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Mass Spectrometric Study of the Vapor-Phase Species of Brominated Polymeric Sulfur Nitride and Tetrasulfur Tetranitride

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The gas-phase species volatilized from $(\text{SN})_x$ treated with bromine and tetrasulfur tetranitride (S_4N_4) treated with Br_2 and ICl were studied using mass spectrometric techniques. Conventional electron impact, chemical ionization, modulated molecular beam, and phase-angle mass spectrometry techniques were used to identify the gas-phase species. The species volatilized from brominated $(\text{SN})_x$ and brominated S_4N_4 were identical, consisting of Br_2 , NSBr , $(\text{SN})_4$ isomers, and smaller amounts of HBr , S_2Br_2 , and other sulfur-nitrogen compounds. The gas-phase species observed over S_4N_4 treated with ICl were I_2 , ICl , S_4N_4 , NSCl , HCl , HI , and small amounts of S_2Cl_2 and other sulfur-nitrogen compounds; Cl_2 and NSI were not observed. The vapors of S_4N_4 brominated in CS_2 solution were examined and found to yield HSCN , BrSCN , and CS_3N_2 species, in addition to HBr , NSBr , Br_2 , and sulfur-nitrogen compounds. The gas-phase products formed on exposure of brominated samples to air were also studied.

Introduction

It has recently been reported that the addition of bromine to polymeric sulfur nitride, $(\text{SN})_x$, results in the formation of blue-black brominated $(\text{SN})_x$ crystals.¹⁻³ On exposure to Br_2 vapor, the $(\text{SN})_x$ crystals swell in directions perpendicular to the $(\text{SN})_x$ chains and form fibrous crystals of composition $(\text{SNBr}_{0.5})_x$.^{1,3} By evacuation at 10^{-5} Torr for 1 h, a small amount of bromine is removed, resulting in a final composition of $(\text{SNBr}_{0.4})_x$.³ It has also been reported^{1,3} that brominated $(\text{SN})_x$ may be sublimed to form brominated $(\text{SN})_x$ films, analogous to the behavior of $(\text{SN})_x$.⁴ Recent work by Smith et al.⁵ has shown that the major gas-phase species of $(\text{SN})_x$ is a noncyclic $(\text{SN})_4$ isomer having properties quite different from tetrasulfur tetranitride, S_4N_4 . The $(\text{SN})_4$ isomer spontaneously polymerizes on cool surfaces to form $(\text{SN})_x$ films.⁵

We have studied the vapor-phase species using a variety of mass spectrometric techniques in order to identify the vapor-phase species formed upon sublimation of $(\text{SNBr}_{0.4})_x$, to better understand the mechanism of bromination and vaporization, and to characterize the species involved in film formation. Additionally, we have examined the vapor-phase species of the analogous compounds formed when S_4N_4 is halogenated with Br_2 and ICl and when S_4N_4 is brominated in CS_2 solution. Brominated S_4N_4 is of particular interest since work reported elsewhere⁶ has found physical and chemical properties nearly indistinguishable from those of $(\text{SNBr}_{0.4})_x$. In the present work, we identify the major gas-phase species for each of these compounds and show that the spectra of brominated $(\text{SN})_x$ and brominated S_4N_4 are nearly identical.

Experimental Section

Samples of $(\text{SN})_x$ and S_4N_4 modified by reaction with Br_2 and ICl were prepared as described previously.^{1,3}

Two mass spectrometers were used in this study. The first was a modulated molecular beam instrument with two regions of differential pumping, equipped with an Extranuclear Laboratories

crossed-beam analyzer and quadrupole mass filter and designed to operate in both the crossed-beam and axial modes. Samples to be studied were placed in a Teflon Knudsen cell which may be operated at temperatures between 20 and 200 °C. The molecular beam effusing through a 1-mm orifice into the first differentially pumped region (maintained at $\leq 10^{-1}$ Torr) is directed at a molecular beam skimmer, which allows a well-collimated molecular beam to enter the analyzer section. The molecular beam is modulated using a rotating toothed wheel and subsequently passes through the ion source. The molecular-beam technique allows one to study unstable or reactive species in the effusive beam because of the total absence of surface-related phenomena; the molecules studied do not collide with surfaces after leaving the Knudsen cell. Modulation of the beam allows the complete elimination of background species from the mass spectra. Mass spectra were obtained at 10, 15, 20, 25, 70, and 100 eV and at temperatures from 40 to 150 °C. Individual samples were examined over extended periods (up to 12 h) to identify species which may be selectively volatilized. The technique of phase-angle spectrometry was used to determine the molecular weight of the gas-phase species obtained by sublimation of brominated $(\text{SN})_x$ and halogenated S_4N_4 samples.⁵ In this technique, the distance between the chopper and the ionizer is increased from 1 to 16 cm. The phase shifts resulting from the mass-dependent flight times of molecular species are related to the molecular weight after calibration with known species.

