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Ion/molecule reactions with S_2F_{10}: detection of $S_2F_{10}^{\cdot+}$, $S_2F_{11}^{+}$ and two isomers of SF_5^{+}

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Abstract

The chemical ionization of S_2F_{10} has been investigated with measurements of ion/molecule reactions between S_2F_{10} and the ions $Ar^{\cdot+}$, $CO_2^{\cdot+}$, $SO_2^{\cdot+}$, $HBr^{\cdot+}$, $C_2H_2^{\cdot+}$ $COS^{\cdot+}$, $C_{60}^{\cdot 3+}$ and C_{60}^{2+} using the selected-ion flow tube (SIFT) technique at 294 ± 2 K in helium at a total pressure of 0.35 Torr. $S_2F_{10}^{\cdot+}$, SF_5^{+}, SF_3^{+} and $S_2F_6^{\cdot+}$ were observed as primary product ions with all reagent ions except C_{60}^{n+}. The occurrence and failure of charge transfer were used to bracket $IE(S_2F_{10}) = 11.25 \pm 0.15\,eV$ and to provide $\Delta H^{\circ}_{f,298}(S_2F_{10}^{\cdot+}) = -221.7 \pm 8.5\,kcal\,mol^{-1}$. Two states of SF_5^{+} of different chemical reactivity were identified and tentatively ascribed to square pyramid and trigonal bipyramid isomers. The SF_5^{+} produced in the nearly thermoneutral charge-transfer reaction with $COS^{\cdot+}$ is seen to react further with S_2F_{10} by F^{+} transfer to produce $S_2F_{11}^{+}$ and is proposed to have a trigonal-bipyramid (D_{3h}) structure, while the SF_5^{+} produced at high excess energies which reacts with S_2F_{10} to produce SF_3^{+} rather than $S_2F_{11}^{+}$, is proposed to have a higher-energy square-pyramid (C_{4v}) structure. With regard to the detection of S_2F_{10} by chemical ionization, the experimental results demonstrate that $S_2F_{10}^{\cdot+}$ (and $S_2F_6^{\cdot+}$) ions can be formed in trace amounts from S_2F_{10} by charge-transfer chemical ionization in helium at 294 ± 2 K. Also, it is suggested that F^{+} transfer to produce $S_2F_{11}^{+}$, as observed with SF_5^{+}, might be generally suited for the detection of S_2F_{10}.

Key words: Sulfur decafluoride; Charge-transfer chemical ionization

1. Introduction

Disulfur decafluoride (S_2F_{10}) is a highly toxic impurity which may appear, along with SOF_2, SO_2F_2, SO_2, SF_4, etc., in electrical discharges of sulfur hexafluoride (SF_6), a commonly-used dielectric. The threshold-limit-value for S_2F_{10} in the USA is 10 p.p.b. [1], three orders of magnitude lower than those for other impurities. The necessity for a method suitable for the determination of low concentrations of S_2F_{10} in SF_6 was recognized long ago [2,3]. Since then, gas chromatography (GC) [4–6] and the combination of GC and infrared spectroscopy (IR) [3,7], have been used in several laboratories with detection limits to 10 p.p.m., and preliminary trapping of

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S_2F_{10} improved the detection limit down to 1 p.p.m.

The first positive-ion electron-impact mass spectrum of S_2F_{10} was reported by Cohen and McDiarmid [8] and later confirmed by others [5,9]. The mass spectrum is very similar to those of SF_6 or SF_6/SF_4 mixtures. There is no evidence for the formation of either the parent ion $S_2F_{10}^{\cdot+}$ or any other ion containing two sulfur atoms. Although the ion-fragment intensities (SF_n^+, $n = 1$–5) in S_2F_{10} differ from those in SF_6, especially at electron energies below 20 eV, they cannot be used as a basis for an accurate concentration measurement; the presence of S_2F_{10} in SF_6 is hardly recognizable even at the 10% level. Farber et al. [10] reported the observation of an m/z 254 peak (corresponding to $S_2F_{10}^{\cdot+}$) in the electron-impact mass spectrum of an arced mixture of SF_6 (90%) and O_2 (10%), but independent evidence for the actual presence of S_2F_{10} in this mixture was not provided. No characteristic ion fragments have been found in the negative-ion mass spectrum of S_2F_{10} [11]: the mass spectrum includes $SF_6^{\cdot-}$, SF_5^-, and F^- ions but these are also present in the SF_6 mass spectrum. The CH_4 and NH_3 positive and negative chemical-ionization mass spectra for S_2F_{10} reported by Jenssen [5] also are not characteristic.

