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A STUDY OF THE REACTIONS BETWEEN GASEOUS AMMONIA AND SULFUR CHLORIDES

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**A STUDY OF THE REACTIONS BETWEEN
GASEOUS AMMONIA AND SULFUR CHLORIDES**

Berkeley, California

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Milagros Villena-Blanco

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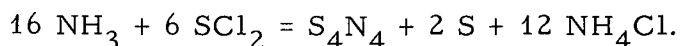
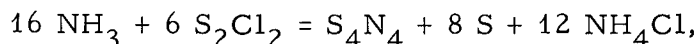
ABSTRACT

The reaction between gaseous ammonia and sulfur chlorides (S_2Cl_2 and SCl_2) has been studied under various conditions of temperature, flowrate of ammonia, concentration and type of sulfur chloride, solvent, and duration of run, for the purpose of determining the optimum conditions for the preparation of S_4N_4 and S_7NH .

Adsorption-column chromatography on alumina and silica gel columns was employed for the quantitative separation of the reaction products.

I. INTRODUCTION

Ammonia has been found to react with sulfur chlorides in a suitable solvent, presumably according to the following equations:



These colorful reactions were first observed in 1838 by Soubeiran,¹⁶ who passed gaseous ammonia into a solution of disulfur dichloride (S_2Cl_2) in carbon disulfide. Since that time, numerous investigators have studied the reactions under a variety of conditions. Francis and Davis⁷ used both sulfur chlorides and found that S_2Cl_2 was inferior to SCl_2 for the preparation of tetrasulfur tetranitride (S_4N_4); but it was reported later¹⁸ that S_2Cl_2 gave a higher yield of S_4N_4 . However, recent studies⁹ showed that conversion of S_2Cl_2 to SCl_2 , by chlorination prior to the introduction of ammonia, greatly increased the yield of S_4N_4 .

The cited authors not only varied the type of sulfur chlorides used but also carried out the reaction in different solvents. A large number of solvents have been used including benzene,¹⁵ carbon disulfide,⁶ chloroform,¹³ ether,¹⁸ carbon tetrachloride,⁹ and dimethylformamide.¹⁰ From their reports of yield of S_4N_4 it seemed that solvent played an important role in the reaction. Macbeth and Graham¹³ did preliminary experiments with these various solvents, excluding dimethylformamide, and found that chloroform was very suitable for the preparation of tetrasulfur tetranitride. Later Arnold¹ found that dry carbon tetrachloride was the most suitable solvent, on the basis of the cheapness, noninflammability, and the absence of side reactions.

Macbeth and Graham¹³ attempted to study the course of the reaction by slowly adding a standard solution of ammonia in chloroform to an ice-cold solution of S_2Cl_2 in chloroform until a permanent alkalinity was produced. They found that 1.33 moles of ammonia reacted with each mole of S_2Cl_2 . Besides the product indicated above, they reported having isolated a white, flaky substance which contains

hydrogen besides sulfur and nitrogen, and which was later² proved to be heptasulfurimide (S_7NH). Arnold et al.² modified the method by using gaseous ammonia instead of the standard solution of ammonia and were the first to report that the color of the reaction mixture changed from dark brown to greenish brown to salmon red during the ammonia flow. The ammonia flow was stopped when the reaction mixture reached salmon-red color, and the products were then examined.

Each of the above investigators was attempting to maximize the yield of S_4N_4 since it is the parent compound of numerous other sulfur-nitrogen compounds. However, the conditions of the reaction can be varied so that the heptasulfurimide is the principal product.^{3,10}

Tetrasulfur tetranitride crystallizes as bright yellow-orange needles that are reported to melt at $178^\circ C$.⁹ It has been shown⁴ from the electron diffraction data that the "cradle" structure leads to a satisfactory model for the tetrasulfur tetranitride molecule. This cradle model (Fig. 1) consists of a bisphenoid of sulfur atoms and a square of nitrogen atoms, with $N-S = 1.62 \text{ \AA}$, angle $S-N-S = 112 \text{ deg}$, and angle $N-S-N = 106 \text{ deg}$. The structure probably involves resonance among the following bond structures, of which (I) is considered to be the most important.

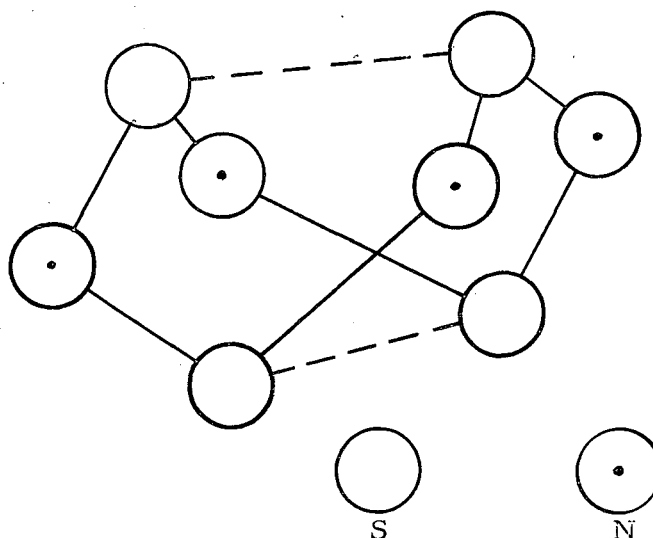
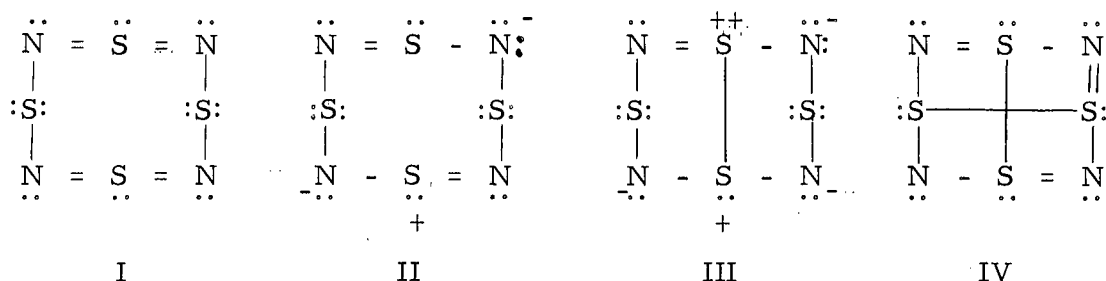


Fig. 1. Model for the tetrasulfur-tetranitride molecule.



S_4N_4 is not explosive with ordinary handling but can be detonated with percussion. It is soluble in dioxane, carbon disulfide, tetrachloroethane, tetrahydrofuran, and benzene. Although readily oxidized in the presence of alkali, it is otherwise stable in air.

The other sulfur-nitrogen compound, S_7NH , is a white, flaky substance which melts at 113.5°C without decomposition. Structurally, it resembles S_8 with an NH group substituted for one of the sulfur atoms. The strong absorption band in the infrared at 3400 cm^{-1} verifies that the hydrogen is bonded to the nitrogen. It produces an evanescent purple color with alcoholic potassium hydroxide. It readily dissolves in benzene, methanol, acetone, and carbon tetrachloride.