Electron impact (EI) and chemical ionization (CI) mass spectra were also obtained using a Hewlett-Packard 5980A mass spectrometer equipped with a dual EI-CI source and a conventional-solids inlet probe. Argon, methane, isobutane, and ammonia were used as CI reagents. The total pressure in the source was approximately 1 Torr in these experiments and all spectra were obtained using an electron energy of 70 eV.

Results

The mass spectra obtained using a conventional ion source and 70-eV EI ionization conditions gave spectra of brominated $(\text{SN})_x$ and brominated S_4N_4 which are essentially indistinguishable. Figure 1(a) shows the spectra obtained for brominated $(\text{SN})_x$ at 120 °C under these conditions. Both the brominated $(\text{SN})_x$ and brominated S_4N_4 show distinct multiplets centered at approximately m/e 358, 438, and 520, with the series of peaks around m/e 358 the most intense. These multiplets may be ascribed to one or more compounds con-

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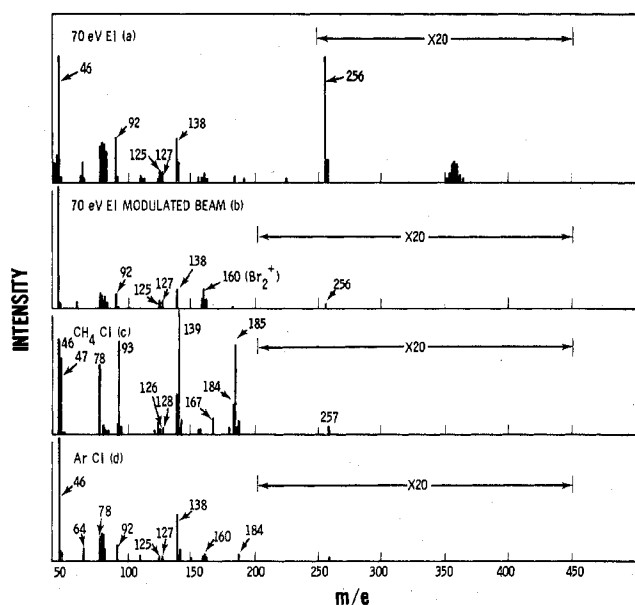


Figure 1. Comparison of the 70-eV EI conventional mass spectrum (a), the 70-eV EI modulated-beam spectrum (b), the methane chemical ionization spectrum (c), and the argon chemical ionization mass spectrum (d).

taining three, four, and five bromine atoms, respectively. It was not possible to identify the other elemental constituents of these species; however, elements other than sulfur and nitrogen are present.

While quite similar ion clusters have been observed in the mass spectra of brominated (SN)_x using other mass spectrometers, the modulated-beam and chemical ionization (CI) studies quite clearly show that these are experimental artifacts, due to surface-related reactions occurring in conventional mass spectrometer ion sources. The 70-eV EI modulated molecular-beam spectra shown in Figure 1(b) show no evidence of the higher mass clusters seen in the conventional mass spectra. The high-mass clusters were not observed in the modulated-beam experiment under any mass spectrometer conditions for temperatures from 50 to 150 °C for either brominated (SN)_x or brominated S₄N₄. The absence of surface-related phenomena in the modulated-beam experiment is due to the "collision-free" conditions after leaving the Knudsen cell. Samples sublimed in the Teflon cell are collimated into a small, solid-angle effusive beam which passes through the mass spectrometer ion source without surface collisions.

Further evidence to support the surface-related origin of the high-mass clusters is provided by the chemical ionization spectra. We failed to observe any ions indicative of these heavier species using argon, methane, isobutane, or ammonia as CI reagents. The reduction in surface-related reactions in the CI mode, as compared to EI ionization, is related to the increased pressure and gas flow, the increased ionization efficiency with the appropriate CI reagent, and decreased importance of diffusion to hot surfaces in the source. The increased importance of sulfur impurity (as S₈⁺, *m/e* 256) in the conventional EI spectra is also due to decomposition of sulfur-nitrogen compounds in the ion source. S₈ is a known product of the thermal decomposition of (SN)_x.⁵ Thus, the high-mass clusters may certainly be dismissed as artifacts related to surface reactions of unstable or reactive compounds in conventional ion sources.

