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REACTIONS OF HEPTASULFUR IMIDE AND THE HEPTASULFUR IMIDE ANION

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REACTIONS OF HEPTASULFUR IMIDE AND  
THE HEPTASULFUR IMIDE ANION

Marshall Harvey Mendelsohn  
(Ph. D. Thesis)

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REACTIONS OF HEPTASULFUR IMIDE AND THE HEPTASULFUR IMIDE ANION

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ABSTRACT

Several experiments were performed to determine whether solutions of the heptasulfur imide anion ( $S_7N^-$ ) could be quantitatively prepared from the parent acid, heptasulfur imide ( $S_7NH$ ). A successful method was found which employed powdered KOH under low temperature ( $-60^\circ$ ) conditions and a controlled stirring time (15 min). Investigations were also carried out on reactions of solutions of the heptasulfur imide anion with several potential reactants. From these experiments, three new derivatives,  $S_7NCO_2C_2H_5$ ,  $S_7NCO_2CH_2C_6H_5$ , and  $S_7NSi(CH_3)_3$ , were prepared and characterized.

A study was made of the reaction of  $S_7NH$  with diborane. New compounds of the formula,  $S_7NBH_2 \cdot \text{ether}$  were made, and the compound  $S_7NBH_2 \cdot (C_2H_5)_2O$  was isolated as a crystalline material and characterized. The new compound  $S_7NBH_2 \cdot \text{pyridine}$  was also isolated and characterized.

Finally, a preliminary study was made of the reaction of sulfur nitride ( $S_4N_4$ ) with aluminum trichloride in nitromethane. The species  $S_2N_2^+$  and  $NH_4^+$  were identified as two of the products of the reaction.

## I. PREPARATION OF THE HEPTASULFUR IMIDE ANION

### A. Introduction

Heptasulfur imide was first isolated by Macbeth and Graham in 1923;<sup>1</sup> however, the correct formulation of the compound as  $S_7NH$  was not made until 1942 by Arnold.<sup>2</sup> Many reactions involving heptasulfur imide have been carried out; however, only one group of workers<sup>3</sup> has prepared and studied reactions of the heptasulfur imide anion,  $S_7N^-$ . In this section we report various attempts at quantitatively preparing solutions of the anion.

### B. Experimental

Reagents and procedures.- Heptasulfur imide was made by standard methods<sup>4,5</sup> and purified by one recrystallization from methanol followed by repeated recrystallizations from carbon tetrachloride until the solutions were colorless and the solid melted at 113-114° (lit. 113.5°).<sup>5</sup> Methyl iodide, trifluoroacetic acid, methyl lithium, and potassium hydroxide were all reagent grade chemicals and were used without further purification. Anhydrous lithium hydroxide was used as received from the Fisher Scientific Company. Liquid ammonia was distilled from sodium. Diglyme was distilled first from potassium hydroxide and then from lithium aluminum hydride at reduced pressure. Tetrahydrofuran was distilled from lithium aluminum hydride. Fluorene and 2,3-dimethylnaphthalene were each recrystallized twice from ethanol and were found

to melt at 116-118° (lit. 116-7°)<sup>6</sup> and 104-104.5° (lit. 104-4.5°)<sup>6</sup>, respectively. Para-dibromobenzene was recrystallized from ethanol and was found to melt at 86.5-88° (lit. 87°).<sup>6</sup>

To determine the yield of  $S_7N^-$  from the reaction of potassium fluorenyl with  $S_7NH$ , methyl iodide was used to convert the  $S_7N^-$  in solution to  $S_7NCH_3$ . A known amount of  $K^+$  fluorenyl $^-$  in diglyme was pipetted into a vessel cooled to -78°, and the solution was quickly diluted with 5 ml of THF to prevent freezing. A 10% excess of  $S_7NH$  dissolved in THF was cooled to -78° and then added to the potassium fluorenyl solution. The resulting solution was stirred for a known amount of time under a  $N_2$  atmosphere, and then a large excess of methyl iodide (1 ml) was added and allowed to react for 20-30 min. After removal of the volatiles under vacuo, the  $S_7NCH_3$  was quantitatively extracted with carbon disulfide, and the amount of  $S_7NCH_3$  formed was determined by proton nmr spectroscopy using a weighed amount of 2,3-dimethylnaphthalene as an internal standard.

To study the reaction of heptasulfur imide with potassium hydroxide and lithium hydroxide, a weighed amount of  $S_7NH$  (0.2-0.5 g) was added to a stirred slurry of KOH or LiOH (2-4 g) in tetrahydrofuran (25.0 ml) at -63°. At various times an aliquot was pipetted from solution and added to an excess of standardized trifluoroacetic acid dissolved in diglyme. The excess acid was titrated with standardized 0.100 M NaOH to neutrality. The endpoint was detected by the first persistent blue color. (The accuracy of this indicator was checked by doing several titrations on a known amount of acid in the presence of some  $S_7NH$ , and

it was found to be as good as a phenolphthalein indicator solution.) We also determined the yields of  $S_7NCH_3$  for various stirring times of a THF solution of  $S_7NH$  with LiOH or KOH. An aliquot of solution at  $-62^\circ$  was pipetted into an excess of  $CH_3I$  (0.5-0.6 ml), and after evaporation of the volatiles, the amount of  $S_7NCH_3$  formed was determined by proton nmr spectroscopy, using  $p-Br_2C_6H_4$  as an internal standard.