The absence of a mass-spectral signature for S_2F_{10} has made the use of mass spectrometry (MS) almost impossible for the analysis of S_2F_{10}/SF_6 mixtures and has significantly restricted the use of GC–MS. Olthoff et al. [12] have proposed the use of a hydrolysis reaction to convert S_2F_{10} into SOF_2 after it has passed through a GC column and to monitor $SOF_2^{\cdot+}$ in a single-ion mode of a GC–MS to provide a measure of S_2F_{10}. The detection limit of this three-step procedure was claimed to be about 10 p.p.b. However, this method is still based on the indirect detection of S_2F_{10} and the results obtained might have been affected by the presence of $S_2F_{10}O$ or $S_2F_{10}O_2$.

A direct and sensitive mass-spectrometric method for the detection of trace S_2F_{10} is still very much in demand as is evidenced by the absence of information about the production of S_2F_{10} inside any industrial equipment filled with SF_6 and by controversial reports about S_2F_{10} formation during laboratory experiments with corona, spark and arc discharges in SF_6 [3–5,13].

In this study we have attempted to discover a soft-ionization method suitable for providing a mass-spectral signature of S_2F_{10}. The method of choice was positive-ion chemical ionization (CI) by charge transfer at room temperature in a selected-ion flow tube (SIFT). In such an apparatus the electron-impact ion source and the ion/molecule reaction region are physically separated, in contrast to conventional CI methods. Also, the SIFT ion source is sufficiently versatile to provide a variety of CI reagents and the conditions in the reaction region (He buffer gas at 0.35 Torr) are favourable for the collisional stabilization of reactant and product ions. Finally, since the temperature in the reaction region is room temperature, the thermal decomposition of the relatively unstable S_2F_{10} before chemical ionization can be avoided (the temperature in conventional CI is usually around 650 to 700 K).

2. Experimental

The experiments were performed with a SIFT apparatus which has been described in detail elsewhere [14]. Helium was used as the buffer gas at pressures of 0.35 Torr and an average gas velocity of 5.8×10^3 cm s^{-1}. The effective reaction length was 47 and 66 cm and the gas temperature was 294 ± 2 K.

Reactions of S_2F_{10} were investigated with the eight different reactant ions $Ar^{\cdot+}$, $CO_2^{\cdot+}$, $SO_2^{\cdot+}$, $HBr^{\cdot+}$, $C_2H_2^{\cdot+}$, $COS^{\cdot+}$, $C_{60}^{\cdot3+}$ and C_{60}^{2+} generated by electron impact at 30–100 eV in the electron-impact source from the pure parent gas or, in the case of C_{60}^{n+}, from a mixture of C_{60} and Ar. All the parent gases were of normal research grade. The fullerene powder was a mixture of C_{60} and C_{70} containing 2–12% C_{70} (Strem Chemicals Co.). The S_2F_{10} was prepared by Professor D. Desmarteau, Department of Chemistry, Clemson University. The sample was checked by IR and GC and had a purity of 99.999%. Impurities below this level may be SF_6, SF_4, SOF_2 and SiF_4. Electron-impact mass spectrometry at 70, 20 and 15 eV

Table 1
Results for the reactions of various cations with S_2F_{10} observed with the SIFT technique at 294 ± 2 K in helium at 0.35 ± 0.01 Torr

Cation	IE (eV)	Primary reaction products [a]				Rate coefficients	
		$S_2F_{10}^{\bullet+}$	$S_2F_6^{\bullet+}$	SF_5^+	SF_3^+	k_{obs} [c]	k_c [d]
$Ar^{\bullet+}$	15.76	1	1	>87	<11	–	2.3
$CO_2^{\bullet+}$	13.77	1	2	93	4	1.3	2.2
$SO_2^{\bullet+}$	12.32	1	1	>83	<15	–	1.9
$HBr^{\bullet+}$	11.66	1	1	90	8	0.99	1.7
$C_2H_2^{\bullet+}$	11.40	1	Obs	70	20[b]	0.82	2.84
$COS^{\bullet+}$	11.17	2	Obs	90	7	0.038	1.94
C_{60}^{3+}	11.09[e]	–	–	–	–	<0.001	
C_{60}^{2+}	<9.7[e]	–	–	–	–	<0.001	

[a] Branching percentage with an estimated uncertainty of ±5.
[b] An ion with m/z 64, presumably $C_2H_2F_2^{\bullet+}$, is also seen as a product (8%).
[c] Observed effective bimolecular rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1} with an estimated accuracy of ±30%.
[d] Calculated collision rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.
[e] Apparent ionization energy: the experimentally determined onset energy for charge transfer [17,18].

indicated an upper limit for any S–O–F molecules of 1000 p.p.m.

