Energetics and Reaction Pathways of some Reactions leading to $SNSAsF_6$ and $SNAsF_6$†

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Our previously reported preparation of $SNSAsF_6$ from S_4N_4, S_8 and AsF_5 was investigated *in situ* by ^{14}N NMR spectroscopy with, and without, traces of Br_2. Reaction pathways are proposed, which were separately investigated by ^{14}N NMR spectroscopy, and an efficient high-yield synthesis of highly crystalline $SNSAsF_6$ developed. The enthalpy of reaction was estimated as -104.6 ± 2 kJ mol^{-1} per $SNSAsF_6$. The compound $SNSAsF_6$ was also formed rapidly and quantitatively from $SNAsF_6$ and S_8 with no observable intermediates (A reaction mechanism is proposed and the enthalpy and entropy of the reaction estimated as -66 ± 28 kJ mol^{-1} and -1.6 J K^{-1} mol^{-1}), from reactions of $S_4(AsF_6)_2$ with $(S_3N_2)_2(AsF_6)_2$ (1:1) and S_4N_4 (2:1), and very slowly in small amounts from $S_4N_4(AsF_6)_2$ with S_8, $S_8(AsF_6)_2$ or $S_4(AsF_6)_2$. The compounds $S_4(AsF_6)_2$ and S_4N_4 gave $(S_3N_2)_2(AsF_6)_2$ and an IR spectrum of the pure material is reported. The compounds $(S_3N_2)_2(AsF_6)_2$ was oxidised by AsF_5 to give equimolar amounts of $SNAsF_6$ and $SNSAsF_6$ in SO_2 solution, the reaction proceeding faster with traces of Br_2. The enthalpy of reaction of S_4N_4 and AsF_5 leading to $SNAsF_6$ was estimated as -40 ± 28 kJ mol^{-1} per $SNAsF_6$ and subsequently the reaction was shown to occur in about 30% yield. As part of an investigation into the course of this reaction, polymeric $(S_5N_5AsF_6)_x$ was prepared in high yield, from S_4N_4 and $S_4N_4(AsF_6)_2$, which on oxidation with AsF_5 and traces of Br_2 gave $SNAsF_6$ in a 30% yield. In addition, $(S_3N_2)_2NAsF_6$ was oxidised by AsF_5 with traces of Br_2 to give $SNSAsF_6$, $SNAsF_6$ and N_2.

The dithionitryl cation SNS^+ (*cf.* ONO^+) has a simple but extensive chemistry.[1] It was first prepared as the $SbCl_6^-$ salt in unspecified yield by the reaction of S_7NH, S_7NBCl_2, or 1,4-$S_6N_2H_4$ with $SbCl_5$ in liquid SO_2.[2] Concurrently, we had investigated the reaction of $S_8(AsF_6)_2$ with NaN_3 in liquid SO_2 which gave $SNSAsF_6$ in *ca.* 20% yield.[3a] Our discovery that the oxidising power of AsF_5 with the chalcogens is enhanced by trace amounts of Br_2[4a] (or I_2, Cl_2, $AsCl_4AsF_6$)[4b,c] led us to develop a high-yield synthesis of pure $SNSAsF_6$ [1.7 g, 54%,‡ equation (1)],[3a] with is now carried out on a larger scale (*e.g.*

$$S_8 + 2S_4N_4 + 12AsF_5 \xrightarrow[\text{trace Br}_2]{SO_2} 8SNSAsF_6 + 4AsF_3 \qquad (1)$$

13 g, 90% yield). Although various other routes to the dithionitryl salt have been reported,[2,5–7] none has been demonstrated to give the salt in large quantities (a table containing a detailed comparison of these reactions has been deposited as SUP 56873). In addition, other SNS^+ salts may not have the same extensive simple chemistry as that of $SNSAsF_6$ due to involvement of the anion.[8]

Prior to this work, the kinetics and energetics of reaction (1) [described by equation (1)] were unknown and the purification[3a] of $SNSAsF_6$ was slow (5–7 d). Therefore the objectives of the present work were to understand the course of this intriguing reaction with and without traces of Br_2, to improve and optimise the yield of $SNSAsF_6$, to minimise the time necessary to prepare a large quantity of pure sample, and also to explore the possibility of preparing new S_xN^+ ($x > 2$) cations.

We have shown that ^{14}N NMR spectroscopy is a useful technique for the detection of SN^+, SNS^+, and other small SN-containing species.[9a] We therefore studied reaction (1) and other related reactions [*e.g.* (2) and (3)] by ^{14}N NMR

$$SNAsF_6 + \tfrac{1}{8}S_8 \longrightarrow SNSAsF_6 \qquad (2)$$

$$(S_3N_2)_2(AsF_6)_2 + 3AsF_5 \xrightarrow[\text{trace Br}_2]{SO_2} 2SNSAsF_6 + 2SNAsF_6 + AsF_3 \qquad (3)$$

spectroscopy. The results of these NMR studies and other independently studied reactions have enabled us to propose how reaction (1) proceeds and to improve it significantly.

The enthalpies of reactions (1) and (2) were estimated using published data together with the recently determined[10] enthalpy of formation of $SNSAsF_6$. We also estimated the enthalpy of reaction (4) to be *ca.* -160 ± 112 kJ mol^{-1}.

$$S_4N_4 + 6AsF_5 \xrightarrow[\text{trace Br}_2]{SO_2} 4SNAsF_6 + 2AsF_3 \qquad (4)$$

Experimental

General techniques and apparatus were as described in refs. 11–13, except where stated. Crystals suitable for X-ray analysis were mounted in dry glass capillaries under N_2. Infrared spectra were recorded as Nujol mulls between KBr or CsI plates in the 4000–200 cm^{-1} range using a Perkin-Elmer 683 spectrometer; Raman spectra were obtained from solid samples mounted in sealed capillary tubes using a Spex-Ramalab spectrometer with a slit width of 4 cm^{-1} and a Spectra Physics 164 W argon-ion green laser (5145 Å).

Nitrogen-14 NMR spectra were recorded at room temperature unlocked at 14.450 MHz on a Varian XL-200 spectrometer with nitromethane as an external standard, and acquisition parameters were as described in ref. 9*a*. No line-broadening

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† *Supplementary data available* (No. SUP 56873, 11 pp.) tables of reactions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: Torr ≈ 133 Pa.

‡ Yields given in the text refer to pure $SNSAsF_6$ recovered from the first purification. When the product is purified by successive recrystallisation the overall yield of $SNSAsF_6$ can often be improved by 10–20%.

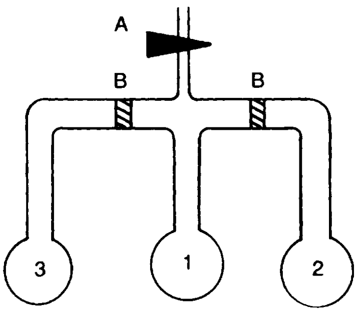

Fig. 1 Reaction vessel: A, J-Young or Rotoflo valve attached to $\frac{1}{4}$ in outside diameter glass tubing; B, medium or coarse frit

functions were applied (SN^+, δ 200, $\nu_{\frac{1}{2}}$ = *ca.* 200 Hz; SNS^+, δ −91, $\nu_{\frac{1}{2}}$ = 8 Hz).[9a] In order to compare integration between ^{14}N NMR spectra an equal number of transients was acquired, and spectra integrated in the absolute-intensity mode.

