Mass-spectrometric Study of the Thermal Pyrolysis of Tetrasulphur Tetranitride over Quartz Wool and Silver Wool

By **Richard D. Smith**, Physical Sciences Department, Battelle, Pacific Northwest Laboratories, Richland, Washington 99352, U.S.A.

Mass-spectrometric techniques have been used to identify the pyrolysis products of S_4N_4 vapours passed over quartz wool and silver wool at 80—400 °C. Tetrasulphur tetranitride was volatilized from solid samples at 60—80 °C in a heated tube and passed into a second reaction tube packed with quartz or silver wool heated to 80—400 °C. The products passing from the reaction tube are examined using modulated molecular-beam techniques in conjunction with measurements of the mass-spectrometric appearance potentials, low-energy electron-impact mass spectrometry, and phase-angle spectrometry. The major product at *ca.* 200 °C is S_2N_2, accompanied by smaller amounts of S_3N_3 and S_4N_2. At higher temperatures (>300 °C) S_2, SN, and N_2 become the major pyrolysis products. The results are examined in terms of their implications for the synthesis of $(SN)_x$ from S_2N_2 and S_4N_4.

THE principal method for the synthesis of $(SN)_x$, polymeric sulphur nitride, involves the thermal decomposition of tetrasulphur tetranitride (S_4N_4) vapours passed over silver wool at 200—300 °C.[1,2] Previous work has shown that S_2N_2 formed in this manner may be collected at liquid-nitrogen temperatures. The S_2N_2 crystals will undergo a slow solid-state polymerization on warming to room temperature and form $(SN)_x$ crystals. The identity and relative abundance of other species produced by S_4N_4 pyrolysis on silver wool are unknown; however, observation and mass-spectrometric studies of species volatilized from products condensed on the liquid-nitrogen trap suggest the existence of other reactive or unstable species in addition to S_4N_2.[3,4] The importance and precise role of silver wool in S_2N_2 formation also remains uncertain.

Previous workers have observed that $(SN)_x$ films may also be formed from S_4N_4 vapours passed over Pyrex or quartz wool.[5,6] While the intermediate species in this process is uncertain, Louis *et al.*[5] have suggested an acyclic isomer of S_4N_4 [previously identified as the major species sublimed from $(SN)_x$[7]] as the intermediate species.[5] While this isomer of S_4N_4 is known to spontaneously polymerize on cool surfaces to yield $(SN)_x$ films, there is no evidence to support its role in this system; processes involving S_2N_2 or another sulphur–nitrogen compound cannot be ruled out. Additionally, while tentative evidence exists for isomerization of the acyclic isomer to form the ' cyclic ' S_4N_4,[7] there is no experimental evidence for an appreciable contribution of a reverse process.

In this work I report the results of a direct mass-spectrometric study, using a unique double-furnace technique, of the products observed on passing S_4N_4 vapours over quartz and silver wool at temperatures from 80 to 400 °C. This study has directly identified the pyrolysis products of S_4N_4, which include the S_3N_3 and SN radicals. The relative concentrations of each of the vapour-phase pyrolysis products are reported as a function of temperature. The acyclic S_4N_4 isomer postulated by previous workers,[5] however, was not detected. The present results generally support established methods for the synthesis of S_2N_2 and $(SN)_x$.

EXPERIMENTAL

A schematic illustration of the apparatus employed in this work is shown in Figure 1. The sample, connector, and reaction regions are constructed of three alumina tubes wrapped separately with nichrome heating coils. Chromel–alumel thermocouples, embedded in the tubes, monitor the temperature in each of the three regions. Tetrasulphur tetranitride was sublimed at temperatures ranging from 60 to 80 °C, controlled to ±0.5 °C. The vapours pass through the connection region and into the reaction tube maintained at between 80 and 400 °C, and containing a 4-cm plug of quartz or silver wool. The temperature in the connector region was initially maintained at 80 °C but increased at higher reaction-tube temperatures (>250 °C), reaching 130 °C at a reaction-tube temperature of 400 °C. The reaction-tube temperature was monitored at three locations, and the temperature gradient across the quartz or silver wool plug was always observed to be <10 °C. Reaction-tube temperatures were controlled and maintained constant to within 1 °C. All the reported measurements were made after allowing at least 20 min for equilibration at each temperature. The pressure in the heating region was varied by altering the temperature of the S_4N_4 sample region and, in most experiments, by a continuous flow of inert gas (He or N_2) over the S_4N_4 sample and through the reaction region.