The preferred method for quantitative preparation of the  $S_7N^-$  anion involves the use of an apparatus described previously in the literature.<sup>7</sup> Reaction flask A was equipped with a stopcock B and was connected to collection flask E (equipped with a stopcock D) through a filtration column C. Reaction flask A was flushed with  $N_2$  through stopcock B and cooled to ca.  $-60^\circ$ . A magnetic stir bar, 25.0 ml of THF, and 2-4 g of freshly powdered KOH were, respectively, added to reaction flask A. After the slurry had stirred for a few minutes, 0.2-0.5 g  $S_7NH$  was added, the time noted, and parts E and C connected to A.  $N_2$  was flushed through stopcock D for a few minutes, and then stopcocks D and B were closed. The solution was allowed to stir for 15 minutes and was then filtered. The filtration was performed by removing the apparatus from the cold bath ( $\sim -62^\circ$ ), inverting it, and briefly applying a vacuum through stopcock D. Filtration was carried out in 5-10 seconds, and several blank runs showed that the temperature of the solution after filtration was  $-30$  to  $-40^\circ$ . After filtration,  $N_2$  was reintroduced through stopcock D. A and C were removed from E, and E was stoppered with a ground-glass sleeve joint attached to an

open stopcock. After a few minutes of flushing, the latter stopcock and stopcock D were almost simultaneously closed. The solutions obtained in the preceding manner were warmed to  $-22$ ,  $0$ , or  $\sim 23^{\circ}$ . At various times, an aliquot (5.0 ml) was pipetted into an excess of  $\text{CH}_3\text{I}$  (0.5-0.6 ml) at  $0^{\circ}$ . The amount of  $\text{S}_7\text{NCH}_3$  formed was determined as described in the previous paragraph.

A chromatographic column with a glass frit and a cooling jacket was used to study the reaction of a solution of  $\text{S}_7\text{NH}$  passed through a column of anhydrous  $\text{LiOH}$ . The apparatus had a sidearm used for flushing and maintaining a  $\text{N}_2$  atmosphere. The column was loaded with  $\text{LiOH}$  to a total height of 5-7 cm, and the cooling jacket was brought to a temperature of  $-55$  to  $-68^{\circ}$  by adding dry ice to acetone. A known amount (about .25 g) of  $\text{S}_7\text{NH}$  dissolved in 25.0 ml of THF was added, and a stopwatch was started. The time of passage through the column varied with the pressure applied from a  $\text{N}_2$  tank. The eluate was collected in a flask, which was attached to the column with a standard 19/38 ground-glass joint. The flask was cooled to  $-78^{\circ}$ , and an aliquot of the eluate was added to an excess of trifluoroacetic acid in diglyme. The equivalents of base in solution per mole of  $\text{S}_7\text{NH}$  was determined by titration as described previously.

Preparation of  $\text{K}^+\text{fluorenyl}^-$ . - An apparatus similar to that referred to previously was used.<sup>7</sup> Solutions of  $\text{K}^+\text{fluorenyl}^-$  were made by adding a known amount of fluorene to 50.0 ml of diglyme and stirring under a  $\text{N}_2$  atmosphere with 3-5 g of powdered  $\text{KOH}$ . The solution was filtered and checked by titration. An aliquot was added to an

excess of standardized 0.100 N HCl, and a few drops of phenolphthalein in methanol were added. The endpoint was detected by the color change yellow to orange. After 16-24 hours of stirring, it was found that 94-100% of the fluorene had been deprotonated.

Instrumentation.- A Varian T-60 was used for the proton nmr spectra, and a Cary 14 spectrophotometer was used to record the uv-vis spectrum.

### C. Results

S<sub>7</sub>NH + liquid NH<sub>3</sub>.- When a small amount of S<sub>7</sub>NH is added to dry liquid ammonia at -78°, a bright yellow colored solution is formed. These dilute solutions ( $\sim 10^{-4}$  M) were found to be highly conducting (two measurements gave molar conductances of 210 and 280 cm<sup>2</sup>/ohm-mole; for comparison to a known ionic compound, the value for Na(N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>) is 235 cm<sup>2</sup>/ohm-mole<sup>8</sup>). When methyl iodide was added to these solutions, it was found that S<sub>7</sub>NCH<sub>3</sub> could be isolated. However, because of the limited solubility of S<sub>7</sub>NH in liquid ammonia and the reactivity of ammonia itself, this solvent system was not investigated further.

S<sub>7</sub>NH + CH<sub>3</sub>Li.- When methyl lithium is allowed to react with excess S<sub>7</sub>NH at -78°, a yellow solution is formed, and in two runs the yields of methane liberated were 88% and 90%. Because we did not find the desired 100% yield and also because of the difficulty of quantitatively handling solutions of methyl lithium, this method was also not investigated further.

S<sub>7</sub>NH + LiOH. - When S<sub>7</sub>NH reacts with LiOH at -63° to -45°, a yellow solution is formed. The number of equivalents of base in solution per mole of S<sub>7</sub>NH was determined under various conditions, and these values are given in Table I for different reaction times. If we had quantitatively prepared a solution of S<sub>7</sub>N<sup>-</sup>, the number of equivalents of base in solution per mole of S<sub>7</sub>NH should be 1.00. As can be noted from Table I, we found that the number of equivalents of base in solution per mole of S<sub>7</sub>NH increased with time to values larger than 1.00. We then checked the yields of S<sub>7</sub>NCH<sub>3</sub> for shorter periods of stirring at -60° and found the following results (± 3%): 2 min, 24%; 5 min, 67%; 15 min, 53%; 30 min, 49%.