The objective of this study was to reinvestigate the reactions between the sulfur chlorides and ammonia, by using quantitative separation of the reaction products. Since crystallization, used in all previous studies, involves losses of 10 to 50%, a portion of this work centered upon developing an efficient method of separation of these products. Chromatographic methods of separation were investigated and employed. Also an attempt to learn the mechanism of the reaction was made. In order to accomplish this, reactions were carried out under various conditions of temperature, flowrate of ammonia, concentration and type of sulfur chlorides, solvent, and duration of the ammonia flow. The effects of each of the variables were determined. The reaction course was followed by taking small samples of the reaction mixture at every distinct color change. The behavior of the samples when mixed with water was noted, and the pH of the aqueous portion was determined.

II. EXPERIMENTAL PROCEDURES

A. Chromatographic Experiments

Preliminary experiments dealt with column partition chromatography. Columns of cellulose powder (Van Waters) and Celite (diatomaceous earth, made by Johns-Mansville) were prepared and several immiscible solvent pairs were examined, e. g., dimethylformamide-pentane, dimethylformamide-isooctane and acetonitrile-hexane. Mixtures of known composition containing sulfur, heptasulfurimide and tetrasulfur tetranitride were introduced into the columns. Qualitative analysis of the fractions from the columns indicated that no separation was accomplished. In view of these results, this method was abandoned and adsorption chromatography was investigated as an alternative.

For reasons discussed in the latter part of this thesis, two columns were required in order to obtain a quantitative separation of the three compounds. In one column (alumina, dried) tetrasulfur tetranitride was separated from sulfur and heptasulfurimide. Using another sample of the three compounds in a second column (silica gel) sulfur and heptasulfurimide were separated from each other, leaving the tetrasulfur tetranitride in the column. A typical procedure is described below.

B. Separation Procedures

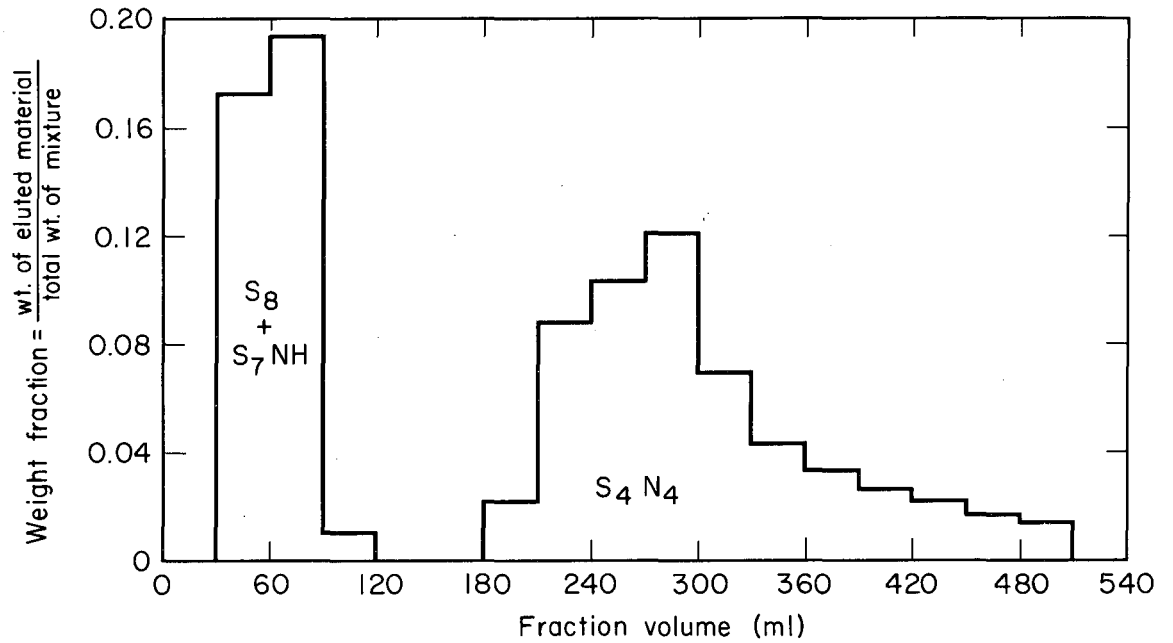
1. Separation of S_4N_4 from S_7NH and S

An alumina column, 18 cm long and 2.54 cm in diameter was prepared by pouring a thin slurry of the alumina (acid, activity grade 1, M. Woelm-Eschwege, Germany, dried at 150° C for 12 hr) in dry benzene into a 2-ft glass column with a reservoir attached to the top of the column by a ground-glass joint. The tubular section of the column was prefilled with dry benzene (dried over P_2O_5 and distilled) so that the solids in the slurry filled the column by settling from the reservoir through the column liquid, forming a sedimentary bed on the fritted glass at the bottom of the column. This process was aided by

allowing the liquid to flow out of the bottom of the column and by frequent tapping of the column. When the solid bed ceased to contract, a 1-cm layer of sand was carefully established by settling. This served to protect the column bed from disturbance during the subsequent application of the sample to the column.

One-half gram of a mixture containing S, S₇NH, and S₄N₄ was dissolved in 50 ml of dry benzene. To readily dissolve the mixture it was often necessary to warm the solution. The cooled solution was added to the top of the column and allowed to flow slowly through the column until the level of the solution fell almost to the top of the sand. At this point elution was commenced. The eluant (pure dry benzene) was allowed to flow through the column at a rate of 1 ml/min (0.2 cm³/cm²-min). Fractions were collected with the aid of an automatic fraction collector at 30-min intervals (i. e., 30-ml fractions). The first fraction was usually free of any material. The next three fractions contained all the sulfur and heptasulfurimide. The following two fractions were free of any eluted material. The S₄N₄ usually came out in the next eleven fractions. The number of fractions actually depended upon the amount of the sample being separated. Figure 2 shows a typical elution in an alumina column. The S₄N₄ was recovered from the benzene solution by evaporating off the solvent in the air at room temperature.

The generally accepted⁹ melting point of S₄N₄ is 178° C, although Arnold, Hugill, and Hutson² reported a melting point of 180° C, and Francis and Davis⁷ reported a "decomposition point" of 185° C. It was found that S₄N₄ which was recrystallized five times from benzene, or which was purified by column chromatography followed by one crystallization, melted at 187 to 187.5° C. This result was obtained by using a calibrated thermometer in either a Mel-Temp apparatus or an oil bath. Heating rates in the neighborhood of two degrees per minute were used. The x-ray diffraction pattern of a sample melting at 187 to 187.5° C yielded structure factors close to those reported by Clark⁵ and yielded d values close to those found by Jaeger and Zanzstra.¹² Hence the purification procedure did not lead to a new modification of S₄N₄.



MU-32500

Fig. 2. Elution profile in Al_2O_3 column. Total weight of mixture is 0.5303 g (mixture composition is given in Table II, dried Al_2O_3); flow rate is $0.2 \text{ cm}^3/\text{cm}^2\text{-min}$; column length is 18 cm.