The data analysis and sources of uncertainty associated with the determination of rate coefficients has been described elsewhere [14,15].

3. Results

The results of the measurements for the eight reactions which were investigated are summarized in Table 1. The reactant ions were chosen with a view to observing the occurrence or non-occurrence of charge transfer and so to bracket the ionization energy of S_2F_{10} and to discover a "soft" (low exothermicity) charge-transfer chemical ionization reaction with S_2F_{10}. The ionization energies of the reactant ions cover a range from IE(Ar) = 15.76 eV to $IE_{app}(C_{60}^{\bullet+})$ < 9.7 eV [16]. For $C_{60}^{\bullet 3+}$ and C_{60}^{2+} the value of IE listed is an apparent ionization energy IE_{app}: the independently determined onset energy for charge transfer [17,18]. Charge transfer involving these latter two ions involve Coulombic repulsion between product ions which gives rise to an activation barrier [17,18].

Table 1 shows that the rate coefficient for reaction drops systematically from a high value close to the collision rate coefficient to $< 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} with decreasing ionization energy, viz. decreasing exothermicity for charge transfer. There is a sharp drop in the rate coefficient below IE = 11.4 eV.

Table 1 also provides branching fractions for the primary reaction products. Figure 1 shows the variations in ion signals recorded for the reaction of $CO_2^{\bullet+}$ with S_2F_{10}. Figure 2 shows the graphical determination of the branching fractions for this reaction. By far the major primary reaction channel observed with all cations is the production of SF_5^+ (see Fig. 1). The second most abundant channel which was observed is the production of SF_3^+. All the cations showed some reactivity with S_2F_{10} to produce trace amounts (~ 1%) of $S_2F_{10}^{\bullet+}$ and $S_2F_6^+$. The very slow reaction with $COS^{\bullet+}$ produces ≈ 2% of $S_2F_{10}^+$. $S_2F_{10}^+$ appears to be unreactive with S_2F_{10}. There is some indication in Fig. 2 that $S_2F_6^{\bullet+}$ reacts further with S_2F_{10}, possibly by charge transfer. Figure 2 also provides evidence for a reaction of SF_5^+ with S_2F_{10} to produce SF_3^+, presumably according to reaction (1):

$$SF_5^+ + S_2F_{10} \rightarrow SF_3^+ + (2SF_6) \qquad (1)$$

and slower than the reaction of $CO_2^{\bullet+}$ with S_2F_{10}.

$S_2F_{11}^+$ was observed to be formed as a secondary product in those experiments involving the primary reactions of $HBr^{\bullet+}$, $C_2H_2^{\bullet+}$ and $COS^{\bullet+}$ with S_2F_{10}

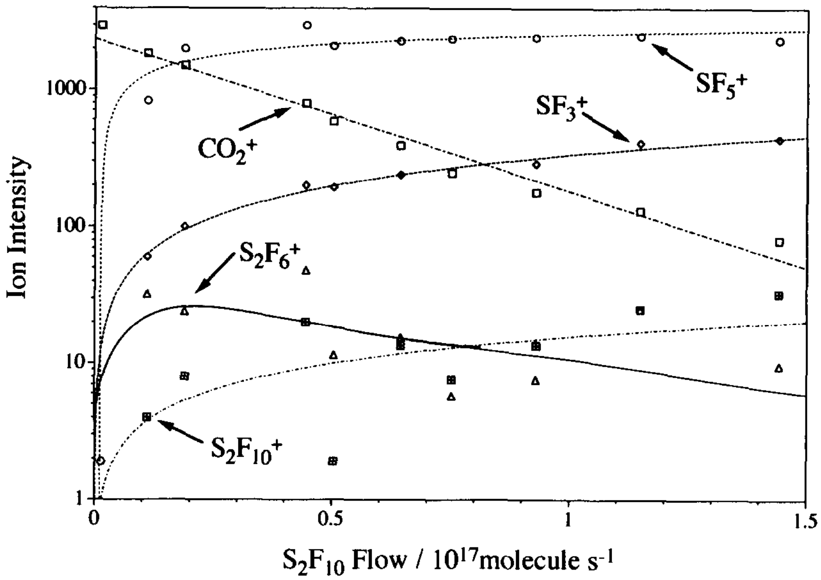

Fig. 1. Observed variation in ion signals with the addition of S_2F_{10} into the reaction region of the SIFT apparatus in which $CO_2^{\cdot+}$ has been selected upstream in helium buffer gas. $P = 0.35$ Torr, $\bar{v} = 5.8 \times 10^3\,\mathrm{cm\,s^{-1}}$, nominal reaction length = 66 cm, and $T = 294$ K. $CO_2^{\cdot+}$ was generated from CO_2 by electron impact at 100 eV. Increasing signals were fitted using a computerized curve-fitting program.