In two experiments with S<sub>7</sub>NH and LiOH, we determined the yield of S<sub>7</sub>NCH<sub>3</sub> and the number of equivalents of base in solution per mole of S<sub>7</sub>NH from the same solution. The results were as follows:

Yield of S <sub>7</sub> NCH <sub>3</sub> (%/100%)	No. of equivalents of base in solution / S <sub>7</sub> NH (mole)
0.59 ± .02	0.83 ± .01
0.27 ± .02	0.30 ± .01

S<sub>7</sub>NH + K<sup>+</sup> fluorenyl<sup>-</sup>. - Four runs were carried out with an excess of S<sub>7</sub>NH, and as can be noted from Table II, the maximum yield of S<sub>7</sub>NCH<sub>3</sub> was found to be 80%.

S<sub>7</sub>NH + KOH. - When S<sub>7</sub>NH reacts with KOH at -63° a yellow solution is first obtained which after several minutes turns green. If the yellow solution is cooled to -78°, it remains yellow, and if the green

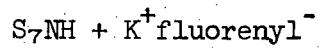
TABLE Ia  
S<sub>7</sub>NH + LiOH

Temp.(°C)	stirring time (hr)	equivalents of base in solution/ S <sub>7</sub> NH (mole)
-63	0.5	1.18
-63	1.0	1.53
-63	3.0	1.69
-45	0.5	1.26
-45	1.0	1.30
-45	2.5	1.70
-45	4.3	2.28

TABLE Ib  
S<sub>7</sub>NH + LiOH

Temp.(°C)	total time through column (min)	equivalents of base in solution/ S <sub>7</sub> NH (mole)
-57	2.2	0.84
-55	3.5	1.01
-68	4.2	1.06
-56	5.0	1.10
-55	5.5	1.15
-57	6.0	1.22

TABLE II



Temp.(°C)	stirring time (hr)	yield of $S_7NCH_3$ (% ± 3%)
-78	0.5	58
-78	0.7	59
-78	4.0	80
-78	24.0	79

solution is warmed to  $0^{\circ}$ , it turns blue. Table III shows the number of equivalents of base in solution per mole of  $S_7NH$ , determined by titration of an aliquot of solution, at various temperatures and stirring times. As can be noted from Table III, it was found that the number of equivalents of base in solution per mole of  $S_7NH$  increased with time to values larger than 1.00. Yields of  $S_7NCH_3$  were determined by addition of an aliquot of the solution made from  $S_7NH$  with KOH at  $-62^{\circ}$  to an excess of  $CH_3I$  at  $0^{\circ}$ . The results were as follows ( $\pm 3\%$ ): 2 min, 68%; 10 min, 101%; 15 min, 102%; 20 min, 103%; 30 min, 95%; 40 min, 94%; 90 min, 85%. These results indicate that a quantitative preparation of the  $S_7N^-$  anion can be realized with KOH by carrying out the reaction at  $\sim -62^{\circ}$  for 15 min  $\pm$  5 min. A yield of  $99\% \pm 2\%$  was found 3 more times from solutions prepared under similar conditions as those described above, during the course of the experiments detailed next.

Temperature behavior of solutions of  $S_7N^-K^+$ . - When a solution of  $S_7N^-K^+$ , made by reacting  $S_7NH$  with KOH in THF at  $-62^{\circ}$  for 15 minutes, was filtered and allowed to stand at room temperature for one hour, it was found that the yield of  $S_7NCH_3$  was  $27 \pm 2\%$  (average of 3 runs). Additional runs were made by allowing the filtered solution of  $S_7N^-$  to warm to  $-22$  and  $0^{\circ}$ . For these runs, the yield of  $S_7NCH_3$  was determined as a function of time. This was also done for a solution which was cooled from  $\sim 50^{\circ}$  to  $0^{\circ}$ . The results are shown in Table IV. The results of the runs performed on going from  $-63$  to  $0^{\circ}$  and from  $50$  to  $0^{\circ}$  show that the yield leveled off in both instances at  $34\% \pm 1\%$ .

TABLE III

S<sub>7</sub>NH + KOH

Temp. (°C)	stirring time (hr)	equivalents of base in solution/ S <sub>7</sub> NH (mole)
-63	0.5	0.97
-63	0.75	1.06
-63	1.0	1.09
[ -78 <sup>a</sup>	0.25	0.98
	0.5	1.07
	1.0	1.09
[ -78 <sup>b</sup>	0.5	0.81
	1.0	0.85
	2.3	1.00
	4.5	1.19

<sup>a</sup> initially at -63° for 3 min

<sup>b</sup> initially at -63° for 2 min

TABLE IV

Time Dependence of Yields of  $S_7NCH_3$   
After a Temperature Change

Time at a specific temperature (min)	Temp. ( $^{\circ}C$ )	Yield of $S_7NCH_3$ ( $\% \pm 2\%$ )
15	-63	99
30	-22	90
50	-22	84
120	-22	66
720	-22	46
15	-63	97
5	0	80
25	0	42
60	0	36
1230	0	34
10	$\sim 50$	25
5	0	37
15	0	35
60	0	33
1200	0	35

The data in Table IV can also be interpreted kinetically. If we assume a first order dependence on the decreasing yield of  $S_7NCH_3$ , we can plot  $\log(\text{yield } S_7NCH_3(\infty) - \text{yield } S_7NCH_3(t))$  vs. time. When this was done for the runs at  $-22$  and  $0^\circ$ , and the best straight line approximated by sight, the following half-times were noted:

Half-time (min)	Temp. ( $^\circ\text{C}$ )
12	0
84	-22

In a separate experiment, a solution which was warmed to room temperature for one hour and which gave a yield of  $S_7NCH_3$  of 26% was kept at approximately  $-35^\circ$  for 11 days. The yield of  $S_7NCH_3$  was rechecked and was found to be 53% (average of 2 aliquots).