2. Separation of S₇NH from S

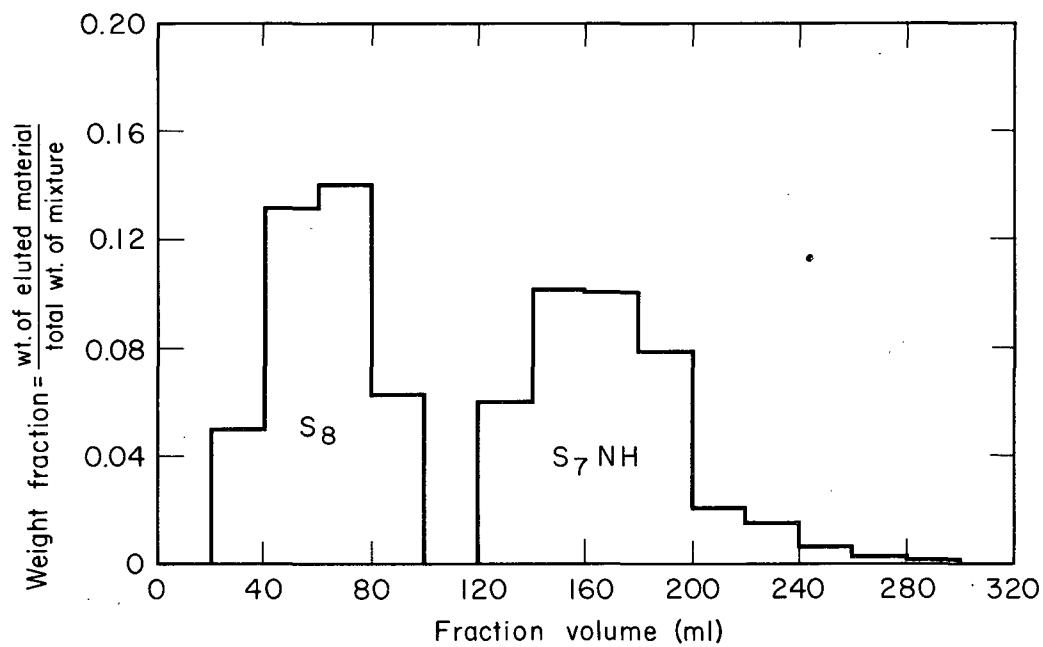
A column of silica gel ("suitable for chromatographic use," J. T. Baker Chemical Co.) was prepared in the same manner as the preparation of the alumina column. One-half gram of the mixture was dissolved (usually aided by heating) in 50 ml of carbon tetrachloride (dried over CaSO₄ and distilled). The cooled solution was added to the top of the column. As soon as the level of the solution had reached the surface of the sand, pure carbon tetrachloride was allowed to flow through the column at the rate of 1 ml/min (0.2 cm³/cm²-min). Fractions were collected at 20-min intervals. The first fraction did not contain any eluted material. The next four fractions contained all the sulfur. The sixth fraction was essentially free of any eluted material. The following nine fractions contained all the S₇NH, which was recovered by evaporating off the solvent in air at room temperature. The S₄N₄ could not be completely recovered from this particular column. A typical elution profile in silica gel is shown in Fig. 3.

C. Reactions of Gaseous Ammonia and Sulfur Chlorides

A 2-liter 3-necked round-bottom flask was used as the reaction vessel. The main neck was fitted with a cork stopper, bored to carry a paddle stirrer. A gas inlet tube was inserted through one of the standard tapered (24/40) side-necks, and a thermometer through the other. The gas inlet tube was connected to a cylinder of anhydrous ammonia through a gas flowmeter (Manostat Flowmeter FM 1043T) calibrated to the ammonia flow according to the procedure described by the manufacturer.

Then 84 g (0.6 mole) of S₂Cl₂ was added to 1.4 liters of dry carbon tetrachloride in the reaction vessel. During brisk stirring, ammonia was introduced at the specified flowrate.

The first reaction was exothermic; yellow-brown fumes were given off, and the contents of the flask turned rose ebony^(8E6) (the superscript after each color indicates the location of the color plate in



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Fig. 3. Elution profile in SiO₂ gel column. Total weight of mixture is 0.5204 g (mixture composition is given in Table II, nondried SiO₂); flow rate is 0.2 cm³/cm²-min; column length is 18 cm.

the Dictionary of Color by Maerz and Paul.¹⁴ After about 30 min the fumes disappeared and the reaction mixture turned grey^(15C6). The temperature continued to rise until the olive drab^(15J5) color appeared, after which it began to drop. The olive drab color lasted for about 5 min, then the color suddenly changed to burnt umber^(15L12), and then gradually brightened up, after 3 hr of reaction, to a golden poppy^(9L12) color; at this point the temperature had reached room temperature.

It should be noted that the time interval for the appearance of each distinct color varied with the conditions of the reactions. For instance, at a slow flowrate (18 liters/hr) of ammonia, the olive drab mixture was formed after 1-1/2 hr of reaction, whereas at a faster flowrate (50 liters/hr), it was formed after 35 min. Besides the differences in time interval of the appearance of each color, there was also a difference in the sequence of color changes. At a slow flowrate of ammonia, the color of the reaction mixture changed from rose ebony to grey to olive drab to burnt umber to golden poppy; at a faster flowrate, the color changed from rose ebony to yolk yellow^(10L5) to yellow ochre^(11L7) to olive drab to burnt umber to golden poppy. Hence the time of formation of the golden-poppy color depended upon the conditions of the reaction, as shown in Table I.

At each distinct color change, a rod was dipped into the reaction mixture and a drop or two of the reaction mixture was taken for observation. About 5 ml of the reaction mixture was also taken and was shaken with 25 ml of distilled water, and the pH of the aqueous portion was determined.

The reaction mixture was filtered on a sintered-glass funnel. The total volume of the filtrate was recorded and two 25-ml aliquots were air-dried in tared evaporating dishes for chromatographic separation.

The damp solid material was immediately stirred with about 500 ml of distilled water to dissolve the ammonium chloride. The remaining solid was filtered off and allowed to air-dry thoroughly for a day or two.

The factors believed to affect the yields of S_4N_4 and S_7NH are the flowrate of ammonia, temperature, concentration and type of sulfur chlorides, solvent, and duration of run. In order to determine the effect of each of these variables, reactions were carried out such that one variable was changed at a time, as summarized in Table I.

In the first four runs reactions were carried out at ambient temperature, with an ammonia flowrate of 18 liter/hr and an initial concentration of 84 g of S_2Cl_2 in CCl_4 . Only the duration of run was varied.

In the fifth run a fast (50 liter/hr) flowrate of ammonia was employed. The temperature was kept at ambient temperature and 84 g of S_2Cl_2 was used. With such a flowrate the color of the reaction mixture changed from rose ebony to yolk yellow to yellow ochre, at which time the temperature was at its peak ($71^\circ C$). Then as the temperature dropped the mixture became olive drab in color and finally turned golden poppy after 2 hr of reaction. The yellow ochre color lasted for about 5 min. In view of these results the sixth run was stopped at the appearance of the yellow ochre color.