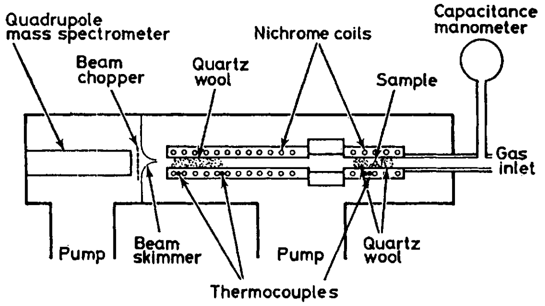

FIGURE 1 Schematic illustration of experimental apparatus. The connector between the sample and pyrolysis regions may be heated separately. For phase-angle spectrometry the distance between the chopper and the mass spectrometer ionizer is increased from 1 to 16 cm

The molecular beam effusing from the final (reaction region) tube enters a differentially pumped region (maintained at $<10^{-7}$ Torr) † and is directed at a molecular beam skimmer, which allows a well collimated molecular beam to enter the analyzer section (see Figure 1). The molecular

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† Throughout this paper: 1 Torr = (101 325/760) Pa; 1 eV ≈ 1.60×10^{-19} J.

beam is modulated, using a rotating toothed wheel, and subsequently passes through the ion source. Mass spectra were obtained at 9, 10, 12, 15, 16, 20, 25, and 100 eV. The modulated molecular-beam technique allows one to study unstable or reactive species in the effusive beam because of the total absence of surface-related phenomena; [7,8] the molecules studied do not collide with surfaces after leaving the alumina tube. Modulation of the beam also eliminates background species from the mass spectra.

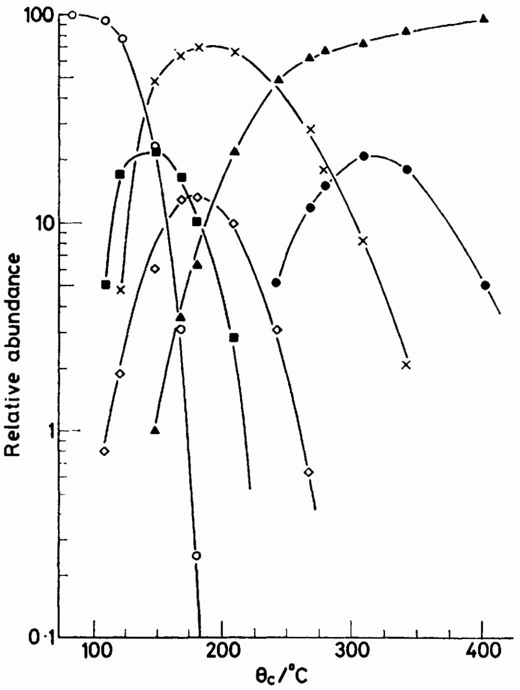

FIGURE 2 Relative abundance of the major pyrolysis products of S_4N_4 passed through a 4-cm plug of quartz wool: (○) S_4N_4, (◇) S_4N_2, (■) S_3N_3, (×) S_2N_2, (●) SN, and (▲) S_2

The technique of phase-angle spectrometry was used to determine the molecular weight of each gas-phase species identified in this work, at each temperature. 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 between the chopper and the ionizer allow one to determine the molecular weight after calibration with known species.[7,8] Further confirmation was provided by the measurement of appearance potentials of the various ions in the mass spectra. These techniques have been discussed in detail elsewhere.[7,8]

RESULTS

The mass spectra of the S_4N_4 pyrolysis products were compared with the results of phase-angle spectrometry to find the highest electron energy where the relative abundance of each species can be determined without interference from ions resulting from fragmentation of heavier species. The optimum electron energy was found to be *ca.* 15 eV. At this energy, all the products of S_4N_4 pyrolysis can be observed, with the exception of N_2. The relative abundance of N_2 as a function of temperature was obtained in separate experiments at 20 eV.