If the following yields are assumed to be equilibrium values (see discussion section) and are plotted as  $\log K$  vs.  $1/T$ , a straight line is obtained which gives  $\Delta H = -2.7$  kcal/mole:

Temp. ( $^\circ\text{C}$ )	Yield of $S_7NCH_3$ (%)
-35	53
-22	46
0	34
20	27

$S_7NH + KOH$  in DMSO. - It was found that at room temperature,  $S_7NH$  reacts with  $KOH$  in dimethyl sulfoxide to give a green colored solution which in a few seconds changes to a deep blue colored solution.

After stirring for 1-2 hours, it was found that the blue solution changes to a deep brown-orange color. No further change was detected after an additional 24 hours of reaction. The brown-orange solution was found to be stable in a  $N_2$  atmosphere for at least two weeks; however, it immediately changes color if exposed to oxygen or if water is added. The solution was titrated with acid when the deep brown-orange color appeared. The equivalents of base in solution per mole of  $S_7NH$  in four separate experiments was found to be 4.00, 3.97, 3.96 and 3.94. A uv-vis spectrum of the brown-orange solution showed two peaks in the visible region at 4700 and 3330 Å. Two peaks in the ultraviolet region were not completely resolved, but appeared at approximately 2880 and 2620 Å.

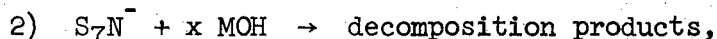
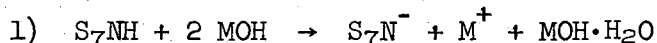
#### D. Discussion

The majority of experimental conditions tested were found unsuitable for the quantitative preparation of solutions of the heptasulfur imide anion. However, we did find that with KOH we could convert greater than 95% of the  $S_7NH$  to the heptasulfur imide anion by carrying out the reaction at low temperature and by carefully controlling the reaction time. This conclusion is based on the assumption that the yield of  $S_7NCH_3$  upon addition of methyl iodide is a quantitative indicator of the species  $S_7N^-$ . We believe that this assumption is at least partially verified by the fact that under certain conditions we do get 100% yields of  $S_7NCH_3$ . Also, it has been shown that  $S_7NH$  and  $CH_3I$  do not react at 35°, <sup>3b</sup> eliminating the possibility of the

$S_7NCH_3$  coming from the  $S_7NH$ . Thus it appears most likely that the formation of  $S_7NCH_3$  is due to the species  $S_7N^-$ .

The basic problem in quantitatively preparing solutions of the heptasulfur imide anion is that another reaction, besides simple deprotonation, is occurring. Because the equivalents of base in solution per mole of  $S_7NH$  becomes greater than 1.0, this other reaction is most likely a base attack on the  $S_7N$  ring to give an open chain species. With KOH, the yield of  $S_7NCH_3$  was 100% after 20 minutes of stirring and then slowly decreased. Because we did obtain a solution which contained only  $S_7N^-$  (and no  $S_7NH$ ) and because at longer times we found that the equivalents of base in solution per mole of  $S_7NH$  is greater than 1.00 and that the yield of  $S_7NCH_3$  (i.e.  $S_7N^-$ ) was decreasing, the attack of the  $OH^-$  anion in this case must be on the  $S_7N^-$  anion. Because we do not find a solution which contains only  $S_7N^-$  for the base LiOH, the following two possibilities must be considered: (1) If the attack were on the  $S_7NH$ , the yield of  $S_7N^-$  would always be less than the equivalents of base in solution per mole of  $S_7NH$ ; (2) If the attack were on the  $S_7N^-$ , then at very low yields of  $S_7N^-$ , the equivalents of base in solution per mole of  $S_7NH$  may be equal to the yield of  $S_7N^-$ . The results of two runs with LiOH, in which we determined the yield of  $S_7NCH_3$  (i.e.  $S_7N^-$ ) and the equivalents of base in solution per mole of  $S_7NH$  for the same solution, suggest that the second hypothesis is correct. Therefore, our data show that for the bases KOH and LiOH, the complicating reaction is a base attack of the  $S_7N^-$  anion.