Chemical analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen. Sulfur (Fischer Scientific) was vacuum dried. Anhydrous sulfur dioxide (Matheson) was distilled onto and stored over calcium hydride. Bromine (Fischer Scientific) and CCl_3F (Matheson) were distilled onto and stored over P_4O_{10} and 3 Å molecular sieves, respectively. Arsenic pentafluoride (Ozark Mahoning) was used without further purification. The compound S_4N_4 was prepared as previously described,[10] and vacuum dried prior to use, m.p. 176–178 °C (lit.,[14] 187–187.5 °C). This was used routinely and contains S_8 as an impurity to decrease the chance of an S_4N_4 explosion [Found (Calc.) for S_4N_4: N, 30.2 (30.4); S, 69.4 (69.6%)]. Purer S_4N_4, m.p. 182–185 °C [Found (Calc.): N, 30.4 (30.4); S, 69.7 (69.6%)]. **CAUTION**: S_4N_4 will explode on grinding, scratching or on subjection to shock or heat; the explosive nature increases with purity. The melting point of S_4N_4 having a different purity is specified where it is appropriate in the text. The compounds $SNAsF_6$[15] and $(S_3N_2)_2NAsF_6$[1b] were prepared by our published methods, and the purity assessed by Raman and ^{14}N NMR ($SNAsF_6$) and IR spectroscopy [$(S_3N_2)_2NAsF_6$]; $S_4(AsF_6)_2{\cdot}nSO_2$ ($n \leq 1$)[4] and $S_8(AsF_6)_2$[16] were prepared as previously described, and the former subjected to dynamic vacuum for 5 h to remove the SO_2. The compound $S_4N_4(AsF_6)_2$ was prepared according to the procedure described in ref. 17 with slight modifications. The impure product (containing $SNAsF_6$ and $SNSAsF_6$, see below) was heated at 110 °C *in vacuo* (*ca.* 10^{-3} Torr) to sublime out the $SNAsF_6$. The residual brown solid was washed with SO_2 in a two-bulb vessel to remove $SNSAsF_6$ giving a white solid. Isolated in this manner $S_4N_4(AsF_6)_2$ is less sensitive to traces of moisture although its IR spectrum was very similar to that reported.[17]

Reactions were carried out in flame-dried three-bulb Pyrex-glass vessels incorporating a medium sintered-glass frit and closed with a Teflon-stemmed glass valve (J. Young) (see Fig. 1), except where stated. NMR samples were prepared in 10 mm thick-walled precision NMR tubes (Wilmad Glass, Buena, NJ) fitted with an O-ringette valve (PTFE stopcock, model BST/2) so that volatile materials (SO_2, AsF_5, *etc.*) could be condensed into the NMR tube through the valve. Traces of Br_2, 0.03–0.04 mmol (for small scale) or 0.09–0.1 mmol (for preparative scale), were condensed at −196 °C into the reaction mixture after addition of SO_2 and AsF_5.

Preparation of $SNSAsF_6$ *According to Equation* (1) *and Improved Purification from* SO_2–CCl_3F *Solution at* ca. −70 °C.—We recently[10] reported a large-scale preparation of highly crystalline $SNSAsF_6$ (12.8 g, 84% recovered yield) by the route shown in equation (1). The same method is employed here, except for a modification in the purification step.

Sulfur dioxide (12.45 g), AsF_5 [15.15 g, 86.16 mmol; a 2% excess relative to equation (1)], and a trace of Br_2 were successively condensed onto a mixture of S_8 [1.62 g, 6.33 mmol; a 10% deficit relative to equation (1)] and S_4N_4 (2.60 g, 14.07 mmol). A deep blue solution which formed at room temperature (r.t.) became yellowish brown over a yellow solid after stirring for 12 h. Volatile materials (SO_2, AsF_3) were removed. The crystalline brownish yellow solid (14.65 g) was treated with S_8 (0.890 g, 3.48 mmol) in fresh SO_2 (17.25 g) producing a deep blue solution which rapidly (< 1 min) changed to intense red-brown over a brown solid. Stirring was stopped after 12 h to allow unreacted S_8 to aggregate for 1 d; this was then separated from the soluble product by filtration into the second bulb. The soluble product was recrystallised four times by slow removal of the solvent. The amount of SO_2 was then reduced to 7.40 g, and CCl_3F (total 4.46 g) was added in aliquots until a dark brown solution (mainly S_x^{2+}, x = 16–22)[18–20] formed over a yellow solid ($SNSAsF_6$) when cooled to −78 °C. The cold solution was swirled gently and then filtered into the first bulb. The solvent was recondensed onto the solid and the process repeated five times. The brown material was separated from the unreacted S_8 by washing it into the third bulb and the solvent was removed giving highly crystalline $SNSAsF_6$ [13.40 g, 50.20 mmol, 90% recovered yield based on S_4N_4 used and equation (1)] in the second bulb, unreacted S_8 (0.303 g, Raman spectrum) in the first bulb and an intractable brown solid (1.621 g) in the third bulb. The $SNSAsF_6$ was then heated at *ca.* 60 °C under dynamic vacuum (10^{-3} Torr) for 14 h to sublime out small remaining traces of S_8 giving pure $SNSAsF_6$ (IR and Raman spectra). It was critical to use well dried apparatus and reagents and to add all the required amount of AsF_5 and traces of Br_2 before the reaction mixture warmed to r.t. in order to obtain a high yield of $SNSAsF_6$. Related reactions were monitored by ^{14}N NMR spectroscopy in the absence and presence of traces of Br_2 (see Table 1, experiments 1–3).

Other Reactions leading to $SNSAsF_6$.—S_4N_4 *with* $S_4(AsF_6)_2$ (*1:2 ratio*). Sulfur dioxide (10.25 g) was condensed onto a mixture of S_4N_4 (1.375 g, 7.47 mmol) and $S_4(AsF_6)_2$ (7.55 g, 14.92 mmol) at −78 °C producing a dark blue solution on warming to r.t. An intense red-brown solution formed above a pale yellow solid after stirring for about 10 min. The reaction mixture was stirred for 24 h and then left at r.t. without stirring for 48 h in order to precipitate and aggregate the S_8 by-product (see below). The solution was filtered into the third bulb and the solid was washed with SO_2 until all the soluble materials were transferred, leaving a pale yellow solid (S_8, 0.40 g, Raman spectrum) in the first bulb. The product was purified by successive recrystallisation[3a] using the third and second bulbs. The solvent was removed giving a yellow crystalline solid, $SNSAsF_6$ (4.88 g, IR spectrum) in *ca.* 60% recovered yield [based on S_4N_4 used and equation (9b) given below], in the third bulb. The brown solid (2.78 g) in the second bulb contained $SNSAsF_6$, $(S_3N_2)_2NAsF_6$, $S_4N_3AsF_6$ and $(S_3N_2)_2(AsF_6)_2$ (IR spectrum).