In the seventh run, conditions were similar to that of Run No. 1 except that the ammonia flow was stopped when the reaction mixture turned olive drab.

In the eighth, ninth, and tenth runs the reaction vessel was kept under ice throughout the duration of the run. With the ammonia flowrate of 18 liters/hr and an initial concentration of 84 g of S_2Cl_2 , the duration of the ammonia flow was varied. The golden poppy color appeared earlier than if the reaction was carried out at ambient temperature.

In the eleventh run, the reaction mixture was cooled in ice until the appearance of the olive drab color. While continuing the passage of ammonia, the ice bath was removed and the temperature was allowed to rise to room temperature.

Run No. 12 was carried out under the same conditions as Run No. 1 except that the concentration of S_2Cl_2 was doubled.

In Run No. 13, 84 g of S_2Cl_2 was used. However, it was chlorinated prior to the introduction of ammonia. During brisk stirring, Cl_2 gas (dry) was allowed to pass into the solution until a distinctly

Table I. Tabulated summary of experimental procedure

Run No.	Duration of run (hr)	Flowrate of NH ₃ (liters/hr)	Temp.	Conc. of S ₂ Cl ₂ (g)	Type	Solvent
1 ^a	3	18	Ambient	84	S ₂ Cl ₂	CCl ₄
2	4	18	Ambient	84	S ₂ Cl ₂	CCl ₄
3	5	18	Ambient	84	S ₂ Cl ₂	CCl ₄
4	7	18	Ambient	84	S ₂ Cl ₂	CCl ₄
5	2	50	Ambient	84	S ₂ Cl ₂	CCl ₄
6	0.5	50	Ambient	84	S ₂ Cl ₂	CCl ₄
7	2	18	Ambient	84	S ₂ Cl ₂	CCl ₄
8 ^a	2.5	18	Ice-cooled	84	S ₂ Cl ₂	CCl ₄
9	3.5	18	Ice-cooled	84	S ₂ Cl ₂	CCl ₄
10	6.5	18	Ice-cooled	84	S ₂ Cl ₂	CCl ₄
11	2.5	18	Initially ice-cooled ^(b)	84	S ₂ Cl ₂	CCl ₄
12 ^a	6.0	18	Ambient	168	S ₂ Cl ₂	CCl ₄
13	6	18	Ambient	84	S ₂ Cl ₂ ^(c)	CCl ₄
14	1	18	Ambient	84	S ₂ Cl ₂	Dimethyl formamide
15	1	18	-5° C	84	S ₂ Cl ₂	Dimethyl formamide
16	1	18	Ambient	84	S ₂ Cl ₂	Tetrahydrofuran
17	2.3	18	Ambient	84	S ₂ Cl ₂	CCl ₄
18	3.0	18	> 35° C	84	S ₂ Cl ₂	CCl ₄
19	6.0	18	Ice-cooled	168	S ₂ Cl ₂	CCl ₄

^aDuplicate run was done.

^bIce bath was removed at the olive drab color.

^cObtained by chlorination of S₂Cl₂.

green layer of the Cl_2 gas was observed over the solution. At this point the flow of chlorine was stopped and the gas inlet tube was connected to the ammonia cylinder. Ammonia was passed at the rate of 18 liters/hr. Initially, dense white fumes formed, but soon disappeared. A yellow-brown mass was rapidly formed in the flask, which slowly became grey. Next the color changed to olive drab, and then gradually to golden poppy after 6 hr.

In the next three runs the solvent was changed. In Run No. 14, 84 g of S_2Cl_2 was added to 1.4 liters of dimethylformamide (dried over CaH_2 and distilled) at ambient temperature. As ammonia was allowed to pass at the rate of 18 liters/hr, the contents of the flask turned deep blue. The first reaction was somewhat violent, and sometimes a back pressure occurred in the ammonia line. However, this could be avoided by cooling the reaction mixture in ice during the ammonia flow. Ammonia was passed for 1 hr. No solid material could be filtered off. Upon standing in air the deep blue color of the dimethylformamide solution disappeared. A 25-ml aliquot gave a cream-colored residue, indicating the absence of S_4N_4 .

In Run No. 15 a reaction similar to that described by Goehring et al.¹⁰ was carried out.

In Run No. 16, 1.4 liters of tetrahydrofuran (dried over dri-Na and a little LiAlH_4 added prior to distillation) and 84 g of S_2Cl_2 were mixed. The ammonia flow was kept at 18 liters/hr. The contents of the flask remained golden poppy in color throughout the entire run. No cooling was necessary. The reaction was stopped after 2-1/2 hours. Very little solid material (bright yellow) was isolated after the water washings.

In Run No. 17 the mode of operation was altered: 1.4 liters of dry carbon tetrachloride was saturated with ammonia (at 18 liters/hr) prior to the addition of S_2Cl_2 . Then, through one of the side-necks, S_2Cl_2 was added in 2-ml portions at 5-min intervals. A total of 50 ml of S_2Cl_2 was added. The ammonia flow was stopped when the temperature dropped to room temperature (after 2-1/3 hr).

Run No. 18 was carried out under the same conditions as Run No. 8 except that the concentration of S_2Cl_2 was doubled.

High temperatures seemed to significantly affect the yield of S_7NH . Hence Run No. 19 was carried out such that the temperature was kept above $35^\circ C$. After 84 g of S_2Cl_2 was added to the carbon tetrachloride, the solution was heated to $35^\circ C$. After removing the hot-water bath, ammonia was passed at the rate of 18 liters/hr. Unlike Run No. 1 the initial rose ebony color did not appear. The color changed from yellow brown to yolk yellow to olive drab and finally to golden poppy. The temperature was not allowed to fall below $35^\circ C$.

Duplicates of runs number 1, 8, and 12 were carried out to verify the reproducibility of the reaction.

III. RESULTS AND DISCUSSION

A. Chromatographic Method of Separation

The water-insoluble reaction products include S, S₇NH, S₄N₄, and possibly S₆(NH)₂ in trace amounts. Quantitative separation of these compounds from each other offers some difficulties. Due to their almost similar behavior towards solvents, extraction methods do not give a good separation, and crystallization involves losses of about 10 to 50% of the yield. Several investigators report having obtained a good separation of S and S₇NH by adsorption-column chromatography. For instance, Heal¹¹ obtained pure S₇NH by elution from a silica gel column by using cyclohexane-carbon disulfide (1:1) as eluant; Weiss¹⁹ separated S and S₇NH and S₆(NH)₂ in an (neutral, Merck) alumina column by using pure dry benzene as eluant. More recently, Tavs et al.¹⁷ reported having separated S and S₇NH from the three isomers of S₆(NH)₂ in a silica gel column by elution with hexane; the three isomers were then separated from each other in an alumina column. All these investigators carried out the reaction between S₂Cl₂ and ammonia as described by Goehring et al.,¹⁰ in which case S₄N₄ is not one of the reaction products. It was also noted that in all these chromatographic separation methods, a preliminary extraction was done to minimize the amount of sulfur in the mixture to be separated in the column.

The present chromatographic investigation was centered upon developing a quantitative separation of S₄N₄ from the rest of the reaction products.