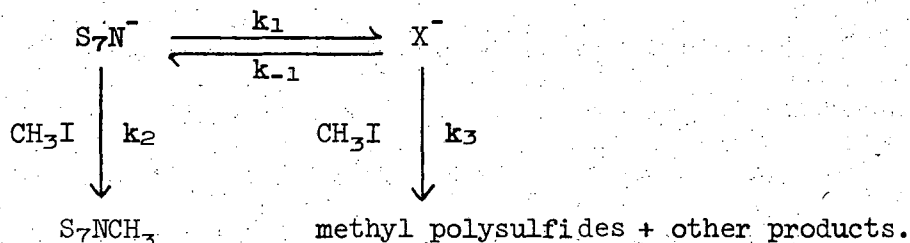
If the decomposition reaction is a base attack on the  $S_7N^-$ , then we can consider the following two consecutive reactions to be true:



where  $M = K$  or  $Li$ . In order to detect the intermediate,  $S_7N^-$ , reaction 1 must be faster or of about the same speed as reaction 2. We find that with  $LiOH$  and  $KOH$ , the yield of  $S_7NCH_3$  (i.e. the amount of  $S_7N^-$ ) does build to a maximum and then slowly declines. Therefore, the deprotonation reaction is faster or of about the same speed as the subsequent decomposition reaction at low temperatures.

We believe that the yellow color observed at low temperatures (from  $S_7NH$  with  $NH_3$ ,  $CH_3Li$ ,  $LiOH$  or  $KOH$ ) is from the  $S_7N^-$  anion, and that the anion is not blue, as previously suggested.<sup>3b</sup> Three observations lead us to believe that the  $S_7N^-$  anion can be in equilibrium with another species (possibly the blue species). First, Olsen found that the yield of  $S_7NCH_3$  was constant over a three day period for a solution of  $S_7N^-$  which was allowed to sit at room temperature.<sup>3b</sup> We have found that at  $0^\circ$ , the yield of  $S_7NCH_3$  levels off after the temperature of a solution of the anion has been raised from  $-62$  to  $0^\circ$ . Secondly, we found that a yield of 34% is reached at  $0^\circ$  when approached from either a higher temperature or a lower temperature. Finally, we found an increase in the yield of  $S_7NCH_3$  from 26% to 53% when a solution was cooled from room temperature to approximately  $-35^\circ$ .

The question arises, however, whether the addition of  $\text{CH}_3\text{I}$  actually quenches the equilibrium. That is, does the yield of  $\text{S}_7\text{NCH}_3$  represent the true amount of  $\text{S}_7\text{N}^-$  at the time of addition of the  $\text{CH}_3\text{I}$ ? The proposed reaction scheme is as follows:



We first note that over the temperature range  $-35$  to  $20^\circ$   $k_1 \approx k_{-1}$ . This approximate equality simplifies the conditions to two inequalities ( $k_2 \gg k_1$  and  $k_3 \gg k_1$ ) which must be simultaneously satisfied in order to assert that the yield of  $\text{S}_7\text{NCH}_3$  does indicate the actual  $\text{S}_7\text{N}^-$  present. Our data do not permit us to say whether or not both of these conditions are simultaneously met. If  $k_2 \gg k_1$  at some low temperature and if  $E_{a2}$  (activation energy)  $> E_{a1}$ , then  $k_2 \gg k_1$  would be true at all higher temperatures. From our kinetic data for runs at  $-22$  and  $0^\circ$ , we can estimate that  $E_{a1} = 12$  kcal/mole. The activation energies for the reaction of methyl iodide with  $\text{C}_2\text{H}_5\text{O}^-$ ,  $\text{Br}^-$ ,  $\text{S}_2\text{O}_3^{=}$ , and o, m, and p- $\text{CH}_3\text{C}_6\text{H}_4\text{O}^-$  are all known<sup>9</sup> and all fall in the range 18.8 ( $\text{S}_2\text{O}_3^{=}$ ) - 21.4 ( $\text{Br}^-$ ) kcal/mole. It is plausible then that  $E_{a2} > E_{a1}$ . It is more difficult to speculate on  $E_{a3}$ , because we do not know what the species  $\text{X}^-$  is (our best guess is some open chain species). However, there is an indication that either one or both of the conditions is not true at temperatures above  $\sim 20^\circ$ . This is because the yield of

$S_7NCH_3$  at room temperature was 27%, and approximately the same value was found for higher temperatures. Therefore, we can only assume that our data from  $-35$  to  $20^\circ$  give us the true equilibrium value, and in order to prove this assumption, further experiments need to be done.

The reaction of  $S_7NH$  with  $KOH$  in  $DMSO$  stops when the equivalents of base in solution per mole of  $S_7NH$  is 4.0. However, the species in this solution have not been identified. The species are probably interesting intermediates in the base decomposition of  $S_7NH$  and should be investigated further.

Although we have shown that solutions of the heptasulfur imide anion can be quantitatively prepared, their usefulness is at least partially limited by their difficult preparation and equilibration at ordinary temperatures with a seemingly equally reactive species. However, several reactions have been investigated, and some of these are reported in the next section.

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## II. REACTIONS OF THE HEPTASULFUR IMIDE ANION

### A. Introduction

In section I, we reported various experiments leading to a successful method for quantitative preparation of solutions of the heptasulfur imide anion ( $S_7N^-$ ). In this section, we report the preparation of three new heptasulfur imide derivatives by reaction of  $ClCO_2C_2H_5$ ,  $ClCO_2CH_2C_6H_5$  and  $ClSi(CH_3)_3$  with solutions of  $S_7N^-$  made with LiOH or KOH. We also briefly describe the results of the reactions of several potential reactants with  $S_7N^-$ , which either failed to react or gave unstable products.