$(S_3N_2)_2(AsF_6)_2$ *with* $S_4(AsF_6)_2$ (*1:1 ratio*). Sulfur dioxide (5.32 g) was condensed onto a mixture of $(S_3N_2)_2(AsF_6)_2$ (0.673 g, 1.08 mmol) and $S_4(AsF_6)_2$ (0.549 g, 1.08 mmol) producing a dark blue solution at r.t. which changed to dark reddish brown above a brown precipitate after stirring for *ca.* 15 min. The solution was filtered into the third bulb and the precipitate was washed three times with SO_2 (*ca.* 1 cm³), giving a pale yellow solid (S_8, 0.04 g, Raman spectrum) in the first bulb. The red-brown soluble product was purified by successive recrystallisation[3a] giving yellow crystalline $SNSAsF_6$ [0.748 g, IR spectrum, *ca.* 70% recovered yield based on S_4N_4 used and equation (8)] in the third bulb. The red-brown solid in the second bulb contained mainly $SNSAsF_6$ and small amounts of unreacted $(S_3N_2)_2(AsF_6)_2$ (IR spectrum).

$SNAsF_6$ *with stoichiometric and excess of* S_8. Sulfur dioxide (3.24 g) was condensed at −78 °C onto a mixture of $SNAsF_6$ (0.594 g, 2.53 mmol) and S_8 (0.080 g, 0.32 mmol) in a 10 mm thick-walled NMR tube. The sample was frozen at −196 °C until the ^{14}N spectrum was obtained. The reaction mixture was warmed to r.t. producing a blue solution which gradually changed to transparent light blue after 2 h and finally to claret after *ca.* 18 h. However, the ^{14}N spectra obtained after 5 and 100 min were identical, showing only the presence of equal amounts of SNS^+ (see Table 1, experiment 4). The solvent was removed giving 0.676 g $SNAsF_6$ (IR, Raman spectra, 100% yield).

A similar reaction of $SNAsF_6$ and excess of sulfur [relative to equation (2)] produced a blue solution at r.t. which rapidly (< 1 min) changed to claret. The experimental weights and ^{14}N NMR results are summarised in Table 1, experiment 5. Unreacted S_8 (Raman spectrum) initially dissolved and gradually precipitated as light yellow crystals but the claret colour still remained.

Reactions of $S_4N_4(AsF_6)_2$ *with* (*i*) $S_8(AsF_6)_2$, (*ii*) S_8 *and* (*iii*) $S_4(AsF_6)_2$.—The objective of these reactions was to verify whether or not $S_4N_4(AsF_6)_2$ is formed as an intermediate in reaction (1) [described by equation (1)]. Three separate reactions of $S_4N_4(AsF_6)_2$ with (*i*) $S_8(AsF_6)_2$, (*ii*) S_8 and (*iii*) $S_4(AsF_6)_2$ were carried out in a two-bulb vessel in liquid SO_2. The weights of reagents and products are included in SUP 56873. In each case there was no observable colour change of the solution after 3 weeks and the IR spectra of the solids obtained after removal of the solvent showed mainly the presence of $S_4N_4(AsF_6)_2{\cdot}nSO_2$ ($n \leqslant 1$) and a small amount of $SNSAsF_6$ indicating that the reactions were incomplete.

Reaction of S_4N_4 *with* $S_4(AsF_6)_2$ (1:1 *ratio*) *leading to* $(S_3N_2)_2(AsF_6)_2$.—The compounds S_4N_4 (1.83 g, 9.92 mmol) and $S_4(AsF_6)_2$ (5.07 g, 10.02 mmol) in SO_2 (8.82 g) produced an intense red-brown solution over a pale yellow solid in 10 min. After 48 h the solution was filtered into the third bulb, and the solid was washed several times with SO_2 to remove all the soluble material giving a pale yellow solid (S_8, 0.527 g, Raman spectrum) in the first bulb. The compound CCl_3F (6.23 g total) was added in small aliquots until black crystals began to precipitate at r.t. and then left unstirred for 6 h allowing more crystals to precipitate. The transparent yellowish brown solution was filtered into the second bulb and the crystals were washed with SO_2 (*ca.* 2 cm^3). The solvent was removed giving black shiny crystals (3.04 g) in the third bulb and a brownish black more soluble solid [3.05 g; a mixture of $(S_3N_2)_2(AsF_6)_2$, $S_4N_3AsF_6$, $(S_3N_2)_2NAsF_6$ and S_4N_4 (IR spectrum)] in the second bulb. The black crystals were identified as $(S_3N_2)_2(AsF_6)_2$ [4.86 mmol, 60% recovered yield based on S_4N_4 and equation (5)] from the cell dimensions of a single crystal which were identical to those reported[21] for $(S_3N_2)_2(AsF_6)_2$. However, there were significant differences between the IR spectrum of the black crystals and those reported[21] (*e.g.* bands at 1203m, 1164m, 1149m, 1068s, and 1035m cm^{-1} in ref. 21 were not observed here). We repeated the reported preparation of $(S_3N_2)_2(AsF_6)_2$ from S_4N_4 and $S_8(AsF_6)_2$ (1:1 ratio) and found that the bulk product contained small amounts of $SNSAsF_6$ and $S_4N_3AsF_6$ (IR spectrum). However, the IR spectrum obtained on purification was identical to that of the black crystals. We have therefore obtained an IR spectrum (see SUP 56873) of a pure sample of $(S_3N_2)_2(AsF_6)_2$. Data for Nujol mull: 1010 (sh), 975vs, 890vw, 808 (sh), 715vs, 690 (sh), 665 (sh), 580s, 565 (sh), 545m, 460w, 450 (sh), 396vs and 365m cm^{-1}.

Oxidation of $(S_3N_2)_2(AsF_6)_2$ *and* $(S_3N_2)_2NAsF_6$ *with* AsF_5.—Arsenic pentafluoride (0.765 g, 4.50 mmol) was condensed at −196 °C onto $(S_3N_2)_2(AsF_6)_2$ (0.816 g, 1.18 mmol) in SO_2 (5.5 g) in a 10 mm NMR tube producing an opaque black solution at r.t. The ^{14}N NMR spectrum acquired after 5 h showed weak resonances assignable to SN^+ and SNS^+ in a 1:1 integration ratio. A trace of Br_2 was added to the solution and the colour changed from black to transparent yellow (with a tint of blue) in *ca.* 30 min. The ^{14}N NMR spectrum acquired after 1 h of addition of Br_2 showed strong SN^+ and SNS^+ peaks in a 1:1 integration ratio (see Table 1, experiment 6). The total integration of SN^+ and SNS^+ was eight times that obtained from the spectrum acquired prior to addition of Br_2. The volatile materials were removed after 2 d and the IR spectrum of the yellowish brown solid (1.142 g) showed the presence of $S_3N_2(AsF_6)_2$,[9b] $S_3N_2FAsF_6$* and a weak band attributable to $SNSAsF_6$.