and increased in importance with decreasing ionization energy. Less than 1% of the SF_5^+ produced in the reaction with $HBr^{\cdot+}$, about 10% of the SF_5^+ produced from $C_2H_2^{\cdot+}$, and essentially all of the SF_5^+ produced in the reaction with $COS^{\cdot+}$ appeared to form $S_2F_{11}^+$. Figure 3 shows the results obtained with $COS^{\cdot+}$. Figure 4 shows that $S_2F_{11}^+$ arises from the F^+ transfer reaction of SF_5^+ with

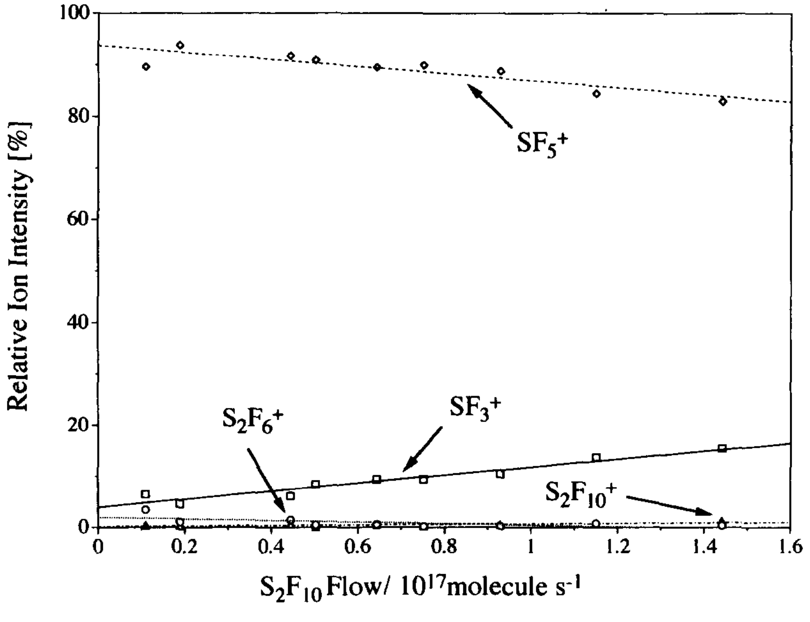

Fig. 2. The percent abundance of product ions recorded in Fig. 1. The intercepts at zero flow of S_2F_{10} provide a measure of the primary product distribution and the ion profiles provide an indication of the occurrence of secondary reactions.

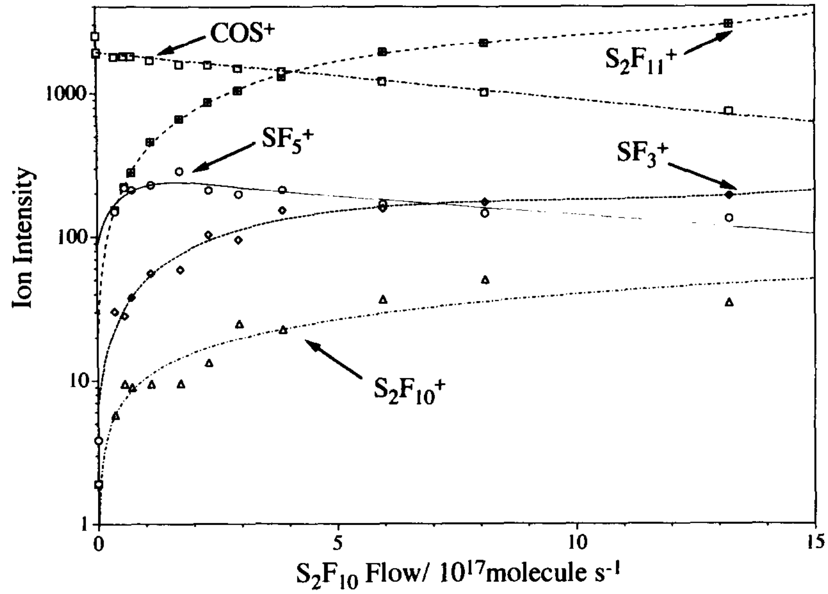

Fig. 3. Observed variation in ion signals with the addition of S_2F_{10} into the reaction region of the SIFT apparatus in which $COS^{\cdot+}$ has been selected upstream in helium buffer gas. $P = 0.36$ Torr, $\bar{v} = 5.9 \times 10^3\,\mathrm{cm\,s^{-1}}$, nominal reaction length = 66 cm, and $T = 294$ K. $COS^{\cdot+}$ was generated from CO_2 by electron impact at 30 eV. Increasing signals were fitted using a computerized curve-fitting program.