### B. Experimental

Reagents and procedures.- Ethyl chloroformate, benzyl chloroformate, boron trifluoride ether complex, antimony trichloride, trimethylchlorosilane, and trimethyl tin chloride were all reagent grade chemicals and were used without further purification. Standard methods were used in the preparation of  $B(CH_3)_3$ <sup>1</sup> and  $(C_5H_5)_2TiCl_2$ .<sup>2</sup> Pyridine was dried with KOH and distilled. Reagent grade carbon disulfide and carbon tetrachloride were used. Spectroquality hexane was used without further purification.

Solutions of  $S_7N^-$  were prepared from  $S_7NH$  (0.2-0.5 g) and powdered KOH (2-4 g) in an apparatus similar to that described previously.<sup>3</sup> After stirring for 15 minutes, the solution of  $S_7N^-$  in THF (15-25 ml)

was filtered. The non-volatile reactants,  $(C_5H_5)_2TiCl_2$ ,  $SbCl_3$ , or  $(C_6H_5)_3SnCl$ , were each dissolved in THF and added directly to the  $S_7N^-$  solution, which was cooled to  $-78^\circ$ . For the volatile reactants,  $BF_3 \cdot$  ether,  $(CH_3)_3SiCl$ , and  $B(CH_3)_3$ , the vessel containing the  $S_7N^-$  solution was first evacuated on a vacuum line, and then the reactant condensed in, while the vessel was held at  $-78^\circ$  with a dry ice-acetone bath. In all cases, the reaction mixture was held at  $-78^\circ$  for 5-15 minutes with occasional agitation. The vessel was then warmed to room temperature, and, after 15-60 minutes, the THF and excess volatile reactant were removed by pumping to leave the crude product.

In the reaction of  $S_7N^-$  with  $BF_3 \cdot$  ether, 20 ml of pyridine was condensed into the vessel containing the crude product. A portion of the crude product was insoluble in the pyridine. The insoluble material was quickly filtered in the air, and the white solid collected was washed with acetone. An infrared spectrum of a Nujol mull of the white solid was recorded and was identical to that reported for  $KBF_4$ .<sup>4</sup> From 0.22 g  $S_7NH$ , 0.11 g  $KBF_4$  were recovered, corresponding to 0.93  $KBF_4$ (mmol)/ $S_7NH$ (mmol). In one case, methanol was added to the filtrate and after evaporation to a small volume ( $\sim 5$  ml), a solid was collected by filtration and identified as  $S_7NH$  from its infrared spectrum. In another experiment, the filtrate was first brought to dryness by evaporating the pyridine. The residue was treated with  $CCl_4$  which was then decanted and evaporated to a small volume (2-3 ml). Again, the solid precipitate was isolated and identified as  $S_7NH$ . In both experiments, a water soluble white solid was isolated from the filtrate (solid was soluble in methanol but not in  $CCl_4$ ) but was not identified.

For preparation of the derivatives  $S_7NCO_2C_2H_5$  and  $S_7NCO_2CH_2C_6H_5$ , an all-glass apparatus was used. This consisted of a 100 ml round bottom flask with an extended neck (ca. 25 cm) which contained a fritted disc. The fritted disc was 20 cm below the top of the neck. A second tube (25 cm long and 10 mm od) was attached to the top of the flask at a slight angle ( $\sim 20^\circ$ ) to the neck. The apparatus could be flushed with  $N_2$  through a side-arm attached 2 cm from the top of the neck. A solution of  $S_7NH$  (.2-.5 g) in THF (25 ml) was then passed into the flask through a column of anhydrous LiOH as described in section I. A 10-fold excess of  $ClCO_2CH_2C_6H_5$  or  $ClCO_2C_2H_5$  was then pipetted through the second tube into the solution containing  $S_7N^-$ , and the flask was agitated. After 5-15 minutes, the reaction mixture was poured into a flask, from which the solvent and excess reactant could be removed by pumping to leave the crude product.

Purification and chemical analysis.- The product  $S_7NCO_2CH_2C_6H_5$  was purified by first adding  $CS_2$  (20 ml) to the crude product and filtering the mixture. The filtrate was saved and the  $CS_2$  allowed to evaporate. The remaining residue was recrystallized twice from 10 ml of a 9:1  $CS_2$ :hexane solvent. The resulting white precipitate was collected and melted sharply at  $98-99^\circ$  (uncorrected). The yield was 0.10 g (25%) from 0.28 g  $S_7NH$ . Anal. Calcd for  $S_7NCO_2CH_2C_6H_5$ : C, 25.72; H, 1.87; N, 3.75; S, 60.09. Found: C, 25.68; H, 1.96; N, 3.90; S, 60.24.

The product  $S_7NCO_2C_2H_5$  was purified by first adding  $CS_2$  to the crude product and filtering the mixture. The filtrate was saved and

the CS<sub>2</sub> allowed to evaporate. A boiling 9:1 hexane:CS<sub>2</sub> solvent was added to the remaining residue, and the solution was then decanted. The soluble fraction was saved and after evaporation of the solvent to ~ 1 ml, a yellow liquid, which was more dense than the solvent, separated from the solution. The solvent was then decanted and the process repeated until the infrared spectrum of the yellow liquid showed the absence of a peak at 3330 cm<sup>-1</sup>. The yield was 0.20 g (45%) from .37 g S<sub>7</sub>NH. Anal. Calcd for S<sub>7</sub>NCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>: C, 11.56; H, 1.61; N, 4.49; S, 72.07. Found: C, 11.43; H, 1.53; N, 4.61; S, 72.18.