The modulated-beam mass spectra of brominated (SN)_x and brominated S₄N₄ contain peaks due to both binary sulfur-nitrogen compounds and several halogen-containing compounds. The spectra of these compounds obtained under essentially identical conditions are given in Table I.

Table I. Comparison of 25-eV Electron Impact Spectra for Brominated (SN)_x and Brominated S₄N₄ at 90 °C^a

<i>m/e</i>	Principal ion ^b	Brominated (SN) _x	Brominated S ₄ N ₄
46	SN ⁺	100	100
47	SNH ⁺ , i	2.1	2.3
48	i	5.0	4.6
64	S ₂ ⁺	2.0	1.5
78	S ₂ N ⁺	12.4	12.6
79	Br ⁺	3.3	1.8
80	HBr ⁺	1.9	1.5
81	Br ⁺	3.1	1.3
82	HBr ⁺ , i	0.5	0.3
92	S ₂ N ₂ ⁺	26	32
93	S ₂ N ₂ H ⁺ , i	1.6	1.9
94	i	2.3	3.1
110	S ₃ N ⁺	1.0	0.9
111	SBr ⁺	1.0	0.5
113	SBr ⁺	1.0	0.5
124	S ₃ N ₂ ⁺	1.5	1.8
125	NSBr ⁺	4.4	2.1
127	NSBr ⁺	4.4	2.1
138	S ₃ N ₃ ⁺	21	20
139	S ₃ N ₃ H ⁺ , i	1.1	1.2
140	i	3.0	2.8
156	S ₄ N ₂ ⁺	0.5	0.5
158	Br ₂ ⁺	0	0
160	Br ₂ ⁺	0	0
162	Br ₂ ⁺	0	0
184	S ₄ N ₄ ⁺	1.0	0.6

^a These spectra were obtained under identical instrumental conditions after heating at 60–90 °C under vacuum for 3 h.

^b Significant isotopic contributions of ³³S, ³⁴S, or ¹⁵N to S_xN_y⁺ ions are indicated by i.

Table II. Molecular Weights of the Molecular Precursor of Ions Determined by Phase-Angle Spectrometry (PAS)

Sample	Ion (<i>m/e</i>)	Mol wt by PAS	Neutral precursor
S ₄ N ₄	S ₄ N ₄ ⁺ (184)	185 ± 5	S ₄ N ₄
	S ₃ N ₃ ⁺ (138)	185 ± 5	S ₄ N ₄
	S ₂ N ₂ ⁺ (92)	185 ± 5	S ₄ N ₄
	SN ⁺ (46)	185 ± 5	S ₄ N ₄
(SN) _x	S ₃ N ₃ ⁺ (138)	187 ± 6	(SN) ₄
	S ₂ N ₂ ⁺ (92)	180 ± 10	(SN) ₄
	SN ⁺ (46)	180 ± 6	(SN) ₄
	S ₃ N ₃ H ⁺ (139)	220 ± 15	?
	S ₂ N ₂ H ⁺ (93)	220 ± 15	?
	SNH ⁺ (47)	220 ± 15	?
Brominated (SN) _x and Brominated S ₄ N ₄	S ₂ Br ₂ ⁺ (224)	220 ± 20	S ₂ Br ₂
	Br ₂ ⁺ (160)	160 ± 5	Br ₂
	S ₃ N ₃ ⁺ (138)	178 ± 10	(SN) ₄
	NSBr ⁺ (125, 127)	131 ± 10	NSBr
	SBr ⁺ (111, 113)		NSBr, S ₂ Br ₂ ^a
	S ₂ N ₂ ⁺ (92)	160 ± 28	(SN) ₄ , S ₂ N ₂ ^a
	HBr ⁺ (80, 82)	78 ± 5	HBr
	Br ⁺ (79, 81)		Br ₂ , NSBr, HBr ^a
SN ⁺ (46)	173 ± 15	(SN) ₄ , NSBr ^a	
S ₄ N ₄ + ICl	I ₂ ⁺ (254)	250 ± 20	I ₂
	S ₄ N ₄ ⁺ (184)	184 ± 10	S ₄ N ₄
	ICl ⁺ (162, 164)	160 ± 15	ICl
	S ₃ N ₃ ⁺ (138)	182 ± 10	S ₄ N ₄
	HI ⁺ (128)	130 ± 10	HI
	I ⁺ (127)		I ₂ , HI, ICl ^a
	S ₂ Cl ⁺ (99, 101)	97 ± 8	S ₂ Cl ₂
	NSCl ⁺ (81, 83)	79 ± 6	NSCl
SCI ⁺ (67, 69)		NSCl, S ₂ Cl ₂ ^a	

^a In each of these cases, more than one neutral precursor may contribute to formation of a given ion.