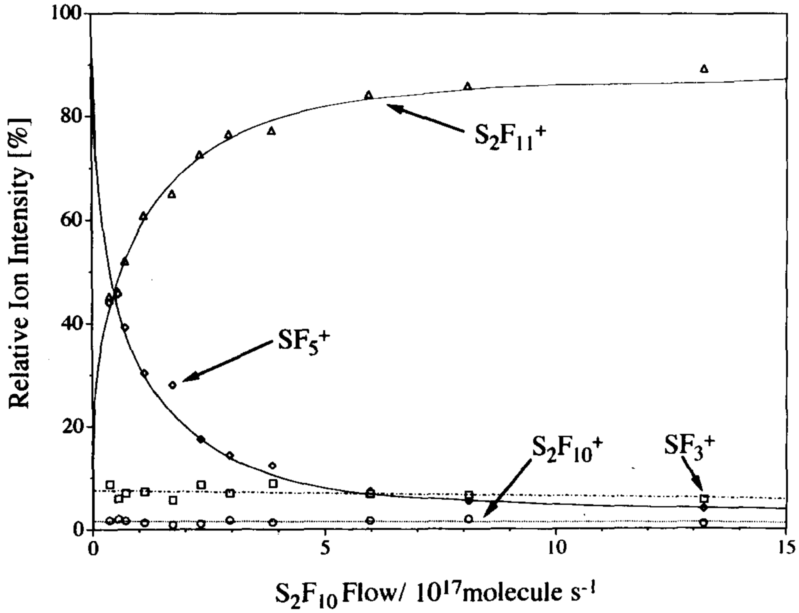

Fig. 4. The percent abundance of product ions recorded in Fig. 3. The intercepts at zero flow of S_2F_{10} provide a measure of the primary product distribution and the ion profiles provide an indication of the occurrence of secondary reactions.

S_2F_{10}, viz. reaction (2):

$$SF_5^+ + S_2F_{10} \rightarrow S_2F_{11}^+ + SF_4 \qquad (2)$$

Figure 3 shows that reaction (2) is rate-limited by its production from $COS^{\cdot +}$, viz. $k_2 \geqslant 3.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

4. Discussion

4.1. Ionization of S_2F_{10}

None of the reactions with S_2F_{10} observed in the experiments reported here, both the primary and the secondary reactions, have been reported previously, to the best of our knowledge. The observed primary production of $S_2F_{10}^{\cdot +}$ can be attributed to charge-transfer reactions of type (3):

$$X^{\cdot +} + S_2F_{10} \rightarrow S_2F_{10}^{\cdot +} + X \qquad (3)$$

An increasing amount of internal energy is expected to be deposited in $S_2F_{10}^{\cdot +}$ with increasing ionization energy of X. Excited $(S_2F_{10}^{\cdot +})^*$ may dissociate or be collisionally stabilized according to the following reactions:

$$(S_2F_{10}^{\cdot +})^* \rightarrow SF_5^+ + SF_5^{\cdot} \qquad (4a)$$

$$\rightarrow SF_3^+ + F_2 + SF_5^{\cdot} \qquad (4b)$$

$$\rightarrow S_2F_6^{\cdot +} + 2F_2 \qquad (4c)$$

$$\xrightarrow{He} S_2F_{10}^{\cdot +} \qquad (4d)$$

This means that SF_5^+, SF_3^+ and $S_2F_6^{\cdot +}$ may be produced by dissociative charge transfer at sufficiently high excess energies. Alternatively, these ions may be formed by complex formation leading to neutral products which may involve chemical-bond formation with X.