The mass spectra of S_4N_4 [7,9] and S_2N_2 [7] have been reported previously and were determined for the experimental conditions used in this work. The mass spectrum of S_4N_2 has also been reported previously,[10] and these results indicate that $[S_4N_2]^+$ accounts for nearly all the ionization at 15 eV. An examination of the mass spectra and the results of phase-angle spectrometry clearly showed that the major neutral species resulting from the pyrolysis of S_4N_4 are S_4N_2, S_3N_3, S_2N_2, S_2, SN, and N_2. Much smaller amounts of S_3N_2 and S_2N were also observed, but may be neglected in the present analysis. With the knowledge of the mass spectra of S_4N_4, S_4N_2, and S_2N_2, and the experimental observation that at 15 eV only S_2 will produce $[S_2]^+$ ions, we only require an estimate for the mass spectra of S_3N_3 to allow a semiquantitative calculation of the relative abundance of the various sulphur–nitrogen species as a function of temperature. This is simplified by the fact that only S_4N_4 may affect calculation of the relative S_3N_3 abundance, since S_4N_4 (or its acyclic isomer) is the only other species present which may yield $[S_3N_3]^+$ ions.

The simple assumptions described above allow one to calculate the relative abundance of S_4N_4, S_4N_2, S_3N_3, S_2N_2, S_2, and SN for S_4N_4 pyrolysis over both quartz and silver wool. The results are given in Figure 2 for quartz wool and Figure 3 for silver wool, and include estimated corrections for the relative ionization cross section at 15 eV, and for the transmission and detection efficiency of the quadrupole mass spectrometer. Due to these uncertainties, the relative concentration of the various species at a given temperature may be in error by as much as ±50%. However, the relative concentration (partial pressure) of a given species *as a function of temperature* is estimated to have an error of $< \pm 10\%$ of the species' abundance for quartz wool. The error limits are assumed to be somewhat larger for S_3N_3 since the mass spectrum for S_3N_3 had to be estimated

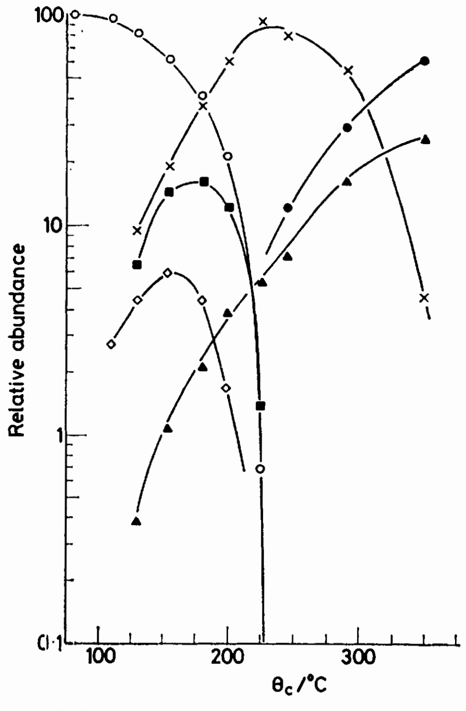

FIGURE 3 Relative abundance of the major pyrolysis products of S_4N_4 passed through a 4-cm plug of silver wool. Key as in Figure 2

by subtraction of contributions from S_4N_4, S_4N_2, S_2N_2, and possibly SN. Additional uncertainty exists for the contribution of SN at a relative abundance of $<10\%$, due to $[SN]^+$ formation from S_4N_4, S_4N_2, S_3N_3, and S_2N_2.

The identity of the neutral precursor of each ion was determined separately using phase-angle spectrometry; these experiments confirmed the semiquantitative product distributions calculated from the mass spectra. Phase-angle spectrometry also allowed one to rule out the existence of other possible species which might contribute to the formation of particular ions. For example, the acyclic S_4N_4 isomer formed by sublimation of $(SN)_x$ does not yield a parent ion on electron impact, but rather shows $[S_3N_3]^+$ as the major ion.[7] Hence, phase-angle spectrometry is required to determine the origin of $[S_3N_3]^+$ ions.