Phase-angle spectrometry⁵ was utilized to determine the approximate molecular weight of the important ions in the mass spectra; these results are summarized in Table II along with the suspected neutral precursor. Also included are results

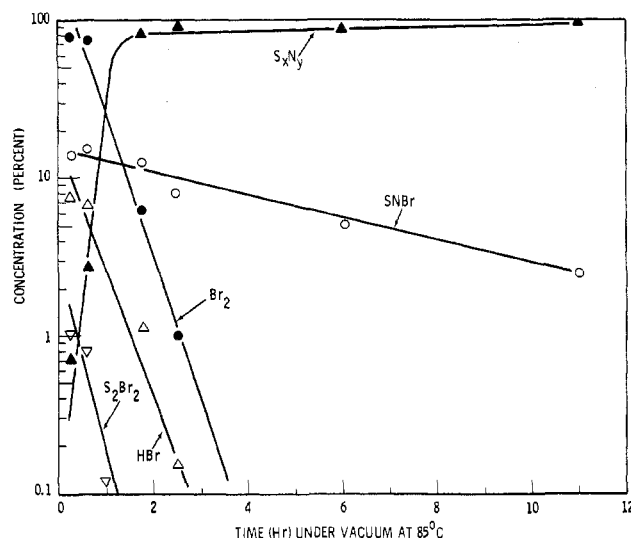


Figure 2. Concentration as a function of time for the various gas-phase species volatilized from brominated $(\text{SN})_x$ upon heating at 85°C . The absolute concentrations may differ by a factor of 2.

for S_4N_4 , $(\text{SN})_x$, and S_4N_4 treated with ICl .

The identification of the gas-phase species allowed a semiquantitative determination of the concentrations of the various components over brominated $(\text{SN})_x$ and brominated S_4N_4 . Figure 2 gives the approximate concentrations corrected for estimated multiplier response and ionization cross sections of the various vapor-phase species in brominated $(\text{SN})_x$. The sample was quickly heated (<15 min) to 85°C and the relative concentrations of the various species were observed for 11 h. The concentrations reported in Figure 2 may be in error by as much as a factor of 2 due to uncertainties in the transmission efficiencies and the estimated relative ionization cross sections of the molecular species. Results similar to those in Figure 2 were obtained for brominated S_4N_4 ; however, volatilization of the brominated species was approximately twice as rapid, leading to greater initial concentrations.

As indicated by Figure 2, the mass spectra of brominated $(\text{SN})_x$ and halogenated S_4N_4 were quite dependent on the sample history. Different heating rates result in differing concentrations of the brominated species at higher temperatures (e.g., 100 – 150°C). For example, heating brominated $(\text{SN})_x$ at 80°C for 3 h removes essentially all of the molecular bromine. Further heating will yield NSBr as the only brominated compound. If samples are heated more rapidly (to 150°C in less than 15 min), Br_2 will be observed over the entire course of the heating and be absent after ~ 30 min at 150°C . Similar behavior was observed for S_4N_4 treated with Br_2 or ICl ; however, loss of Br_2 occurs approximately twice as fast in S_4N_4 than $(\text{SN})_x$ and the halogenated compounds in the latter sample (I_2 , ICl , HI , NSCl) were observed to volatilize at even lower temperatures ($\geq 45^\circ\text{C}$).

We have also examined the mass spectra of S_4N_4 samples brominated in CS_2 solution. The mass spectra of this orange solid (as compared to the blue-black product of the gas-phase bromination) contains all species observed for samples prepared by gas-phase bromination of S_4N_4 , along with additional species due to reaction with CS_2 . The major species containing carbon have been identified as BrSCN , CS_3N_2 , and HSCN (thiocyanic acid).