A similar reaction of $(S_3N_2)_2NAsF_6$ with AsF_5 in SO_2 with a trace of Br_2 in a 10 mm NMR tube produced a blue solution at r.t. which changed to transparent yellow after *ca.* 12 h. The ^{14}N NMR spectrum acquired after 1 h, and then after 1 week of reaction, showed resonances attributable to SNS^+ and SN^+ in an essentially 1:1 integration ratio. The weights of reagents and product and the ^{14}N NMR results are given in Table 1, experiment 7. Volatile materials were removed and the IR spectrum of the yellowish brown solid showed the presence of $S_3N_2(AsF_6)_2$,[9b] $S_3N_2FAsF_6$ and a weak peak attributable to $SNSAsF_6$.

Reaction of S_4N_4 *with* $S_4N_4(AsF_6)_2$ (1:1 ratio).†—Sulfur dioxide (6.52 g) was condensed at −78 °C into a mixture of S_4N_4 (0.199 g, 1.08 mmol) and $S_4N_4(AsF_6)_2$ (0.645 g, 1.14 mmol) in a two-bulb vessel producing an intense green solution at r.t. which changed to red-brown over a black solid after 18 h. The solvent was removed and the resulting black solid (0.868 g) was washed with continuous refluxing SO_2 in an extraction vessel[22] joined to two bulbs. A greenish black solid (0.333 g) as the more soluble product and a black non-crystalline solid (0.480 g) which remained on the frit were obtained after 24 h. Chemical analysis of the black non-crystalline solid gave an empirical formula of $S_5N_5AsF_6$ and an IR spectrum and m.p. as reported[23] for $(S_5N_5AsF_6)_x$ [Found (Calc. for $S_5N_5AsF_6$): As, 17.80 (17.85); F, 26.90 (27.20); N, 16.60 (16.70); S, 38.10 (38.25%)].

The IR spectrum of the more soluble greenish black extracted product showed bands attributable to $(S_5N_5AsF_6)_x$ and unassigned bands at 1065m, 1030w, 1005w, 990vw, 690s (AsF_6^-), 580w, 515w, 440w and 390m (AsF_6^-) cm^{-1}.

Oxidation of $(S_5N_5AsF_6)_x$ *with* AsF_5 *and a trace of* Br_2.—Arsenic pentafluoride (1.06 g, 6.22 mmol) and a trace of Br_2 were successively condensed at −196 °C onto a suspension of $(S_5N_5AsF_6)_x$ (0.378 g, 0.90 mmol) in SO_2 (4.02 g) in a 10 mm thick-walled NMR tube producing a dark blue solution at r.t. which changed to opaque yellowish green after 18 h. The ^{14}N NMR spectrum showed a broad resonance due to $S_4N_4^{2+}$ at *ca.* δ −78 and to SN^+ at δ 204.2, $\nu_{\frac{1}{2}}$ = 195.3 Hz in the integration ratio of 2.6:1 (*i.e.* SN^+ = 27% of total integrated area) and a trace amount of SNS^+. After 2 d volatile materials were removed under dynamic vacuum over a period of 45 min giving a yellowish green solid (0.858 g) which was mainly $S_4N_4(AsF_6)_2{\cdot}nSO_2$ ($n \leqslant 1$) (IR spectrum) [calc. weight 0.716 g, equation (11c) below].

A similar reaction of $(S_5N_5AsF_6)_x$ (0.534 g, 1.27 mmol) with AsF_5 (1.30 g, 7.62 mmol) in SO_2 (7.28 g) with a trace of Br_2 in a vessel (25 mm long, outside diameter 14 mm, equipped with a valve) produced an opaque greenish yellow solution after 18 h. Volatile materials were removed after 3 d and the resulting greenish yellow solid (0.983 g) was heated at 60 °C *in situ* under dynamic vacuum for 1 h 40 min to almost a constant weight in order to sublime out $SNAsF_6$ and to remove SO_2 solvate from $S_4N_4(AsF_6)_2$. The resulting yellowish green solid was mainly $S_4N_4(AsF_6)_2$ (IR spectrum) [0.764 g, calc. 0.713 g on the basis of equation (11c) (below) and $(S_5N_5AsF_6)_x$ used].

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* On removal of the volatile materials $SNSAsF_6$ and $SNAsF_6$ gave some $S_3N_2(AsF_6)_2$ which on grinding abstracted a fluoride ion to give $S_3N_2FAsF_6$ and AsF_5. A detailed account of the preparation and isolation of $S_3N_2(MF_6)_2$ (M = As or Sb) is given elsewhere.[9b]

† This reaction was designed to give $S_4N_4AsF_6$ but the formation of $(S_5N_5AsF_6)_x$ indicates that, in fact, it proceeded with the mole ratio S_4N_4: $S_4N_4(AsF_6)_2$ of 1.5:1.

Reaction of S_4N_4 *with* $S_4N_4(AsF_6)_2$ *(1.5:1 ratio) at* −70 °C *followed by Oxidation with* AsF_5 *and a Trace of* Br_2.—The compound S_4N_4 (0.202 g, 1.09 mmol) and $S_4N_4(AsF_6)_2$ (0.414 g, 0.74 mmol) were gently shaken in SO_2 (3.20 g) at −78 °C [$(S_5N_5AsF_6)_x$ forms at r.t.] producing a green solution which changed to dark blue within 2 min. When all the solid had dissolved, AsF_5 and a trace of Br_2 were successively added at −196 °C producing a blue solution at r.t. which changed to yellowish green and then to brownish yellow after 10 min with all materials in solution. The ^{14}N NMR spectrum at r.t. showed the presence of a broad peak at δ −78.3, $\nu_{\frac{1}{2}}$ = 375 Hz ($S_4N_4^{2+}$), as well as peaks due to SN^+ and SNS^+ in the integration ratio of *ca.* 1:0.6:0.03. Volatile materials were removed giving a yellowish brown solid (1.377 g) [mainly $S_4N_4(AsF_6)_2 \cdot nSO_2$ ($n \leqslant 1$) and small amounts of $SNSAsF_6$, IR spectrum].

Attempted Preparation of $SNAsF_6$ *by Oxidation of* S_4N_4 *with* AsF_5 *and a Trace of* Br_2.—A large excess of AsF_5 (9.54 g, 56.18 mmol) relative to the amount required by equation (4) and a trace of Br_2 were successively condensed at −196 °C onto S_4N_4 (1.72 g, 9.36 mmol) in SO_2 (7.54 g) in a two-bulb vessel. A green solution which formed at r.t. changed to yellowish brown after 1 h. After 14 d the volatile materials were removed by a dynamic vacuum (*ca.* 45 min), and the resulting yellowish brown solid (6.94 g) was finely ground and loaded into a glass tube (300 mm long, outside diameter 30 mm) fitted with a J-Young valve. The product was heated at 110 °C for 3 d *in vacuo* (*ca.* 10^{-3} Torr) as previously described,[15] but the vessel was periodically cooled and evacuated, resulting in 2.44 g of $SNAsF_6$ [Raman, ^{14}N NMR spectra; 28% recovered yield based on equation (4) and S_4N_4 used]. The unsublimed brown solid (4.46 g) contained mainly $S_4N_4(AsF_6)_2$ and a small amount of $SNSAsF_6$ (IR spectrum). The amount of $SNAsF_6$ formed from the oxidation of slightly impure S_4N_4 (m.p. 176–178 °C) and pure S_4N_4 (m.p. 182–185 °C) at r.t. were monitored by ^{14}N NMR spectroscopy *in situ* over 2 weeks and estimated as 20 and 26%, respectively. The presence of Br_2 did not affect reaction rates. The results of these and related experiments are in SUP 56873.