The phenomenon of adsorption depends on the nature of both the solid and the liquid phase; for this reason the choice of solvent is as important as that of the adsorbent itself. A large number of solvents were examined by using various adsorbents, e. g., alumina (acid, neutral, basic; activity grade 1, by M. Woelm-Eschwege, Germany) and silica gel ("suitable for chromatographic use," J. T. Baker Chemical Co.). The solvents examined included hexane, cyclohexane, benzene, carbon tetrachloride, dioxane, carbon disulfide, ether,

acetone, dimethylformamide, acetonitrile, and methanol. A systematic study was carried out to determine which solvent or mixtures of these solvents would give a good chromatographic separation of the three compounds. No attention was devoted to the separation of $S_6(NH)_2$ inasmuch it was reported¹⁷ to be formed in trace amounts. The results of our experiments showed that if a benzene or carbon tetrachloride solution of the test mixture was used to put the mixture onto the (acid) alumina column, pure, dry benzene could be used to elute out the sulfur and heptasulfurimide, leaving the tetrasulfur tetranitride on top of the column. Finally, benzene-acetonitrile (95-5% by volume) slowly removed tetrasulfur tetranitride from the column. However, it was found that the recovery of the materials from the column was not very good. In view of these results numerous experiments were done on the (acid) alumina column to obtain a good chromatogram and a maximum recovery.

It is significant to note the difference in the results obtained when using dried (150° C for 12 hr) and nondried (acid) alumina. These results are shown in Table II. In the case of the nondried alumina, about 30% of S_4N_4 was lost in the column. In an attempt to aid removal of S_4N_4 , the polarity of the eluant was increased by gradually increasing the concentration of acetonitrile in benzene. However, an oily orange liquid was obtained, the composition of which could not be established. This substance most probably resulted from the decomposition of the unrecoverable S_4N_4 .

On the other hand, dried alumina gave 90 to 97% recovery of S_4N_4 and the oily substance was no longer obtained. However, dried alumina failed to adequately separate S and S_7NH , whereas the nondried adsorbent gave a fair separation.

Nondried silica gel gave an excellent separation of S and S_7NH but, as in the case of nondried alumina, only 30% of the S_4N_4 was recovered. Silica gel dried at 200° C for 12 hr gave 86 to 91% recovery of S_4N_4 but it no longer separated S and S_7NH . Thus two columns are necessary to quantitatively separate the three compounds.

Table II. Effect of moisture in the adsorbent. Length of column is 18 cm, diameter is 2.54 cm.

	Nondried Al ₂ O ₃		Dried Al ₂ O ₃		Nondried SiO ₂ gel		Dried SiO ₂ gel	
	Taken (g)	Recovered (g)	Taken (g)	Recovered (g)	Taken (g)	Recovered (g)	Taken (g)	Recovered (g)
S ₈	0.2352	0.2345	0.1765	} 0.1952	0.1906	0.1900	0.1770	0.1954
S ₇ NH	0.0105	0.0092	0.0227		0.2015	0.2051	0.1900	0.1698
S ₄ N ₄	0.1242	0.0882 + oily liq.	0.3311	0.3106	0.1283	0.0394	0.2002	0.1821

It is apparent that on the dried adsorbents, S and S₇NH behave identically, whereas on the non-dried adsorbents S₇NH is held more strongly—probably through the formation of hydrogen with traces of water. The loss or decomposition of S₄N₄ in the columns can also be attributed to the presence of traces of water.

It was found that a column of 2.54-cm inside diameter gave maximum separation consistent with a convenient flowrate. The results given in Table III show that the 18-cm length was chosen as a compromise between separation of the bands and material lost in the column. A longer column (35 cm) provided a better band separation; however, the recovery of materials decreased by 10%. A shorter column gave better recovery but not a very satisfactory separation.

Experiments showed that it was necessary to evaporate the original carbon tetrachloride portion of the reaction mixture and redissolve the residue prior to separation in the column.

Table III. Effect of length of column. Adsorbent was acidic alumina (dried at 150° C for 12 hr).

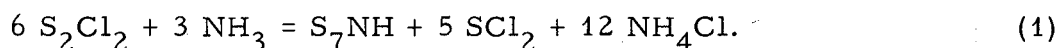
	35 cm long		18 cm long		9.5 cm long	
	Taken (g)	Recovered (g)	Taken (g)	Recovered (g)	Taken (g)	Recovered (g)
S ₈	0.2932	0.2793	0.1765	0.1952	0.3151	0.3138
S ₇ NH	0.0619	0.0353	0.0227		0.0539	
S ₄ N ₄	0.1138	0.0972	0.3311	0.3106	0.1526	0.1500 ^a

^a Infrared analysis showed bands due to S₇NH.

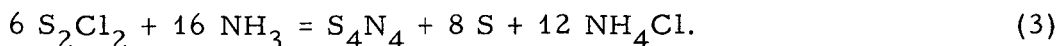
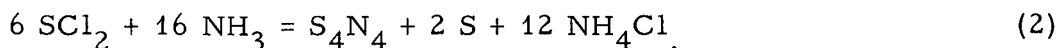
B. Reactions Between Ammonia and Sulfur Chlorides

A series of color changes—namely, rose ebony to olive drab to golden poppy—occurred when gaseous ammonia reacted with sulfur chlorides in a suitable solvent. The reaction was exothermic up to the formation of the olive drab mass, after which the temperature began to drop as the color gradually turned golden poppy.

The changes in color of the reaction mixture are one of the signs of the complexity of the reaction between ammonia and disulfur dichloride. Undoubtedly, there are numerous reactions occurring that lead to the final products. One of them, which leads to the formation of S_7NH , was proposed by Goehring.⁸ Although there is no evidence of the formation of S_7NH , the proposed equation seemed very logical:



Assuming that Eq. (1) does occur, then the formation of S_4N_4 could probably result from two reactions, namely,



The SCl_2 in Eq. (2) was assumed to come from Eq. (1).

All these reactions are believed to be completed in a step-wise manner, as shown from the observation that as the reaction proceeded no S_7NH or S_4N_4 could be isolated. At each color change a drop or two of the reaction mixture was drawn out for observation. After evaporation of the solvent a black residue was left. If the reaction was stopped at the olive drab stage the filtered solid material was an unworkable brown mass, insoluble in benzene and carbon tetrachloride. The solid material was probably composed of insoluble intermediates. It is also believed that the relative rates of each of the determining steps of the above reactions depend upon the conditions of reaction.

The course of the reaction was also followed by drawing out about 5 ml of the reaction mixture at each distinct color change. This sample

was shaken with 25 ml of distilled water and the pH of the aqueous portion was determined. It was found that the pH increased as the reaction proceeded, and remained constant after the formation of the golden poppy color.

The increasing pH can only be used as an indication of the completeness of the reaction. The pH increased from 2.0 to 8.75, at which point the golden poppy color appeared.

It is important to note the pH of the aqueous extract, since results showed that at a fast flowrate of ammonia (50 liters/hr) the orange color appeared twice during the reaction. The first orange color appeared after 30 min and the temperature was at its peak. This color lasted only for about 5 min; the pH of the aqueous extract was 3.25. When the reaction was stopped at this stage the filtered solid material contained no S_4N_4 , and evaporation of the filtrate left a black plastic-like substance.