Figures 2 and 3 omit contributions due to S_3N_2 and S_2N. While the presence of S_3N_2 and S_2N was established using phase-angle spectrometry, the relative abundances of these species were always less than a few percent, and were not amenable to a quantitative treatment. As discussed above, the concentration of N_2 was measured in separate experiments, and was observed at temperatures as low as *ca.* 90 °C for both quartz and silver wool. At higher temperatures the N_2 concentration increases greatly and mirrors the behaviour of S_2. Since N_2 concentrations were recorded at different electron energies (20 eV) in separate experiments, these results were not included in the Figures, or as part of the total products.

DISCUSSION AND CONCLUSIONS

The results in Figures 2 and 3 show that there are distinct differences in the abundances of products formed by passing S_4N_4 vapours over quartz and silver wool. The relative abundances of the sulphur–nitrogen products were found to be only slightly dependent on pressure (of either S_4N_4 or inert gas). Over the range of S_4N_4 partial pressures employed in this work (*ca.* 10^{-6}—10^{-4} Torr) there was no evidence for the occurrence of bimolecular gas-phase reactions between the various sulphur–nitrogen species. Greater variations in the experimental results were observed by decreasing the density of the quartz wool or by greatly increasing the flow of inert gas. Significant shifts in the temperature dependences were observed with the amount of quartz and silver wool. The experiments with quartz wool generally involved considerably greater surface areas. The increased surface area allows the surface reactions to occur at greater rates, shifting the maxima for pyrolysis products to lower temperatures; this undoubtedly plays a role in the faster rate of S_4N_4 consumption in Figure 2 compared to Figure 3.

The data for S_4N_4 pyrolysis over silver wool were much more variable, and are subject to greater uncertainty. This behaviour may be related to the formation of a silver sulphide surface layer, which is often assumed to act as a catalyst in the decomposition of S_4N_4.[2,6,10] The product distribution appeared to be somewhat dependent on the condition of the silver surface. While experiments with quartz wool were reproducible to ±5% (relative ion intensities), the variability with silver wool was ±30% over the course of several experiments, with no evident trends.

The results in Figures 2 and 3 allow speculation concerning the mechanism of S_4N_4 pyrolysis. At low temperatures three (apparently competing) reactions may occur. Reaction (1) is suggested by the observation

$$S_4N_4 \longrightarrow S_4N_2 + N_2 \qquad (1)$$

$$S_4N_4 \longrightarrow S_3N_3 + (SN) \qquad (2)$$

$$S_4N_4 \longrightarrow 2S_2N_2 \qquad (3)$$

of N_2 at temperatures as low as 100 °C; however, S_4N_2 is usually assumed to result from a reaction of S_2N_2 with S_2.[2] Since the rates of gas-phase bimolecular reactions are too slow to contribute to the present results, one must either invoke reaction (1) or a gas–solid reaction of S_2N_2 involving sulphur present on quartz- or silver-wool surfaces.

The nature of reaction (2) producing the S_3N_3 radical is uncertain. The formation of both S_3N_3 and SN gas-phase species cannot be ruled out since appearance-potential measurements suggest the presence of SN at temperatures as low as 140 °C. Unfortunately, a quantitative measurement of the SN concentration is not feasible since $[SN]^+$ ions are also readily formed by all sulphur–nitrogen compounds. An alternative rationalization of these observations would entail a surface-related process producing $S_3N_3(g)$ and SN on the quartz or silver surfaces which might combine with other SN species to produce S_2N_2 or S_2 and N_2.

At temperatures above *ca.* 150 °C, S_2N_2 begins to dominate the reaction products. Reaction (3) is the most likely source of most of the S_2N_2; however, subsequent reaction of the S_3N_3 and S_4N_2 products may also be of importance. At temperatures above 250 °C,

$$S_3N_3 \longrightarrow S_2N_2 + SN \qquad (4)$$

$$S_4N_2 \longrightarrow S_2N_2 + S_2 \qquad (5)$$

dissociation to the elements becomes increasingly important. The results suggest that the competing reaction for decomposition of S_2N_2 *via* reaction (6) is more important at low temperatures.