The observed occurrence and failure of charge transfer to produce $S_2F_{10}^{\cdot +}$ contains information about the ionization energy of S_2F_{10}. The standard-enthalpy change, ΔH°_{298}, for the charge-transfer reaction (3) is related to the standard free-energy change, ΔG°_{298}, and standard-entropy change, ΔS°_{298}, according to relation (5) and to adiabatic ionization energies, IE, according to relation (6):

$$\Delta H^\circ_{298} = \Delta G^\circ_{298} + T\Delta S^\circ_{298} \qquad (5)$$

$$\Delta H^\circ_{298} = \mathrm{IE}(S_2F_{10}) - \mathrm{IE}(X) \qquad (6)$$

Accordingly, when $\Delta G^\circ_{298} \leqslant 0$ is used as a criterion for spontaneity and $T\Delta S^\circ_{298}$ is assumed to be negligible, the observation of charge transfer can be used to place an upper limit to IE(S_2F_{10}), and the failure to observe charge transfer can be used to set a lower limit to IE(S_2F_{10}). Thus the fast reaction observed with $C_2H_2^{\cdot +}$ which appears to proceed largely by dissociative charge transfer and the failure to observe charge-transfer with C_{60}^{3+} can be used to bracket the adiabatic ionization energy of S_2F_{10} to be 11.25 ± 0.15 eV. The standard enthalpy of formation of S_2F_{10}, $\Delta H^\circ_{f,298}(S_2F_{10}) = -480.9 \pm 5.0$ kcal mol^{-1} [19], then provides a value for $\Delta H^\circ_{f,298}(S_2F_{10}^{\cdot +}) = -221.7 \pm 8.5$ kcal mol^{-1}.

4.2. Production of SF_5^+

The measured product distributions (summarized in Table 1) indicate that SF_5^+ predominates as a product in all of the reactions which occurred with a measurable rate coefficient. Presumably this ion arises from S–S bond scission, although recent calculations by Gutsev [20(a)] suggest that the stable structure of S_2F_{10} is best described as an adduct, $SF_4 . SF_6$ with an S–F–S linkage. Furthermore, the observed secondary reactions of SF_5^+ to produce $S_2F_{11}^+$ in the experiments with $HBr^{\cdot +}$, $C_2H_2^{\cdot +}$ and $COS^{\cdot +}$ and the observed secondary reactions of SF_5^+ to produce SF_3^+ in the experiments with $Ar^{\cdot +}$, $CO_2^{\cdot +}$ and $SO_2^{\cdot +}$ suggest the production of two states of SF_5^+ with distinctly different chemical reactivities. We have tentatively assigned these states to a low-energy D_{3h} (trigonal bipyramid, tb) isomer formed at the lower excess energies and a high-energy C_{4v} (square pyramid, sp) isomer formed at the higher excess energies. The two isomers appear not to interconvert under our experimental conditions at thermal energies. The existence of two isomers of SF_5^+, and by implication $SF_5^{\cdot}$, leads to at least four possible channels in the dissociation of $S_2F_{10}^{\cdot +}$ to $SF_5^+ + SF_5^{\cdot}$; $sp^+ + sp$, $sp^+ + tb$, $tb^+ + sp$ and $tb^+ + tb$.

A recent theoretical study by Gutsev [20(b)] of the structures and stabilities of the $SF_5^{\bullet}$ radical and its cation has predicted C_{4v} symmetry for the ground state of the radical and D_{eh} symmetry for the cation. This means that the energetically most favourable channel for the dissociation of $S_2F_{10}^{\bullet +}$ corresponds to the formation of $tb^+ + sp$. To calculate the energy associated with this dissociation we choose as the best available $\Delta H_f^{\circ}(SF_5^{\bullet})$ the value of -218.7 ± 4.2 kcal mol^{-1} reported recently by Fisher et al. [21] which becomes -221.1 ± 4.2 kcal mol^{-1} at 298 K and we assign this value to the low energy C_{4v} isomer, and choose as the best available $\Delta H_f^{\circ}(SF_5^+)$ the value of -2.7 ± 4.4 kcal mol^{-1} reported by Fisher et al. [21] which becomes -0.3 ± 4.4 kcal mol^{-1} at 298 K and we assign this value to the low energy D_{3h} isomer. Adopting also the $\Delta H_{f,298}^{\circ}(S_2F_{10}^{\bullet +})$ of -221.7 ± 8.5 kcal mol^{-1} derived above, we compute a standard enthalpy change at 298 K of $+0.9 \pm 17.1$ kcal mol^{-1} for the dissociation shown in Eq. (7):

$$S_2F_{10}^{\bullet +} \rightarrow SF_5^+(D_{3h}) + SF_5^{\bullet}(C_{4v}) \qquad (7)$$

Therefore, the dissociation appears to be slightly endothermic, although the uncertainty is quite large. Taking the standard entropies of $SF_5^{\bullet}$ and SF_5^+ at 298 K as 72.8 ± 2.0 and 71.26 ± 2.0 e.u. respectively [22], and assuming $S_{298}^{\circ}(S_2F_{10}^{\bullet +}) = S_{298}^{\circ}(S_2F_{10}) = 94.87 \pm 2.0$ e.u. [22], we obtain an entropy term $T\Delta S^{\circ}$ at 298 K of 15.1 ± 1.8 kcal mol^{-1} which is more than sufficient to overcome the endothermicity of the dissociation, $\Delta G_{298}^{\circ} = -14.2 \pm 18.9$ kcal mol^{-1}. Apparently the production of SF_5^+ by dissociative charge transfer is possible already for the thermoneutral charge transfer.