Results and Discussion

Preparation of $SNSAsF_6$.—In situ ^{14}N *study of reaction* (1) [*described by equation* (1)] *in* SO_2 *solution.* Small-scale reactions gave only SNS^+ and were complete within 1 h (^{14}N NMR spectrum, colour changes) with traces of Br_2. In large-scale reactions (Table 1, experiment 1, footnote *f*) small amounts of SN^+ were also observed (^{14}N NMR spectrum).

The colour of reaction (1) without Br_2 (see Table 1, experiment 2) was blue (indicative of S_8^{2+}) after 1 week and the SNS^+ concentration was less than that from a similar reaction including Br_2 after 4 h. The recovered yield of $SNSAsF_6$ was low (30%).[3a] These results clearly show that reaction (1) is slow and non-quantitative in the absence of traces of Br_2.

Large-scale synthesis and purification. The large-scale preparation of $SNSAsF_6$ according to equation (1) gave 13.4 g of purified crystalline product in 90% recovered yield. The impure product from reaction (1) contained some $SNAsF_6$ (^{14}N NMR spectrum) when a deficit of S_8 (10%) was used. This was converted into $SNSAsF_6$ according to equation (2) on reaction with S_8. The quantity of S_8 (0.587 g, 2.29 mmol) taken up was more than that expected if only $SNAsF_6$ was present, suggesting the presence of $S_4(AsF_6)_2$ as a product in the impure material. The transitory blue colour of $S_8(AsF_6)_2$, into which $S_4(AsF_6)_2$ is converted on addition of S_8, was consistent with this proposition. The compound $S_8(AsF_6)_2$ then rapidly reacted with S_8 to give $S_x(AsF_6)_2$ (x = 16–22)[18–20] which gave the final red-brown colour of the reaction mixture and likely constituted less than 5% of the product. Thus using a 10% deficit of S_8 some $SNAsF_6$ was formed (see below) and the amount of unreacted $S_4(AsF_6)_2$ and hence $S_x(AsF_6)_2$ was reduced which facilitated the subsequent purification of $SNSAsF_6$.

$$S_8 + 2S_4N_4 + 12AsF_5 \xrightarrow[\text{trace } Br_2]{SO_2} 8SNSAsF_6 + 4AsF_3 \quad (1)$$

$$S_8 + 6AsF_5 \xrightarrow[\leqslant 5 \text{ min}]{\text{trace } Br_2} 2S_4(AsF_6)_2 + 2AsF_3 \quad \text{(i)}$$

$$2S_4(AsF_6)_2 + 2S_4N_4 \xrightarrow{\leqslant 1 \text{ h}} 2(S_3N_2)_2(AsF_6)_2 + \tfrac{1}{2}S_8 \quad \text{(ii)}$$

$$\tfrac{1}{2}S_8 + 3AsF_5 \xrightarrow[\leqslant 5 \text{ min}]{\text{trace } Br_2} S_4(AsF_6)_2 + AsF_3 \quad \text{(i')}$$

$$(S_3N_2)_2(AsF_6)_2 + 3AsF_5 \xrightarrow[\leqslant 1 \text{ h}]{\text{trace } Br_2} 2SNSAsF_6 + 2SNAsF_6 + AsF_3 \quad \text{(iii)}$$

$$S_4(AsF_6)_2 + (S_3N_2)_2(AsF_6)_2 \xrightarrow{\leqslant 1 \text{ h}} 4SNSAsF_6 + \tfrac{1}{4}S_8 \quad \text{(iv)}$$

$$\tfrac{1}{4}S_8 + 2SNAsF_6 \xrightarrow{\leqslant 5 \text{ min}} 2SNSAsF_6 \quad \text{(v)}$$

Scheme 1

Prior to this work, the impure $SNSAsF_6$ prepared according to equation (1) was purified by successive recrystallisations[3a] in liquid SO_2 requiring at least 5–7 d. Recrystallisation from SO_2–CCl_3F (*ca.* 2:1 ratio) in which $SNSAsF_6$ is virtually insoluble but $S_x(AsF_6)_2$ (x = 16–22) readily dissolves at *ca.* −70 °C produced 13.40 g (90% yield) of crystalline $SNSAsF_6$ within 4 h after reaction with S_8. As far as we are aware, this is the only route which has been demonstrated to give high yields of a crystalline, soluble, SNS^+ salt in large amounts.

Proposed Reaction Pathways for the Formation of $SNSAsF_6$ *by Reaction* (1).—*With a trace of* Br_2. In the presence of a trace of Br_2 we proposed that the key steps in the formation of $SNSAsF_6$ according to equation (1) are as shown in Scheme 1. Each of these reactions have been studied independently. There was no evidence (IR spectroscopy) for the presence of $S_4N_4(AsF_6)_2$ in the reaction products. Under these conditions S_8 is quantitatively oxidised by excess of AsF_5 in less than 5 min according to equation (i) (Scheme 1) to give $S_4(AsF_6)_2$.[4a,b] A full account of the kinetics of this reaction is given elsewhere.[4c] Since the formation of $S_4(AsF_6)_2$ and its subsequent reaction with S_4N_4 to give $(S_3N_2)_2(AsF_6)_2$ proceed very rapidly the oxidation of S_4N_4 by AsF_5 to give $S_4N_4(AsF_6)_2$ (a slow reaction) is precluded.

The significance of each reaction shown in Scheme 1 may change as the overall reaction proceeds. The oxidation of S_8 by AsF_5 to give $S_4(AsF_6)_2$ and its subsequent reaction with S_4N_4 to give $(S_3N_2)_2(AsF_6)_2$ are the dominant reactions at the beginning. However, at an intermediate stage, S_8 produced in reaction (ii) would be oxidised by AsF_5 according to (i′) and thereby compete with $(S_3N_2)_2(AsF_6)_2$ for AsF_5. This implies that only 3 mol of AsF_5 would be available to oxidise 1 mol of $(S_3N_2)_2(AsF_6)_2$ according to equation (iii). Reactions (iv) and (v) are therefore likely to be important at the end of the overall sequence.

Many of the proposed cationic intermediates are very electrophilic especially SN^+ and S_4^{2+}, and consistently high yields of $SNSAsF_6$ were only obtained when rigorously anhydrous apparatus and reagents were used. We also found that yields were decreased when the required amounts of AsF_5 and Br_2 were not added at once. Side reactions became more likely with a deficit of AsF_5. For example, the reactions of $SNSAsF_6$ with S_4N_4 to give $(S_3N_2)_2NAsF_6$[1b] [equation (6) below], and its subsequent disproportionation[1b] [equation (7) below], or further reaction with AsF_5 with loss of N_2 [equation (12) below] become dominant.