The product S<sub>7</sub>NSi(CH<sub>3</sub>)<sub>3</sub> was dissolved by addition of 20 ml of a 50:50 hexane:CS<sub>2</sub> solvent or CCl<sub>4</sub> to the crude product in a dry box. The insoluble material was filtered from the solution. Upon evaporation of the filtrate to a volume of 2-3 ml, a solid precipitate was observed. The solid was filtered off and identified as S<sub>7</sub>NH by its infrared spectrum. The filtrate was saved and upon evaporation yielded a yellow liquid. We were unable to induce this yellow liquid to crystallize or to purify it by sublimation or separation of a pure liquid phase by cooling or addition of another liquid. However, we were able to remove the remaining S<sub>7</sub>NH, as determined from the disappearance of the peak at 3300 cm<sup>-1</sup> in the infrared, by cooling a hexane solution of the yellow liquid to -78° and collecting the filtrate. The yield was 0.10 g (15%) from 0.50 g S<sub>7</sub>NH. Anal. Calcd for S<sub>7</sub>NSi(CH<sub>3</sub>)<sub>3</sub>: C, 11.55; H, 2.89; N, 4.49; S, 72.05. Found: C, 14.98, 13.91; H, 3.09, 3.08; N, 4.39; S, 70.74.

Infrared spectra.- Infrared spectra were recorded with a Perkin-Elmer Model 137B Infracord Spectrophotometer. The following lines were observed for a neat sample of  $S_7NCO_2CH_2CH_3$  pressed between two NaCl plates ( $cm^{-1} \pm 10 cm^{-1}$ ): 2967(m-s), 2924(sh), 1730(s), 1456(m), 1437(m), 1389(m), 1364(m-s), 1292(m), 1208(vs), 1111(w), 1096(m), 1053(m), 999(s), 985(s), 926(m), 834(m-s), 801(m), and 758(s). The following lines were observed for  $S_7NCO_2CH_2C_6H_5$  dissolved in  $CS_2$ , except for the peak at  $839 cm^{-1}$  which was seen in the Nujol mull ( $cm^{-1} \pm 10 cm^{-1}$ ): 3030(w-m), 2941(w-m), 1739(s), 1376(m), 1250(sh), 1199(vs), 1043(m), 1031(m), 1005(w), 976(m), 952(m), 917(w), 839(m), 755(s), 741(s), 694(s). Other peaks were hidden by the  $CS_2$ . The following lines were observed for a neat sample of  $S_7NSi(CH_3)_3$  pressed between two NaCl plates ( $cm^{-1} \pm 10 cm^{-1}$ ): 2959(w-m), 2899(sh), 1401(w), 1364(sh), 1248(m-s), 870(vs), 842(s), 793(m), 756(w-m), and 685(w).

$^1H$  nmr spectra.- The samples were dissolved in  $CS_2$ , and the spectra were recorded with a Varian T-60 spectrometer. All chemical shifts are given relative to internal TMS and are to low field of TMS. For  $S_7NCO_2C_2H_5$ , a triplet centered at 1.33 ppm and a quartet centered at 4.22 ppm were observed. The relative intensity of the triplet to the quartet was 3:2, with  $J_{H-H} = 8$  Hz. For  $S_7NCO_2CH_2C_6H_5$ , two singlets were observed at 7.27 ppm and 5.16 ppm. Their relative intensities were 5:2, indicating that the lower field singlet is from the protons on the phenyl group. For  $S_7NSi(CH_3)_3$ , a singlet was observed at 0.33 ppm.

Mass spectra.- The mass spectra of  $S_7NCO_2C_2H_5$  and  $S_7NSi(CH_3)_3$  were recorded at 70 eV with a Consolidated Electrodynamics Corporation Type 21-103C mass spectrometer. The mass spectrum of  $S_7NCO_2C_2H_5$  gave the following peaks (peaks < 4% of the most intense peak are not given) (m/e, relative peak height, and assignment, respectively): 315, 4,  $^{34}S_2^{32}S_5CO_2C_2H_5^+$ ; 313, 24,  $^{34}S^{32}S_6NCO_2C_2H_5^+$ ; 312, 7,  $^{33}S^{32}S_6NCO_2C_2H_5^+$ ; 311, 75,  $^{32}S_7NCO_2C_2H_5^+$ ; 260, 4,  $^{34}S_2^{32}S_6^+$ ; 258, 18,  $^{34}S^{32}S_7^+$ ; 257, 4,  $^{33}S^{32}S_7^+$ ; 256, 53,  $^{32}S_8^+$ ; 247, 4,  $^{32}S_5NCO_2C_2H_5^+$ ; 239, 4,  $^{32}S_7NH^+$  (imp); 215, 7,  $^{32}S_4NCO_2C_2H_5^+$ ; 194, 4,  $^{34}S^{32}S_5^+$ ; 192, 11,  $^{32}S_6^+$ ; 162, 26,  $^{34}S^{32}S_4^+$ ; 161, 6,  $^{33}S^{32}S_4^+$ ; 160, 100,  $^{32}S_5^+$ ; 151, 4,  $^{32}S_2NCO_2C_2H_5^+$ ; 143, 6,  $^{32}S_4NH^+$  (imp); 130, 6,  $^{34}S^{32}S_3^+$ ; 129, 4, na; 128, 26,  $^{32}S_4^+$ ; 119, 6,  $^{32}SNCO_2C_2H_5^+$ ; 111, 7,  $^{32}S_3NH^+$  (imp); 107, 5,  $^{32}S_2NC_2H_5^+$ ; 97, 6, na; 96, 15,  $^{32}S_3^+$ ; 93, 8,  $^{32}S_2C_2H_5^+$ ; 80, 4,  $^{34}S^{32}SN^+$ ; 78, 33,  $^{32}S_2N^+$ ; 75, 13,  $^{32}SNC_2H_5^+$ ; 73, 6,  $CO_2C_2H_5^+$ ; 66, 6,  $^{34}S^{32}S^+$ ; 65, 4, na; 64, 56,  $^{32}S_2^+$ ; 61, 5,  $^{32}SC_2H_5^+$ ; 58, 8,  $NO_2^+$ ,  $CO_2CH_2^+$ ; 57, 4,  $COC_2H_5^+$ ; 47, 9,  $^{32}SNH^+$  (imp); 46, 8,  $^{32}SN^+$ ; 43, 22,  $NC_2H_5^+$ ,  $CoCH_3^+$ ; 32, 20,  $^{32}S^+$ ,  $O_2^+$ ; 29, 65,  $C_2H_5^+$ ; 28, 50,  $C_2H_4^+$ ,  $CO^+$ ; 27, 11,  $C_2H_3^+$ .