Another interesting result of the Gutsev calculations is the prediction that the separation energy of the two isomers of SF_5^+ is quite small, in the range from 0.2 to 0.3 eV [20(b)]. This result is consistent with the observed fall-off in the production of $S_2F_{11}^+$ (a signature of the low-energy isomer, SF_5^+ (D_{3h})) to 10% in the reaction with $C_2H_2^{\bullet +}$ and less than 1% in the reaction with $HBr^{\bullet +}$ for which the excess energy, IE(X) – IE(S_2F_{10}), is 0.15 ± 0.15 and 0.41 ± 0.15 eV, respectively. However, if the entropy term were important in effecting the dissociation, an additional 15 kcal mol^{-1} (0.65 eV) in the separation energy of the two isomers could be accommodated by our experimental results.

4.3. Reactions of SF_5^+

Our observations indicate that the low energy (D_{3h}) isomer of SF_5^+ reacts with S_2F_{10} to produce $S_2F_{11}^+$ and that the high-energy (C_{4v}) isomer reacts with S_2F_{10} to produce SF_3^+. This difference in reactivity is very intriguing, particularly in view of the possible role of geometric constraints in determining the nature of the reaction products. Possible reactions of SF_5^+ with S_2F_{10} include charge transfer, dissociative F^- transfer and F^+ transfer as indicated in reaction (8):

$$SF_5^+ + S_2F_{10} \rightarrow S_2F_{10}^{\bullet +} + SF_5^{\bullet} \qquad (8a)$$

$$\rightarrow SF_3^+ + 2SF_6 \qquad (8b)$$

$$\rightarrow S_2F_{11}^+ + SF_4 \qquad (8c)$$

To begin with, the failure to observe charge transfer with the high-energy isomer is noteworthy. Charge transfer to produce the low-energy (C_{4v}) isomer of $SF_5^{\bullet}$ is geometrically favourable but may not be favourable on thermodynamic grounds. The ionization energy of S_2F_{10} (11.25 ± 0.15 eV) is quite high. The ionization energy of the low-energy isomer of $SF_5^{\bullet}$, presumably to give the low-energy (D_{3h}) isomer of SF_5^+ apparently is only 9.60 ± 0.05 eV which makes the charge transfer channel (8a) endothermic by at least 1.6 eV with SF_5^+ (D_{3h}). The separation energy for the two isomers of SF_5^+ calculated by Gutsev [20] would then also make the charge-transfer reaction with the high-energy (C_{4v}) isomer of SF_5^+ endothermic.

The production of SF_3^+ (channel 8(b)) may be regarded as proceeding by F^- transfer which is thermodynamically allowed for both the high-energy and low-energy isomers of SF_5^+. Adopting the values previously indicated for $\Delta H_{f,298}^{\circ}(SF_5^+)$ and $\Delta H_{f,298}^{\circ}(S_2F_{10})$, and taking $\Delta H_{f,298}^{\circ}(SF_3^+)$ as 84.66 kcal mol^{-1} [23], we compute an exothermicity of 18 kcal mol^{-1} for this reaction involving the low-energy isomer of SF_5^+. Channel 8(b) is also geometrically favourable for the reaction with the high-energy isomer in that the transfer of F^- to

SF_5^+ (C_{4v}) will not require significant geometric changes to produce octahedral SF_6. In contrast, significant structural changes are required with the low-energy D_{3h} isomer of SF_5^+ so that this channel would be geometrically less favourable.

The thermodynamics of the F^+ transfer reactions (channel 8(c)) are unknown: the F^+ affinity of S_2F_{10} has not been determined. But we can say that the observed occurrence of F^+ transfer with the low-energy SF_5^+ isomer would make the F^+ transfer with the high-energy isomer also energetically favourable. So why should F^+ transfer be preferred with the low-energy isomer? We suggest that here too, geometric factors may well play a role in determining the kinetics. SF_4 has C_{2v} geometry (nearly trigonal bipyramid (including the lone pair of valence electrons)). Consequently, F^+ transfer from the low-energy isomer is geometrically very favourable while that with the high-energy isomer is unfavourable.