Table 1 Determination of the effect of traces of Br_2 on the course of experiments leading to $SNSAsF_6$ monitored by ^{14}N NMR spectroscopy

	Reagents (g, mmol)				Reaction condition and time[a]	Colour changes of solution	Integration of $SNSAsF_6$ mm ± 5%		Weight of $SNSAsF_6$ (g)	
No.	S_8	S_4N_4	AsF_5	SO_2					Calc.[b]	Obs.[c]
1	0.42, 1.64	0.60, 3.28	4.20, 24.72	5.76	1 h 30 min	*e*	40[f]		3.50[g]	3.48
					Trace Br_2 added[d]	*h*	100[f]			
					8 min					
2	0.109, 0.43	0.169, 0.92[i]	1.11, 6.55	3.81	*ca.* 10 min		25		0.982	0.974[g,j]
					ca. 2 h	*e*	32			
					2 h 50 min		36			
					1 week	*k*	58			
3	0.120, 0.47	0.169, 0.92[i]	1.02, 6.0	3.57	Trace Br_2				0.982	0.994
					ca. 10 min		60			
					1 h 40 min		71			
					4 h	*l*	73			
					1 week		76			
	$NSAsF_6$	S_8	SO_2							
4	0.594, 2.53	0.080, 0.32	3.24		*ca.* 5 min	*m*	64		0.675	0.676
					1 h 40 min		67			
5	0.576, 2.45	0.157, 0.61	3.32		*ca.* 5 min	*m*	62		0.654	0.658
		Excess			1 h 50 min		64		Unreacted	
									S_8(0.079 g)	0.077
										Observed weight (g) of product
	$(S_3N_2)_2(AsF_6)_2$	AsF_5	SO_2				$SNSAsF_6$	$SNAsF_6$		
6	0.816, 1.18	0.765, 4.50	5.50		5 h	*m*	5	5		1.142
					Trace Br_2 added[d]		39	42		
					1 h					
	$(S_3N_2)_2NAsF_6$	AsF_5	SO_2							
7	0.344, 0.76	2.15, 12.65	3.72		Trace Br_2					0.752
					1 h	*m*	12	13		N_2(0.006 g)
					1 week		16	18		(expected, 0.011 g)

[a] Refers to time elapsed after reaction mixture had warmed to r.t. under the specified conditions, before the acquisition of the ^{14}N NMR spectrum. [b] Based on S_4N_4 used and equation (1) for experiments 1–3 and on equation (2) for experiments 4 and 5 (see text). [c] Weight of NMR tube plus solid after removal of volatile materials minus weight of empty NMR tube. The $SNSAsF_6$ (yellowish brown solid) was characterised by IR spectroscopy. It was further characterised by Raman spectroscopy in the case of experiments 4 and 5. [d] A trace of Br_2 (0.04 mol) was added to the same sample at −196 °C then the ^{14}N NMR spectrum was acquired after the time(s) indicated. [e] Intense blue solution. [f] A weak resonance due to SN^+ was also observed on this reaction scale. [g] In a separate experiment using *ca.* 10% deficit of S_8 the IR spectrum of the black solid isolated after 2 h of reaction showed mainly the presence of $SNSAsF_6$ and weak bands assignable to $S_4N_4(AsF_6)_2$ and $(S_3N_2)_2(AsF_6)_2$. [h] A transparent yellow solution formed above a yellow crystalline solid which was dissolved by the addition of more SO_2 (12.67 g total). The dilution factor was taken into account in obtaining the integration. [i] Purer S_4N_4 (m.p. 182–185 °C) was used in this experiment. [j] A mixture of yellow and black solids, the IR spectrum of which showed the presence of $SNSAsF_6$. [k] A transparent light blue solution. [l] A blue solution which formed at r.t. changed to transparent yellow after *ca.* 1 h. [m] Experimental details, colour changes of solution and product identification are described in the Experimental section.

Without a trace of Br_2. The IR spectrum of the product isolated from reaction (1) carried out without a trace of Br_2, after 2 h of reaction, showed a strong $SNSAsF_6$ band and weak peaks attributable to $(S_3N_2)_2(AsF_6)_2$ and $S_4N_4(AsF_6)_2$ (see Table 1, footnote *g* and ref. 24). This shows that the courses of reaction (1) with and without traces of Br_2 are not the same. We propose some of the reaction steps in the reaction without Br_2 in Scheme 2. In the absence of Br_2, an excess of AsF_5 reacts with S_8 to give only $S_8(AsF_6)_2$,[4b,c] and its presence in the reaction was implied by the blue-black colour of the solution and product. The formation of $S_8(AsF_6)_2$, its reaction with S_4N_4 to give $(S_3N_2)_2(AsF_6)_2$, and the oxidation of the latter compound by AsF_5 are all much slower than the analogous reactions carried out in the presence of traces of Br_2. It is therefore likely that some S_4N_4 is oxidised by AsF_5 to give $S_4N_4(AsF_6)_2$ consistent with our experimental results. However, the reactions of $S_4N_4(AsF_6)_2$ with S_8, $S_8(AsF_6)_2$ or $S_4(AsF_6)_2$ proceeded slowly to give small amounts of $SNSAsF_6$ but were incomplete after 3 weeks.

Reaction of $SNAsF_6$ *with* S_8.—Mews[25] has shown that the reaction of $SNAsF_6$ and S_8 leads to $SNSAsF_6$. We repeated[15] this reaction on a small scale using a large excess of S_8 [relative to equation (2)] and obtained 50% recovered yield of highly crystalline $SNSAsF_6$.

We reinvestigated reaction (2) more thoroughly in order to determine the course and speed of this simple reaction. The reaction was followed *in situ* by ^{14}N NMR spectroscopy using stoichiometric and excess of S_8 [see Table 1, experiments (4) and (5)]. Only SNS^+ was observed in the ^{14}N NMR spectrum of both reactions, and therefore it is likely that the reaction did not proceed *via* any long-lived S_xN^+ ($x > 2$) intermediates. This reaction, which gave only $SNSAsF_6$, was quantitative and complete within 5 min (^{14}N NMR and IR spectra of products). The weights of $SNSAsF_6$ and of unreacted S_8 (Raman spectrum) were consistent with those calculated according to equation (2). Thus, reaction (2) still proceeds quantitatively with an excess of S_8, although we recommend the use of a

$$S_8 + 2S_4N_4 + 12AsF_5 \xrightarrow{Br_2\ absent} 8SNSAsF_6 + 4AsF_3 \quad (1')$$

$$S_8 + 3AsF_5 \xrightarrow{ca.\ 18\ h} S_8(AsF_6)_2 + AsF_3 \quad (i)$$

$$S_8(AsF_6)_2 + S_4N_4 \xrightarrow{ca.\ 24\ h} (S_3N_2)_2(AsF_6)_2 + \tfrac{3}{4}S_8 \quad (ii)$$

$$(S_3N_2)_2(AsF_6)_2 + 3AsF_5 \xrightarrow{ca.\ 12\ h} 2SNSAsF_6 + 2SNAsF_6 + AsF_3 \quad (iii)$$

$$S_4N_4 + 3AsF_5 \xrightarrow{ca.\ 18\ h} S_4N_4(AsF_6)_2 + AsF_3 \quad (iv)$$

$$\tfrac{3}{4}S_8 + \tfrac{9}{4}AsF_5 \xrightarrow{ca.\ 18\ h} \tfrac{3}{4}S_8(AsF_6)_2 + \tfrac{3}{4}AsF_3 \quad (v)$$

$$2SNAsF_6 + \tfrac{1}{2}S_8(AsF_6)_2 \xrightarrow{\leqslant 5\ min} 2SNSAsF_6 + \tfrac{1}{2}S_4(AsF_6)_2 \quad (vi)$$