The criterion for completion of reaction is the formation of the golden poppy mixture, the aqueous extract of which has a pH of 8.75.

The final products of the reaction are tetrasulfur tetranitride, heptasulfurimide, sulfur, and ammonia chloride. Recently, however, it has been reported that three isomers of the hexasulfurdiimide, $S_6(NH)_2$, have been isolated.¹⁷ However, no attention has been devoted to the qualitative and quantitative determination of these isomers since reports showed that they are formed in trace amounts.

The relative amounts of the final reaction products depend upon the conditions of reactions. In view of this fact, reactions were carried out under various conditions to determine the optimum conditions for the preparation of S_4N_4 and S_7NH .

1. Effect of the Duration of Ammonia Flow

The yields of S_4N_4 , S_7NH , and S depend upon the duration of the ammonia flow, as long as the golden poppy color has not been reached. It was found that in Run No. 7, when the ammonia flow was stopped at the formation of the olive drab mixture, the carbon tetrachloride portion of the reaction mixture left a black residue after evaporation, and

the solid material contained no S_4N_4 . However, after the formation of the golden poppy mixture the amount of S_4N_4 and S_7NH remained constant, independent of the duration of the ammonia flow, as shown in Table IV. It could also be seen from the Table that the weight of the dry solid mixture (obtained after water washings) increased; chromatographic separation of the solid mixture showed that the percentages of the three compounds decreased with increase in time of ammonia flow.

The solid material was composed of S_4N_4 , S_7NH , S, and unknown compounds. The weight of the unknown compound increased as more ammonia was allowed to pass. The mixture of unknown compounds liberated ammonia gas upon standing. The bottles containing the solid materials smelled strongly of ammonia.

2. Effect of Temperature

As shown in Table V, the formation of S_4N_4 and S_7NH depended upon the temperature of the reaction. At ambient temperature 9.4 g of S_4N_4 could be isolated. However, when the reaction mixture was cooled in an ice bath throughout the duration of the ammonia flow, only 3.6 g of S_4N_4 was found in the carbon tetrachloride portion of the reaction mixture. The filtered solid material, after water washings, spontaneously decomposed, liberating ammonia gas and leaving a residue of sulfur and ammonia chloride. More S_7NH was obtained from the reaction carried out at ice temperature than at ambient temperature.

Although Arnold¹ made no mention of the effect of low temperature on the yield of S_4N_4 , he stated that it was desirable to conduct the preparation of S_4N_4 at temperatures between 20 and 50° C. It seems that the rates of the above reactions are all temperature dependent—that the yield of S_4N_4 increases with increase in temperature, although it does not increase indefinitely with increasing temperature. It remains fairly constant after a certain critical temperature has been reached. Table IV shows that the yield of S_4N_4 was not affected by an increase in temperature resulting from an increase in the flowrate of ammonia. The yield of S_7NH was slightly affected.

Table IV. Effect of duration of run. Flowrate of ammonia is 18 liters/hr; concentration of S_2Cl_2 is 84 g in 1.4 liters of CCl_4 .

Run No.	Duration of run (hr)	Temp.	Phase of mixture portion (A=liquid B=solid)	Total solid (g)	Product yield		
					S_7NH (g)	S_4N_4 (g)	S_8 (g)
1	3	Ambient	A	28.6	7.0	2.2	15.0
			B	10.0	0.0	7.2	1.5
				<u>38.6</u>	<u>7.0</u>	<u>9.4</u>	<u>16.5</u>
1 ^a	3	Ambient	A	28.9	7.2	2.2	15.5
			B	9.4	0.0	7.6	1.5
				<u>38.3</u>	<u>7.2</u>	<u>9.8</u>	<u>17.0</u>
2	4	Ambient	A	26.2	7.0	2.5	13.8
			B	11.4	0.0	7.6	1.5
				<u>37.6</u>	<u>7.0</u>	<u>10.1</u>	<u>15.3</u>
3	5	Ambient	A	28.0	7.6	2.6	15.6
			B	12.0	0.0	7.3	1.0
				<u>40.0</u>	<u>7.6</u>	<u>9.9</u>	<u>16.6</u>
4	7	Ambient	A	27.0	7.0	2.7	14.1
			B	13.4	0.0	7.8	0.8
				<u>40.4</u>	<u>7.0</u>	<u>10.5</u>	<u>14.9</u>
7	2	Ambient	A	Black plastic-like substance			
			B	Brown unworkable mass			
8	2	Ice-cooled	A	29.2	9.7	3.6	8.5
			B	- ^b			
8 ^a	2	Ice-cooled	A	29.5	10.0	3.0	8.6
			B	- ^b			
9	3	Ice-cooled	A	28.3	11.4	4.5	9.4
			B	- ^b			
10	6	Ice-cooled	A	28.1	10.4	4.0	8.1
			B	- ^b			

^a Prime (') indicates duplicate run.

^b Solid decomposed.

Table V. Effect of temperature. Flowrate of ammonia is 18 liters/hr; concentration of S_2Cl_4 is 84 g in 1.4 liters of CCl_4 .

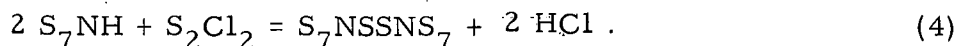
Run No.	Temperature (initial, max, final) (° C)	Phase of mixture portion (A=liquid, B=solid)	Total solid (g)	Product yield		
				S_7NH (g)	S_4N_4 (g)	S_8 (g)
1	21, 49, 23	A	28.6	7.0	2.2	15.0
		B	<u>10.0</u>	<u>0.0</u>	<u>7.2</u>	<u>1.5</u>
			<u>38.6</u>	<u>7.0</u>	<u>9.4</u>	<u>16.5</u>
1 ^a	21, 51, 23	A	28.9	7.2	2.2	15.5
		B	<u>9.4</u>	<u>0.0</u>	<u>7.6</u>	<u>1.5</u>
			<u>38.3</u>	<u>7.2</u>	<u>9.8</u>	<u>17.0</u>
8	2, 18, 2	A	29.2	9.7	3.6	8.5
		B	<u>-^b</u>	<u>-</u>	<u>-</u>	<u>-</u>
			<u>29.5</u>	<u>9.7</u>	<u>3.6</u>	<u>8.5</u>
8 ^a	2, 18, 2	A	29.5	10.0	3.0	8.6
		B	<u>-^b</u>	<u>-</u>	<u>-</u>	<u>-</u>
			<u>29.5</u>	<u>10.0</u>	<u>3.0</u>	<u>8.6</u>
11 ^c	2, 25, 25	A	30.9	10.9	2.5	11.1
		B	<u>10.0</u>	<u>0.0</u>	<u>6.8</u>	<u>1.5</u>
			<u>40.9</u>	<u>10.9</u>	<u>9.3</u>	<u>12.6</u>
18	35, 51, 35	A	31.1	7.7	3.4	16.8
		B	<u>9.6</u>	<u>0.0</u>	<u>6.1</u>	<u>1.0</u>
			<u>40.7</u>	<u>7.7</u>	<u>9.5</u>	<u>17.8</u>

^a Prime (') indicates duplicate run.