Discussion and Conclusions

While the addition of bromine to $(\text{SN})_x$ to form a compound of composition $(\text{SNBr}_{0.4})_x$ has been reported only recently,^{1,3} there have been several literature reports on the bromination of S_4N_4 .⁷⁻⁹ The reaction of bromine with S_4N_4 in CS_2 was originally thought to produce polythiazyl bromide $(\text{NSBr})_x$.⁷

More recent work, however, has suggested that the compound is $\text{S}_3\text{N}_2\text{Br}_2$,⁸ or a mixture of $\text{S}_3\text{N}_2\text{Br}_2$ with $\text{S}_4\text{N}_3\text{Br}$,⁹ and indicated the presence of NSBr as a soluble intermediate in the solution-phase bromination reaction.¹⁰ Our results show monomeric NSBr to be present in the vapors sublimed from S_4N_4 brominated in CS_2 solution but also clearly demonstrate the reactivity of CS_2 , resulting in HSCN (thiocyanic acid), BrSCN , and CS_3N_2 species in the vapors.

The gas-phase species volatilized from brominated $(\text{SN})_x$ and S_4N_4 may be divided into the brominated species (Br_2 , NSBr, and smaller amounts of HBr and S_2Br_2), which dominate upon initial heating at low temperatures ($<80^\circ\text{C}$), and the sulfur-nitrogen compounds which are composed of a number of sulfur-nitrogen species, including one or more isomers of S_4N_4 . Also present in very small amounts is the "hydride impurity" of $(\text{SN})_x$, identified in previous work.¹¹ For S_4N_4 treated with ICl the halogenated gas-phase species are ICl , I_2 , HCl , HI , NSCl , and a very small amount of S_2Cl_2 .

By heating brominated $(\text{SN})_x$ and S_4N_4 for several hours at 70 – 80°C under vacuum, Br_2 , HBr, and S_2Br_2 will be absent from the gas phase (i.e., they amount to less than 0.1 mol % of the vapors). Further heating at temperatures too low for decomposition ($<160^\circ\text{C}$) yields only NSBr, a mixture of sulfur-nitrogen compounds composed primarily of an S_4N_4 isomer, and a very small amount of the sulfur-nitrogen hydride species.⁵ As shown in Figure 2, prolonged heating at relatively low temperatures ($<90^\circ\text{C}$) will ultimately result in $(\text{SN})_x$ crystals which are nearly completely free of bromine. [Visual examination of brominated $(\text{SN})_x$ crystals treated in this fashion revealed the crystals had partially taken on a bronze, metallic luster indicative of $(\text{SN})_x$ prior to bromination.] Thus, the dominant gas-phase bromine species produced upon volatilization of brominated $(\text{SN})_x$ and S_4N_4 are a relatively volatile Br_2 component and less volatile NSBr component. The NSBr isomer is suggested by the fragmentation data.

Two rationalizations of these results are possible. First, bromine is present in the samples in two forms—as loosely bound Br_2 and as a second, more strongly bound form which yields NSBr upon sublimation. The Br_2 may be present in the interfiber region of modified $(\text{SN})_x$ crystals³ and be easily lost upon heating. A more strongly associated component, resulting from actual chemical bonding of bromine to the $(\text{SN})_x$ chains, may yield NSBr upon sublimation. Second, bromine may be present in a form which decomposes upon mild heating to yield Br_2 and a less volatile species yielding gaseous NSBr on sublimation. Recently obtained Raman results suggest that bromine may be present in the $(\text{SN})_x$ crystals as Br_3^- .⁶ The Br_3^- entity may decompose upon heating to yield Br_2 and the more strongly bound bromine species. Regardless of how the bromine is initially present in Br_2 -modified $(\text{SN})_x$, after the initial heating which produced Br_2 in the vapor phase, the present results strongly suggest that the remaining bromine (which yields NSBr upon sublimation) is present as a single form chemically bonded to the $(\text{SN})_x$ chains.

At low temperatures (40 – 80°C) and during the initial heating of both samples, the mass spectra also show the presence of significant amounts (10–30%) of smaller sulfur-nitrogen species (e.g., S_2N , S_2N_2 , S_3N_2 , S_3N_3). These species have been tentatively identified in $(\text{SN})_x$ vapors⁵ and in the thermal decomposition of S_4N_4 vapors.¹² In this work we measured similar low appearance potentials for each of these species and noted shifts in the phase-angle spectrometry results indicating contributions of lower molecular weight species at lower temperature (during the initial heating). The major difference in the mass spectra of brominated $(\text{SN})_x$ and brominated S_4N_4 at less than 80°C is the increased importance of the S_4N_4^+ ion (m/e 184) in the brominated S_4N_4 ,

Table III. Comparison of the Major S_xN_y⁺ Ions in (SN)_x, S₄N₄, and Their Brominated Analogues^a