$$S_2N_2 \longrightarrow 2SN \qquad (6)$$

$$S_2N_2 \longrightarrow S_2 + N_2 \qquad (7)$$

A comparison of results in Figures 2 and 3 also allows for observations concerning the differences between S_4N_4 pyrolysis on quartz or silver wool. For example, S_4N_2 is formed in greater quantities and continues to be an important product at higher temperatures for quartz wool. Also, S_3N_3 and S_4N_2 are observed in appreciable quantities for quartz wool after S_4N_4 has been completely consumed, in strong contrast to silver wool. At higher temperatures the formation of S_2 and N_2 is favoured on quartz wool, whereas SN formation appears more likely on silver wool. Previous workers [11,12] have suggested mechanisms involving sulphur formation on silver wool surfaces and subsequent reaction with S_2N_2 to form S_4N_2. The present results cannot rule out a surface reaction of S_2N_2 with sulphur to yield S_4N_2; however, the results clearly suggest that silver does not play a unique role in S_4N_2 formation.

The present results also show that use of silver wool provides a more favourable route for formation of S_2N_2 crystals. At 225—250 °C, over silver wool, S_2N_2 accounts for *ca.* 90% of the total products. These findings are consistent with previous reports on the synthesis of S_2N_2 from S_4N_4.[1,2,6,10,11] For quartz wool, the optimum temperature for S_2N_2 formation is *ca.* 225 °C; however, at this temperature significant quantities of S_4N_2 and S_2 are also formed. Since the S_2N_2 used in the synthesis of $(SN)_x$ is typically collected at liquid-nitrogen temperatures, these impurities will also be collected at liquid-nitrogen temperatures and may affect the quality of $(SN)_x$ crystals. A mass-spectrometric study of impurities volatilized from the liquid-nitrogen cold-finger used to collect S_2N_2 showed the presence of NH_3, HN_3, SNO, HSNO, and small amounts of other compounds.[3]

The present results also allow an interpretation of recent experiments which found the ' direct ' formation of $(SN)_x$ films from S_4N_4 passed over quartz or Pyrex wool at 275 °C.[5] It was suggested that S_4N_4 rearranged to form the acyclic isomer observed to be the major component in the vapours of $(SN)_x$.[5] The present results show that the acyclic S_4N_4 isomer is not formed in significant quantities by the thermal pyrolysis of ' cyclic ' S_4N_4. (These results do not rule out the possibility of amounts of less than a few mole percent of acyclic S_4N_4 at 150—200 °C.) Thus, it appears that $(SN)_x$ films most likely result from reactions involving other sulphur–nitrogen species. The possible direct roles of SN, S_2N_2, and S_3N_3 in $(SN)_x$ film formation have not been fully investigated; however, $(SN)_x$ is commonly observed coating walls in experiments using SN radicals.[13] It is also observed after the volatilization of presumably pure S_2N_2 at low temperatures.[1] Due to the limited information available, the precursor(s) to $(SN)_x$ films in S_4N_4 pyrolysis over quartz wool remains uncertain.

Several of the sulphur–nitrogen species detected in this work (S_2N, S_3N_2, and S_3N_3) have not been previously observed. There is tentative evidence[7] (appearance-potential measurements) for these species in the vapours of $(SN)_x$; in fact, previous work[7] has indicated that S_3N_3 may account for as much as 15% of $(SN)_x$ vapours. The stability of these species is not known with any certainty, however their mass-spectral observation suggests a greater than transient existence. Additionally, theoretical calculations[14] suggest that S_3N_3 should be quite stable relative to non-cyclic SN and S_2N_2 species.

In summary, I have examined the gaseous species formed on pyrolysis of S_4N_4 on quartz and silver wool. The silver wool does affect the pyrolysis products and increases the yield of S_2N_2. In addition to S_2N_2, I also observed S_4N_2, S_3N_3, S_3N_2, S_2N, S_2, SN, and N_2 species. Since acyclic S_4N_4 was not detected, it is unlikely this species has a role in the direct formation of $(SN)_x$ films when ' cyclic ' S_4N_4 vapours are passed over quartz wool. Film formation is most likely due to S_2N_2 and possibly S_3N_3 and SN.

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