^b Solid decomposed.

^c Ice-bath was removed after formation of olive drab color.

From the results obtained and from the works of other investigators, one plausible explanation could be offered as to the effect of temperature on the formation of S_7NH . Goehring⁸ has reported that S_7NH reacts with S_2Cl_2 or SCl_2 in the following manner:



Since ammonia is a good HCl acceptor, there is a possibility that Eq. (4) would be competing with Eqs. (1), (2), and (3) as ammonia is being passed through the S_2Cl_2 solution. However, the temperature of the reaction greatly affects the rates of each of the above reactions. At low temperatures, the rate of reaction (1) is more favored, whereas at very high temperature ($50^\circ C$) the rate of formation of $S_{16}N_2$ becomes more important. Hence the yield of S_7NH decreased as the temperature increased.

3. Effect of the Flowrate of Ammonia

The results of increasing the flowrate of ammonia are given in Table VI. By a threefold increase in the flowrate, the time of the appearance of the golden poppy color was shortened by about one-third of the original time. The yields of S_4N_4 did not vary with the flowrate.

However, it could be seen from Table VI that there was a decrease in the yield of S_7NH when ammonia was passed at a faster flowrate. This could be due to the fact that at a faster flowrate the temperature rose up rapidly, reaching a maximum that was 20 degrees higher than the maximum temperature of the reaction carried out at a slow flowrate of ammonia. Consequently, with such an increase in temperature, the yield of S_7NH decreased correspondingly.

4. Effect of Concentration and Type of Sulfur Chloride

The results given in Table VII show that the yields of S_4N_4 depend upon the concentration and type of sulfur chlorides. At low or ambient temperature the yield of S_4N_4 doubled when the concentration of S_2Cl_2 was doubled; and as expected, the amount of S_4N_4 was doubled when S_2Cl_2 was chlorinated prior to the introduction of ammonia.

Table VI. Effect of flowrate of ammonia. Concentration of S_2Cl_4 is 84 g in 1.4 liters of CCl_4 .

Run No.	Flowrate of NH_3 (liters/hr)	Temperature (initial, max, final) ($^{\circ}C$)	Phase of mixture portion (A=liquid, B=solid)	Total solid (g)	Product yield		
					S_7NH (g)	S_4N_4 (g)	S_8 (g)
1	18	21, 49, 23	A	28.6	7.0	2.2	15.0
			B	10.0	0.0	7.2	1.5
				<u>38.6</u>	<u>7.0</u>	<u>9.4</u>	<u>16.5</u>
1 ^a	18	21, 51, 23	A	28.9	7.2	2.2	15.5
			B	9.4	0.0	7.6	1.5
				<u>38.3</u>	<u>7.2</u>	<u>9.8</u>	<u>17.0</u>
5	50	24, 71, 21	A	28.4	5.0	2.6	15.5
			B	10.2	0.0	7.4	1.7
				<u>38.6</u>	<u>5.0</u>	<u>10.0</u>	<u>17.2</u>

^a Prime (') indicates duplicate run.

Chlorination of S_2Cl_2 forms sulfur dichloride according to the equation:



Inasmuch as two moles of SCl_2 are produced from each mole of S_2Cl_2 , on the basis of Eqs. (2), (3), and (5), the amount of S_4N_4 should be twice as much as that obtained from a reaction between S_2Cl_2 and ammonia.

It can be seen from Table VII that at ambient temperature the yield of S_7NH remained fairly constant and did not vary with the concentration of S_2Cl_2 . However, at low temperature the amount of S_7NH doubled when the concentration of S_2Cl_2 was doubled. This, again is an evidence of the temperature dependence of the rate of formation of $S_{16}N_2$.

A trace amount of S_7NH was obtained from the reaction between SCl_2 and ammonia.

Table VII. Effect of concentration and type of sulfur chloride. Flowrate of ammonia is 18 liters/hr; duration of run was until appearance of golden poppy color.

Run No.	Conc. of S ₂ Cl ₂ (g)	Type	Temperature (initial, max, final) (° C)	Phase of mixture portion (A=liquid, B=solid)	Total solid (g)	Product yield		
						S ₇ NH (g)	S ₄ N ₄ (g)	S ₈ (g)
1	84	S ₂ Cl ₂	21, 49, 23	A	28.6	7.0	2.2	15.0
				B	10.0	0.0	7.2	1.5
					<u>38.6</u>	7.0	9.4	16.5
1 ^a	84	S ₂ Cl ₂	21, 51, 23	A	28.9	7.2	2.2	15.5
				B	9.4	0.0	7.6	1.5
					<u>38.3</u>	7.2	9.8	17.0
12	168	S ₂ Cl ₂	22, 52, 22	A	29.1	8.2	2.1	14.3
				B	56.5	0.0	17.5	24.9
					<u>85.6</u>	8.2	19.6	39.2
12 ^a	168	S ₂ Cl ₂	20, 54, 22	A	28.6	6.2	2.7	15.7
				B	59.0	2.3	20.0	29.5
					<u>87.6</u>	8.5	22.7	45.2
13	84	SCl ₂ ^b	19, 60, 20	A	6.2	0.4	2.5	1.7
				B	39.0	0.0	17.6	0.6
					<u>45.2</u>	0.4	20.1	2.3
19	168	S ₂ Cl ₂	2, 18, 2	A	40.0	16.4	3.5	10.0
				B	22.4	3.6	4.5	12.1
					<u>62.4</u>	20.0	8.0	22.1

^a Prime (') indicates duplicate run.

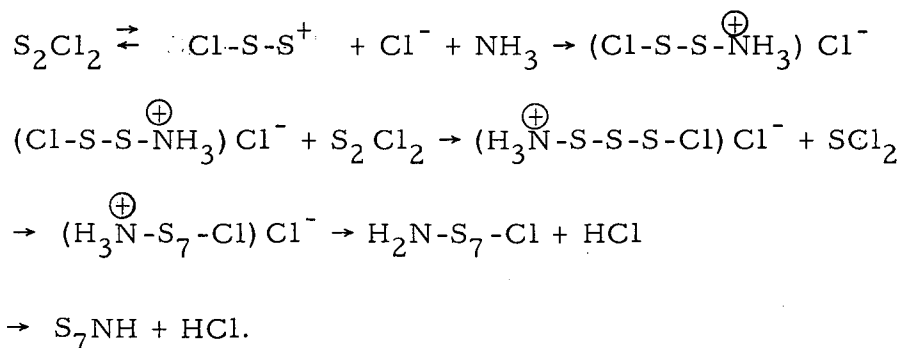
^b Obtained by sufficient chlorination of S₂Cl₂.

There was one puzzling difference in the behavior of the solid materials obtained from the reactions carried out at ice temperature. As mentioned earlier in the discussion, the solid material obtained from a low concentration of S_2Cl_2 spontaneously decomposed after the water washings. However, in Run No. 18, where the concentration of S_2Cl_2 was doubled, a large amount of solid material was filtered off and no decomposition was observed. No explanation for the spontaneous decomposition of the solid could be offered at present—more study on it is necessary.

