through multiple collisions with the buffer gas (either Ar or N₂ of number density N). The shape of this energy distribution depends on E/N , the type of buffer gas used, and the temperature. For fixed N , higher electric field strengths lead to higher mean electron energies. For a given E/N , use of Ar as the buffer gas results in an electron swarm with higher mean electron energies than provided by N₂. The studies presented here cover $E/N = 0.4 - 15 \times 10^{-18}$ V cm² for N₂ ($\bar{\epsilon} = 0.04 - 0.5$ eV) and $0.4 - 6 \times 10^{-18}$ V cm² for Ar ($\bar{\epsilon}$ range of $0.5 - 1.9$ eV).

Electrons can be distinguished from anions, formed by electron attachment, by a simple timing arrangement in which the electrons are admitted into the drift tube as a short (1–2 ms) pulse. The large mass difference between electrons and anions insures that anions arrive at the end of the drift tube after the electrons and over a far broader time window. We can monitor the attenuation of electron pulses as a func-

tion of the admitted reactant gas concentration with little interference from product anions. The density reduced electron attachment coefficient, α , is determined as a function of E/N . Multiplication of α with the mean electron drift speed [23] gives the electron attachment rate constant, k_a , as a function of E/N .

A small orifice in the Faraday plate allows anions formed within the drift tube to enter a differentially pumped region leading to a quadrupole mass spectrometer. Anions formed from electron attachment and secondary anions, resulting from subsequent anion-molecule reactions, can be monitored. In this mode of operation electrons are admitted continuously into the drift tube. Care is taken to insure that anion-molecule reactions, if they occur, are taken into account in determining the primary anion branching ratios.

The sample of SF₅CF₃ was commercially purchased (Apollo Scientific Limited) with a stated purity of 99%, and was used without further purification.

3. Results and discussion

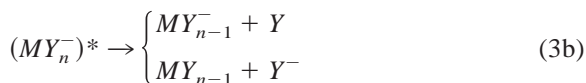
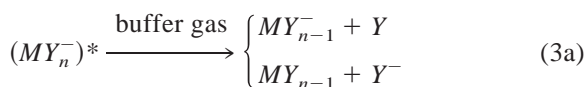
The capture of an electron, e^- , by a molecule, MY_n , leads initially to the formation of an excited parent anion:



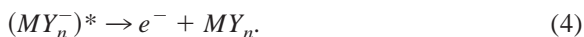
The excited parent anion may be collisionally stabilised:



dissociate:



or it may autodetach:



Reactions (2) and (3) lead to permanent electron attachment, and an observable electron pulse attenuation in swarm experiments. Only dissociative electron attachment (reaction (3)) was observed for electron attachment to SF_5CF_3 . The exclusive anion product detected for $0.04 < \bar{\epsilon} < 1.9$ eV was SF_5^- , formed by the exothermic dissociative attachment reaction:



$$\Delta H = -22 \text{ kJ mol}^{-1} \quad (5)$$

(ΔH corresponds to the enthalpy of the reaction for zero kinetic energy electrons). Enthalpies of formation were taken from the NIST website [24]. $SF_5CF_3^-$ was not detected. This indicates that the lifetime of the transient $(SF_5CF_3^-)^*$ with respect to dissociation is short compared to the time for collisional stabilization to take place in our instrument.

CF_3^- is not an observed anion product from the attachment of low-energy electrons to SF_5CF_3 . This result is consistent with the energetics of the channel:



$$\Delta H = 162 \text{ kJ mol}^{-1} \quad (6)$$

Electrons with a kinetic energy of at least 1.7 eV would be needed to access these products. With Ar as the buffer gas, we were able to operate with $\bar{\epsilon} > 1.7$ eV. Even then CF_3^- was not detected. The dynamics of the dissociation of $(SF_5CF_3^-)^*$ are such that under swarm conditions SF_5^- (+ CF_3) is the sole product. Electron beam studies would be of interest, for they provide data in a collision free environment, and an opportunity to investigate electron attachment processes at higher electron energies. Electron beam studies have been performed on two derivatives of SF_6 : SF_5Cl [10], and SF_5NCO [25]. Only a small yield of SF_5Cl^- is detected, and electron capture to SF_5NCO is not observed to yield the parent anion.

The electron attachment rate constants as a function of $\bar{\epsilon}$ are presented in Fig. 1. Below $\bar{\epsilon} = 0.5$ eV, the data points correspond to electron attachment in a

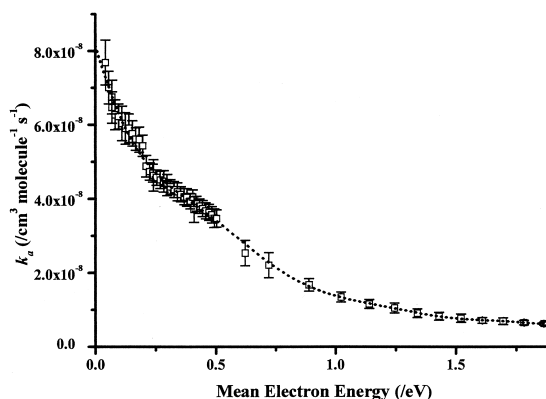


Fig. 1. Electron attachment rate constant, k_a , as a function of mean electron energy, $\bar{\epsilon}$, in atmospheric pressure N_2 ($\bar{\epsilon} < 0.5$ eV) and Ar ($\bar{\epsilon} > 0.5$ eV) buffer gases for SF_5CF_3 . The data points are the average of at least six independent measurements, and the error bars shown represent one standard deviation about the mean value.

N_2 buffer gas. For $\bar{\epsilon} > 0.5$ eV, the results were obtained in Ar. The data show that electron attachment to SF_5CF_3 is fast over the mean electron energies covered in our experiment, with the attachment rate coefficient decreasing with increasing $\bar{\epsilon}$. The dependence of k_a on $\bar{\epsilon}$ indicates that the electron attachment cross section is peaked at zero electron energy.

With N_2 as the buffer gas and using our lowest E/N (4.0×10^{-19} V cm²), the electron energy distribution approximates to Maxwellian, with $\bar{\epsilon} = 0.042$ eV. This is close to $\bar{\epsilon}$ for thermalised electrons at 300 K, 0.038 eV. This leads to the conclusion that the thermal electron attachment rate constant for SF_5CF_3 , $k_{th}(300 \text{ K}) \approx k_a(300 \text{ K}, E/N = 4.0 \times 10^{-19} \text{ V cm}^2) = (7.7 \pm 0.6) \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4. Conclusion

The observations presented in this communication demonstrate that SF_5CF_3 will be destroyed by fast dissociative electron attachment, leading to the products SF_5^- and CF_3 . The destruction of SF_6 in the atmosphere has been modeled by Morris et al. [26]. They conclude that for molecules that are rapidly destroyed by electron attachment, but are otherwise

inert, the atmospheric lifetime will be of the order of 1000 years. Although SF₆ may be regenerated following electron attachment, SF₅CF₃ is destroyed by electron attachment, so that 1000 years is an upper limit to its atmospheric lifetime. The detection of SF₅CF₃ in the stratosphere indicates that it is not degraded in the Earth's lower atmosphere by reactions with hydroxyl radicals. Ion (e.g. O⁺, O₂⁺, H₃O⁺, H₂O.H₃O⁺, O⁻, and O₂⁻), free radical (e.g. O^{1D}), and photo-initiated (e.g. Lyman-α) reactions in the upper stratosphere and mesosphere may provide atmospheric sinks for SF₅CF₃ in addition to the electron attachment channel and reduce its atmospheric lifetime.

Acknowledgements

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