4.4. Production of SF_3^+

Table 1 shows some primary production of SF_3^+: the branching percentage is low except in the case for the reaction with $C_2H_2^{+\cdot}$. There is no clear correlation with SF_5^+ production which might be expected if SF_3^+ is produced by dissociative charge transfer (channel 4(b)). Indeed this channel is energetically unfavourable since it requires an additional 85 kcal mol^{-1} to form $SF_3^+ + F_2$ from the low-energy isomer of SF_5^+ ($\Delta H_f^\circ(SF_3^+)$ has been reported to be 84.66 kcal mol^{-1} [23]). Alternate reaction paths leading directly to SF_3^+ which are likely to be energetically more favourable are possible. For example, reaction (9) may be favourable for the production of SF_3^+ from $C_2H_2^{\cdot+}$.

$$C_2H_2^{\cdot+} + S_2F_{10} \rightarrow SF_3^+ + C_2H_2F_2 + SF_5^{\cdot} \qquad (9)$$

This reaction seems plausible in view of the observation of some $C_2H_2F_2^{+\cdot}$ which suggests the occurrence of a related reaction, perhaps involving charge transfer from SF_3^+ to $C_2H_2F_2$ before separation of the products. Formation of the CH_2CF_2 isomer ($\Delta H^\circ_{f,298}(CH_2CF_2) = -78.5$ kcal mol^{-1}, [24]) in reaction (9) is exothermic by about 50 kcal mol^{-1}.

4.5. Detection of S_2F_{10}

The results of our experimental study could provide the basis for the development of CI MS or CI GC–MS methods for the detection of trace amounts of S_2F_{10}. The ion/molecule reactions which were identified produce characteristic mass spectra for the S_2F_{10} molecule and most proceed at close to the collision rate. Any one of the product ions which were identified (SF_3^+, SF_5^+, $S_2F_6^{\cdot+}$, $S_2F_{10}^{\cdot+}$, $S_2F_{11}^+$) could provide a signature for S_2F_{10} in the presence of SF_6. Even SF_5^+, which is efficiently produced in the ion/molecule reactions with S_2F_{10}, is not readily generated from SF_6 with the same reactant ions. However, in mixtures of SF_6 containing trace amounts of S_2F_{10} (e.g. parts-per-billion levels), even inefficient production of SF_5^+ from SF_6 may obfuscate the detection of S_2F_{10}. Monitoring ions containing two sulfur atoms ($S_2F_6^{\cdot+}$, $S_2F_{10}^{\cdot+}$, $S_2F_{11}^+$) would seem to be much more practical. Positive ion/molecule reactions in SF_6 have been observed by Saporoschenko and coworkers with an ion drift-tube mass spectrometer at $P(SF_6) = 0.1–0.7$ Torr [25] and by Sauers and Harman [26] who directly coupled a corona discharge cell containing SF_6 with a mass spectrometer. Saporoschenko et al. detected the slow formation of $S_2F_7^+$ from $SF_3^+ + SF_6$, $S_2F_9^+$ from $SF_5^+ + SF_6$ and trace amounts of $S_2F_6^{\cdot+}$, and have proposed a mechanism for the formation of $S_2F_9^+$ which includes $(S_2F_{11}^+)^*$ as an intermediate ion [25(b)]. However, neither group found $S_2F_{10}^{\cdot+}$ or $S_2F_{11}^+$ ions.

5. Conclusion

The results demonstrate that $S_2F_{10}^{\cdot+}$ (and $S_2F_6^{\cdot+}$) ions can be formed from S_2F_{10} by chemical ionization in helium at 294 ± 2 K, although they are produced only in trace amounts. However, under "soft" chemical ionization conditions involving nearly thermoneutral charge transfer, the secondary F^+ transfer reaction between SF_5^+ and S_2F_{10} to produce $S_2F_{11}^+$ provides a more sensitive indicator for S_2F_{10}. This latter observation suggests that chemical ionization by F^+

transfer generally might provide a suitable means for the detection of S_2F_{10}.

The observed occurrence and failure of charge transfer provide a bracketed value for $IE(S_2F_{10}) = 11.25 \pm 0.15\,eV$ and $\Delta H^{\circ}_{f,298}(S_2F_{10}^{\cdot+}) = -221.7 \pm 8.5\,kcal\,mol^{-1}$.

The apparent formation of two isomers of SF_5^+ with different chemical reactivities is an interesting result which is now being explored further with computations of the energies and structures of possible isomers of SF_5^+ and the energy for their interconversion. The existence of two stable isomers of SF_5^+ has important consequences for the known thermochemistry of SF_5^+ which are discussed elsewhere [27].

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7. References

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