5. Effect of Solvent

The conditions of reaction were kept similar to that of the first run but the reaction was carried out in various solvents. Table VIII shows that the nature of the solvent seemed to have a tremendous effect on the relative amounts of the reaction products.

It has been postulated⁸ that S_7NH is formed in a step-wise manner, starting from the dissociation of the S_2Cl_2 :



The initial dissociation of S_2Cl_2 should be facilitated in a more polar solvent. However, the results obtained were contrary to this expectation. At low temperatures more S_7NH was formed in a reaction using carbon tetrachloride as solvent than in a reaction using dimethylformamide as solvent. At ambient temperature no S_7NH was isolated from a reaction carried out in dimethylformamide, whereas 8 g of S_7NH was obtained from the carbon tetrachloride solution.

In a more polar solvent the formation of S_4N_4 did not seem to be favored. At no temperature condition was any S_4N_4 obtained from a

reaction carried out in dimethylformamide. However, if tetrahydrofuran (a slightly polar solvent) was used as solvent an appreciable amount of S_4N_4 was formed.

More study on the effect of the nature of solvents is necessary to explain clearly the results obtained.

Table VIII. Effect of solvent. Concentration of S_2Cl_2 is 84 g in 1.4 liters of solvent; flowrate of ammonia is 18 liters/hr.

Run No.	Duration or run (hr)	Temperature (initial, max, final) (°C)	Phase of mixture portion (A=liquid, B=solid)	Total solid (g)	Product yield		
					S_7NH (g)	S_4N_4 (g)	S_8 (g)
1	At orange (3)	21, 49, 23	A	28.6	7.0	2.2	15.0
			B	10.0	0.0	7.2	1.5
				38.6	7.0	9.4	16.5
14	At blue (2)	19, 51, 20		- ^a	- ^b	- ^b	-
15	At blue (1)	-5		16	8.1	- ^b	7.2
16	At orange (1)	21, 51, 39		25.5	- ^b	5.6	13.8

^a Not quantitatively analyzed.

^b Absent.

IV. SUMMARY

Gaseous ammonia and sulfur chlorides in a suitable solvent react to give tetrasulfur tetranitride, heptasulfurimide, sulfur, and ammonia chloride. The relative amounts of these products depend upon the conditions of reaction. For this reason reactions have been carried out under various conditions of temperature, flowrate of ammonia, concentration and type of sulfur chlorides, solvent, and duration of run.

A procedure for the quantitative separation of the reaction products has been established. The S_4N_4 is separated from S and S_7NH on an alumina column by using pure dry benzene as eluant. The S and S_7NH are separated from each other on a silica gel column by elution with pure dry carbon tetrachloride.

I believe that the completion of the reaction yielding S_4N_4 occurs at the formation of the golden poppy mixture, the aqueous extract of which has a pH of 8.75. Beyond this point the yields of S_4N_4 and S_7NH do not vary with the length of time of the ammonia flow.

The results of the numerous runs can be summarized as follows:

(a) The yields of S_4N_4 and S_7NH depend largely upon the temperature of the reaction. At low temperatures very little S_4N_4 and more S_7NH are formed, whereas at higher temperatures a large amount of S_4N_4 is produced but the yield of S_7NH decreases.

(b) Although the yield of S_4N_4 did not vary by a threefold increase in the flowrate of ammonia, the time of completion of reaction was shortened by one-third. The yield of S_7NH decreases with increasing flowrate of ammonia. It is being assumed that at elevated temperatures a side reaction between S_2Cl_2 and S_7NH becomes more favored. For this reason the yield of S_7NH decreases with increasing temperature. Inasmuch as a faster flowrate of ammonia results in an increase in temperature of the reaction mixture, the amount of S_7NH decreases correspondingly.

(c) The yield of S_4N_4 depends upon the concentration and type of sulfur chloride. By using a double amount of S_2Cl_2 the yield of S_4N_4 is doubled. A slightly more than double yield of S_4N_4 is obtained when

S_2Cl_2 is chlorinated prior to the introduction of the ammonia.

(d) As long as the temperature is allowed to rise freely, the yield of S_7NH does not seem to be affected by the change in concentration of S_2Cl_2 . However, at low temperatures, increasing the concentration of S_2Cl_2 increases the yield of S_7NH .

(e) A trace amount of S_7NH is formed if ammonia is passed through a solution of SCl_2 .

(f) The nature of the solvents seems to have a tremendous effect on the relative amounts of the reaction products. If the reaction is carried out in carbon tetrachloride a large amount of S_4N_4 is formed; in tetrahydrofuran less S_4N_4 is obtained; and in a more polar solvent, dimethylformamide, no S_4N_4 is isolated.

(g) Comparable amounts of S_7NH are formed in both the reaction carried out in carbon tetrachloride and dimethylformamide and at low temperatures. The reaction carried out in tetrahydrofuran failed to yield S_7NH .

V. CONCLUSION

The water-insoluble products of the reaction between gaseous ammonia and sulfur chlorides are best quantitatively separated by using two adsorption columns. Separation of S_4N_4 from S and S_7NH is done on an alumina column, using dry benzene as eluant. The S and S_7NH can be separated from each other on a silica gel column by elution with dry carbon tetrachloride.

To obtain the maximum conversion of S_2Cl_2 to S_4N_4 alone, it is best to chlorinate the S_2Cl_2 in carbon tetrachloride prior to the introduction of ammonia. At a moderate flowrate (18 liters/hr) of ammonia no cooling is necessary. It is not advisable to prolong the passage of ammonia beyond the golden poppy color inasmuch as the yield of S_4N_4 does not vary with the duration of the ammonia flow.

The volume of carbon tetrachloride should be proportionate to the initial concentration of S_2Cl_2 . One and four-tenths liters of CCl_4 is sufficient for 168 g (1.2 moles) of S_2Cl_2 to allow a convenient stirring of the reaction mixture. However, if the S_2Cl_2 is to be chlorinated prior to the introduction of ammonia, 1.4 liters is sufficient for 84 g (0.6 mole) of S_2Cl_2 .

If the desired product is S_7NH alone it is best to carry out the reaction at low temperature. An ice bath serves the purpose very well. Carbon tetrachloride is the best solvent to use. Reaction should be stopped at the formation of the golden poppy mixture.

If it is desired to obtain both S_4N_4 and S_7NH in a reaction, it is best to carry out the reaction at ambient temperature and with a moderate flowrate (18 liters/hr) of ammonia.

The changes in color of the reaction mixture are one of the signs of the complexity of the mechanism of the reaction between gaseous ammonia and sulfur chlorides. It seems that the rates of formation of the various products are governed by the temperature of the reaction. The effect of temperature on the formation of S_7NH is very puzzling. It will be interesting to know whether the effect is due either to the reaction between S_7NH and unreacted S_2Cl_2 in the presence of ammonia at elevated temperatures; or whether the rate of formation of S_7NH is greatly slowed down at temperatures above 50° .

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