Ion (<i>m/e</i>)	Brominated			
	(SN) _x ^b	S ₄ N ₄ ^c	(SN) _x ^b	S ₄ N ₄ ^b
SN ⁺ (46)	100	100	100	100
S ₂ ⁺ (64)	3.5	1.1	1.6	2.0
S ₂ N ⁺ (78)	14	28	10	11
S ₂ N ₂ ⁺ (92)	43	42	20	24
S ₃ N ⁺ (110)	0.7	2.7	0.6	0.6
S ₃ N ₂ ⁺ (124)	2.7	0.9	1.0	1.4
S ₃ N ₃ ⁺ (138)	51	58	21	22
S ₄ N ₂ ⁺ (156)	1.0	<0.04	0.4	0.3
S ₄ N ₄ ⁺ (184)	0.8	15.2	1.4	0.9

^a All spectra were obtained under identical instrumental conditions using 25-eV electron impact. ^b Spectra obtained after 2 h at 95 °C. ^c Spectra obtained at 75 °C.

due to the volatilization of some unreacted S₄N₄. At higher temperatures, the spectra become nearly indistinguishable, as indicated in Table I, and phase-angle spectrometry results indicate that the dominant (>80%) sulfur–nitrogen species is an S₄N₄ isomer. The argon, methane, isobutane, and ammonia chemical ionization (CI) spectra of brominated (SN)_x and S₄N₄ are also similar to within experimental limits.

To determine the identity of the S₄N₄ isomer, a series of experiments were undertaken to compare the intensities of the S_xN_y⁺ ions in the spectra of (SN)_x, S₄N₄, and their brominated analogues. The results in Table III suggest the vapors are composed of a mixture of the two S₄N₄ isomers.

Additional evidence for the similarity of brominated (SN)_x and brominated S₄N₄ is provided by the presence of the “hydride impurity” of (SN)_x noted in earlier work. While this species has not been precisely identified, it has a molecular weight of 220 ± 12 from phase-angle spectrometry and does not show a parent ion.¹¹ The concentration of the hydride impurity observed in brominated (SN)_x and brominated S₄N₄ was quite similar, with values ranging from 0.1 to 0.2 atom % hydrogen. The hydride concentration is approximately a factor of 10 smaller than observed in typical (SN)_x samples and apparently is related to the formation of HBr. A possible rationalization of this result is that bromine replaces hydrogen which is bound to the (SN)_x chains, forming HBr and a chemically bonded species which yields NSBr upon sublimation.

Brominated S₄N₄ or (SN)_x exposed to air reacts much more rapidly than (SN)_x^{5,11} to yield several additional products; NH₃, SO₂, HNSO, S_x, S₄N₂, and increased amounts of HBr and the hydride impurity were identified in the vapors of samples exposed to air for 1 day. An unidentified species producing a doublet at *m/e* 173 and 175 was observed and may possibly be attributed to either S₂N₂H₂Br⁺ or S₂NOBr⁺. A rather large contribution of an ion at *m/e* 140 was also observed (possibly S₃N₂O).

The S₄N₄ samples treated with ICl sublimed at a lower temperature and had a negligible hydride impurity. Otherwise,

the samples produced gas-phase species analogous to brominated (SN)_x and brominated S₄N₄: S₂Cl₂, ICl, I₂, and NSCl along with relatively large amounts of HCl and HI.

In summary, the present work has examined the gas-phase species volatilized over brominated (SN)_x and brominated S₄N₄, as well as S₄N₄ treated with ICl. The mass spectra of brominated S₄N₄ and brominated (SN)_x are nearly indistinguishable and suggest that the solid samples may be identical. (This result is quite surprising and further studies of brominated (SN)_x and S₄N₄ are required to answer the interesting mechanistic questions raised by these results.) The major gas-phase species containing bromine are Br₂ and monomeric NSBr. S₄N₄ brominated in CS₂ solution produces an orange solid which sublimates to give BrSCN and CS₃N₂, in addition to S₄N₄, HBr, Br₂, S₂Br₂, and NSBr. For S₄N₄ treated with ICl the major halogen-containing gas-phase species are ICl, I₂, and NSCl. In all cases the major sulfur–nitrogen species is one or a mixture of (SN)₄ isomers.

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Registry No. (SN)_x, 37221-29-7; S₄N₄, 28950-34-7; Br₂, 7726-95-6; ICl, 7790-99-0; NSBr, 52509-85-0; S₂Br₂, 13172-31-1; NSCl, 17178-58-4; S₂Cl₂, 10025-67-9.

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