Scheme 2

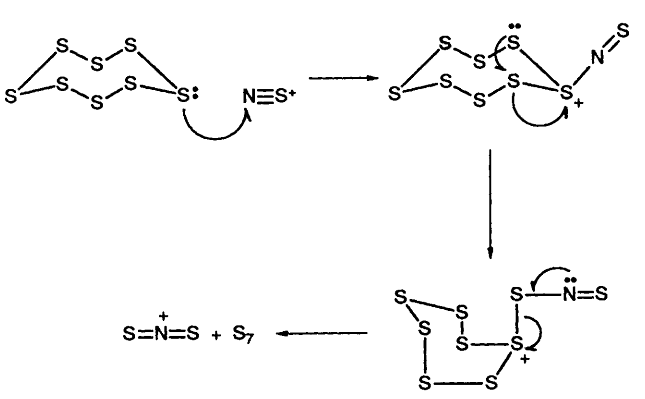

Fig. 2 Proposed reaction pathway for the formation of $SNSAsF_6$ from S_8 and SN^+

stoichiometric (or a slight deficit) amount of S_8 in order to prevent contamination of $SNSAsF_6$.

The reaction of $SNAsF_6$ with S_8 may proceed by donation of a pair of electrons from S_8 into the π^* lowest unoccupied molecular orbital (LUMO) of $SNAsF_6$. This process would result in the lengthening and weakening of the bonds around the resultant three-co-ordinate positively charged sulfur centre,[26] and facilitate the formation of S_7 concurrent with elimination of a sulfur atom from the S_8 ring (see Fig. 2) by SN^+; $S_8{}^+$ derivatives of the proposed intermediate (Fig. 2) are unknown, whereas several S_7X^+ (X = I, Br, $S_5S_7{}^+$ in $S_{19}{}^{2+}$) are stable cations.[19,20,26] The resulting S_7 may isomerise to S_8 or preferentially react with another SN^+ unit in a similar manner giving S_6 and so on.

Preparation of $(S_3N_2)_2(AsF_6)_2$.—The reaction of S_4N_4 and $S_4(AsF_6)_2$ in a 1:1 ratio led to the formation of $(S_3N_2)_2(AsF_6)_2$ [equation (5)] in *ca.* 60% yield in about 1 h (colour changes). Its

$$S_4N_4 + S_4(AsF_6)_2 \longrightarrow (S_3N_2)_2(AsF_6)_2 + \tfrac{1}{4}S_8 \quad (5)$$

infrared spectrum was identical to that of $(S_3N_2)_2(AsF_6)_2$ prepared from the reaction of S_4N_4 and $S_8(AsF_6)_2$ but different from that previously reported[21] (see Experimental section). This is a new synthesis of $(S_3N_2)_2(AsF_6)_2$. The other products of the reaction were S_8 (Raman), $(S_3N_2)_2NAsF_6$ (IR) and $S_4N_3AsF_6$ (IR spectrum). The formation of $(S_3N_2)NAsF_6$ can be accounted for by the reaction of the product, $(S_3N_2)_2(AsF_6)_2$, with $S_4(AsF_6)_2$ starting material, leading to $SNSAsF_6$ [see equation (8) below] which may then react with S_4N_4 to give $(S_3N_2)_2NAsF_6$ [1b] [see equation (6)] which is known to disproportionate[1b] according to equation (7), to give $S_4N_3AsF_6$ and S_4N_4.

$$SNSAsF_6 + S_4N_4 \longrightarrow (S_3N_2)_2NAsF_6 \quad (6)$$

$$2(S_3N_2)_2NAsF_6 \longrightarrow 2S_4N_3AsF_6 + S_4N_4 \quad (7)$$

Other Reactions leading to $SNSAsF_6$.—*Reaction of* $S_4(AsF_6)_2$ *with* $(S_3N_2)_2(AsF_6)_2$ *or* S_4N_4 *according to equations* (8) *or* (9b). The compound $(S_3N_2)_2(AsF_6)_2$ reacted with S_4N_4 to give crystalline $SNSAsF_6$ (IR spectrum) in *ca.* 70% recovered yield [equation (8)] and S_8 (Raman spectrum) within 1 h as indicated by colour changes.

$$(S_3N_2)_2(AsF_6)_2 + S_4(AsF_6)_2 \xrightarrow[\leqslant 1\ h]{SO_2} 4SNSAsF_6 + \tfrac{1}{4}S_8 \quad (8)$$

The reaction of S_4N_4 and $S_4(AsF_6)_2$ [1:2 ratio, equation (9a)], designed to give S_3NAsF_6 (S_3N^+ is isolobal with $S_4{}^{2+}$ and S_2N_2), led instead to the formation of $SNSAsF_6$ in about 1 h [see equation (9b)] in *ca.* 60% recovered yield. The other products were S_8 (Raman), $(S_3N_2)_2(AsF_6)_2$, $(S_3N_2)_2NAsF_6$ and $S_4N_3AsF_6$ (IR spectrum). Reaction (9b) reasonably proceeds *via* equations (5) and (8).

$$S_4N_4 + 2S_4(AsF_6)_2 \not\longrightarrow 4S_3NAsF_6 \quad (9a)$$

$$S_4N_4 + 2S_4(AsF_6)_2 \longrightarrow 4SNSAsF_6 + \tfrac{1}{2}S_8 \quad (9b)$$

Oxidation of $(S_3N_2)_2(AsF_6)_2$ *with* AsF_5.—A preliminary study of this reaction [equation (3)] has been reported,[9a] and an account of the solid $S_3N_2(AsF_6)_2$ is given elsewhere.[9b] Reaction (3) was followed in solution by ^{14}N NMR spectroscopy, and the results are presented in Table 1, experiment 6. Equal amounts of SNS^+ and SN^+ were given, the reaction being facilitated by traces of Br_2. The reaction may proceed through an $S_3N_2BrAsF_6$ intermediate[27] followed by bromide-ion abstraction by AsF_5 to give $S_3N_2(AsF_6)(AsF_5Br)$, the dication then dissociates into SN^+ and SNS^+.[9a,b] The AsF_5Br^- ion may then react with AsF_5 according to equation (10) regenerating the Br_2 facilitator.

$$2AsF_5Br^- + AsF_5 \longrightarrow 2AsF_6{}^- + AsF_3 + Br_2 \quad (10)$$

Preparation of $SNAsF_6$ *by Reaction* (4).—The enthalpy change for reaction (4) was estimated (see below) as −40 ± 28 kJ mol^{-1} per $SNAsF_6$ which implied that the reaction might proceed. It was therefore followed *in situ* by ^{14}N NMR spectroscopy in small-scale reactions with and without traces of Br_2 but no definite difference in the rates were observed. The yield of $SNAsF_6$ was estimated as *ca.* 20–30%. The major product in all reactions (*ca.* 70–80% of the product) was $S_4N_4(AsF_6)_2$ (^{14}N NMR $\delta = -78.3$, $\nu_{\frac{1}{2}} = 375$ Hz; and IR spectra). Small amounts of $SNSAsF_6$ (*ca.* 3% of the product) were also formed. The recovered yield of *ca.* 30% of isolated $SNAsF_6$ obtained on a preparative scale was consistent with the ^{14}N NMR results.

The formation of $S_4N_4(AsF_6)_2$ as a major product in reaction (4) was not surprising as it has been prepared by Gillespie *et al.*[17] according to equation (11a) but without Br_2. It is possible

$$S_4N_4 + 3AsF_5 \longrightarrow S_4N_4(AsF_6)_2 + AsF_3 \quad (11a)$$

$$S_4N_4(AsF_6)_2 + \tfrac{3}{2}S_4N_4 \longrightarrow 2S_5N_5AsF_6 \quad (11b)$$

$$2S_5N_5AsF_6 + 6AsF_5 \longrightarrow 2SNAsF_6 + 2S_4N_4(AsF_6)_2 + 2AsF_3 \quad (11c)$$

that $S_4N_4(AsF_6)_2$, which initially formed, reacted with S_4N_4 to give $S_5N_5AsF_6$ which was then oxidised by AsF_5 as described in equations (11a)–(11c).

In a separate experiment we showed that polymeric $(S_5N_5AsF_6)_x$ was formed from the reaction of S_4N_4 with $S_4(AsF_6)_2$ in liquid SO_2 at r.t. which on oxidation by AsF_5 with traces of Br_2 gave SN^+ and $S_4N_4^{2+}$ in the ratio of 1:2.6 (^{14}N NMR spectroscopy). It is possible that monomeric $S_5N_5AsF_6$ is formed in reaction (4) and that it reacts with AsF_5 according to equation (11c). This was supported by the reaction of $S_4N_4(AsF_6)_2$ with S_4N_4 (both of which are insoluble in SO_2) at −70 °C which gave a solution without a precipitate, which suggested that monomeric, rather than polymeric $(S_5N_5AsF_6)_x$ was generated *in situ*. Reaction of this solution with AsF_5 with a trace of Br_2 gave about 37% yield of $SNAsF_6$ as well as $S_4N_4(AsF_6)_2$ (^{14}N NMR spectroscopy). The $SNAsF_6$ may also arise in part from the S_8 impurity in S_4N_4; S_8 and S_4N_4 in the presence of traces of Br_2 react with AsF_5 to give first $(S_3N_2)_2(AsF_6)_2$ and then $SNSAsF_6$ and $SNAsF_6$ (see Scheme 1). The $SNSAsF_6$ may react with S_4N_4 to give $(S_3N_2)_2NAsF_6$[1b] which on oxidation with AsF_5 gives $SNAsF_6$, $SNSAsF_6$ and N_2.

$$2(S_3N_2)_2NAsF_6 + 9AsF_5 \xrightarrow[SO_2]{\text{trace } Br_2} 4SNAsF_6 + 4SNSAsF_6 + N_2 + 3AsF_3 \quad (12)$$

The $SNSAsF_6$ may further react with S_4N_4 and, by the process given above, multiply the amount of $SNSAsF_6$ and $SNAsF_6$. For an infinite number of cycles the SN^+ to SNS^+ ratio is 2:1. The observed SN^+ to SNS^+ ratio is *ca.* 7:1, implying most (but not all) of the $SNAsF_6$ produced in equation (4) is formed *via* $S_5N_5^+$.

Thermodynamic Aspects of the Preparation of $SNSAsF_6$ *by Equations* (1) *and* (2) *and* $SNAsF_6$ *by Equation* (4).—The recent[10] determination of the enthalpy of formation of $SNSAsF_6$ as −1413.8 ± 1.9 kJ mol^{-1} has enabled us to analyse the thermodynamics of reactions (1) and (2). With ΔH_f $(AsF_3) = -858.14$,[28] ΔH_f $(AsF_5) = 1237 \pm 0.8$[29] and ΔH_f $(S_4N_4) = 469 \pm 1$ kJ mol^{-1},[30] the enthalpy change of reaction (1) is deduced as −836.8 ± 16 kJ mol^{-1} *i.e.* thermodynamically allowed as observed.

The compound $SNSAsF_6$ was also prepared from the reaction of $SNAsF_6$ with sulfur [equation (2)]. The enthalpy of formation of $SNAsF_6$ has been estimated[31] as −1347.5 ± 28 kJ mol^{-1} which gives the enthalpy change for reactions (2) and (4) as −66 ± 28 and −160 ± 112 kJ mol^{-1} (or −40 ± 28 kJ mol^{-1} per $SNAsF_6$). The probable role of entropy in reaction (2) was assessed using Bartlett's[32] relationship for A^+B^- salts [equation (13)] where $S°$ is in J K^{-1} mol^{-1} and V_m is the

$$S° = 1.85V_m \quad (13)$$

molar volume (Å^3) of one unit of A^+B^- in the solid. The molar entropy of S_8 has been experimentally determined as 430.9 J K^{-1} mol^{-1},[33] and those of $SNSAsF_6$ (V_m = 167 Å^3)[3b] and $SNAsF_6$ [V_m(estimated) = 138.8 Å^3][31] were estimated from equation (13) as 308.8 and 256.5 J K^{-1} mol^{-1} respectively. These data give the entropy change of reaction (2) as −1.6 J K^{-1} mol^{-1} (and ΔG as −65.5 kJ mol^{-1} at r.t.).

Conclusion

The energetics and course of the reaction of S_8, S_4N_4 and AsF_5 with and without traces of Br_2, leading to $SNSAsF_6$, are now reasonably well understood. The synthesis of $SNSAsF_6$ has been improved significantly and the time required to isolate large quantities (*ca.* 13 g) of the pure compound was reduced from *ca.* 9 to 2 d. The energetics of the reaction of $SNAsF_6$ and S_8 leading to $SNSAsF_6$ has also been estimated, and the reaction shown to proceed rapidly with no observable (^{14}N NMR spectroscopy) intermediates.

Our estimate of a marginally favourable enthalpy for the reaction of S_4N_4 and AsF_5 to give $SNAsF_6$ (−40 ± 28 kJ mol^{-1} per $SNAsF_6$) led us to reinvestigate this reaction. About 30% yield of $SNAsF_6$ as well as the previously reported $S_4N_4(AsF_6)_2$ were produced. Reaction pathways were proposed for this and the reactions leading to SNS^+, all of which were supported by separate experiments followed by *in situ* ^{14}N NMR spectroscopy.

Our attempts to prepare new sulfur–nitrogen cations (*e.g.* S_3N^+) were unsuccessful, but led to the discovery of new reactions of S_4^{2+}, S_8^{2+}, $S_4N_4^{2+}$ and $(S_5N_5^+)_x$.

This work further[4] illustrates the synthetic potential of AsF_5 as a facile oxidising agent in the presence of traces of Br_2, the utility of ^{14}N NMR spectroscopy in following[9a] the course of reaction of small sulfur–nitrogen cations *in situ*, and the use of energetics as a guide in synthesis.[34]

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