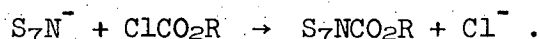
The following peaks were observed for  $S_7NSi(CH_3)_3$  (peaks < 3% of the most intense peak are not given) (m/e, relative peak height, and assignment, respectively): 315, 3,  $^{34}S_2^{32}S_5NSi(CH_3)_3^+$ ; 313, 17,  $^{34}S^{32}S_6NSi(CH_3)_3$ ; 312, 7,  $^{33}S^{32}S_6NSi(CH_3)_3^+$ ; 311, 46,  $^{32}S_7NSi(CH_3)_3^+$ ; 258, 8,  $^{34}S^{32}S_7^+$ ; 256, 20,  $^{32}S_8^+$ ; 249, 3,  $^{34}S^{32}S_4NSi(CH_3)_3^+$ ; 247, 13,  $^{32}S_5NSi(CH_3)_3$ ; 239, 6,  $^{32}S_7NH^+$  (imp); 229, 3, na; 226, 3,  $^{32}S_6^{34}S^+$ ; 224, 10,  $^{32}S_7^+$ ; 220, 11, na; 215, 8,  $^{32}S_4NSi(CH_3)_3^+$ ; 206, 8, na; 205, 26, na; 194, 11,  $^{34}S^{32}S_5^+$ ; 193, 5, na; 192, 44,  $^{32}S_6^+$ ; 191, 35, na; 183, 12,

$^{32}\text{S}_3\text{NSi}(\text{CH}_3)_3^+$ ; 177, 5, na; 168, 4,  $^{32}\text{S}_3\text{NSi}(\text{CH}_3)_2^+$ ; 162, 6,  $^{34}\text{S}^{32}\text{S}_4^+$ ;  
 160, 23,  $^{32}\text{S}_5^+$ ; 153, 9,  $^{34}\text{S}^{32}\text{SNSi}(\text{CH}_3)_3^+$ ; 152, 3,  $^{32}\text{S}_2\text{N}^{29}\text{Si}(\text{CH}_3)_3^+$ ;  
 151, 60,  $^{32}\text{S}_2\text{NSi}(\text{CH}_3)_3^+$ ; 138, 6,  $^{34}\text{S}^{32}\text{SNSi}(\text{CH}_3)_2^+$ ; 137, 4,  
 $^{32}\text{S}_2\text{N}^{29}\text{Si}(\text{CH}_3)_2^+$ ; 136, 39,  $^{32}\text{S}_2\text{NSi}(\text{CH}_3)_2^+$ ; 130, 5,  $^{34}\text{S}^{32}\text{S}_3^+$ ; 128,  
 10,  $^{32}\text{S}_4^+$ ; 121, 9,  $^{32}\text{SNSiCH}_3^+$ ; 120, 11,  $^{32}\text{SN}^{29}\text{Si}(\text{CH}_3)_3^+$ ; 119, 100,  
 $^{32}\text{SNSi}(\text{CH}_3)_3^+$ ; 109, 4,  $^{34}\text{S}^{32}\text{SSiCH}_3^+$ ; 107, 19,  $^{32}\text{S}_2\text{SiCH}_3^+$ ; 105, 5,  
 $^{32}\text{SSi}(\text{CH}_3)_3^+$ ; 96, 5,  $^{32}\text{S}_3^+$ ; 90, 10,  $^{32}\text{SSi}(\text{CH}_3)_2^+$ ; 86, 4, na; 75,  
 10,  $^{32}\text{SSiCH}_3^+$ ; 74, 5,  $^{32}\text{SNSi}^+$ ,  $^{29}\text{Si}(\text{CH}_3)_3^+$ ; 73, 64,  $\text{Si}(\text{CH}_3)_3^+$ ; 64,  
 15,  $^{32}\text{S}_2^+$ ; 45, 5, na; 43, 5,  $\text{SiCH}_3^+$ . Na means that those peaks so  
 designated were not assigned. Imp is noted after fragments which are  
 from  $\text{S}_7\text{NH}$ .

### C. Results and Discussion

In exploratory experiments, we found that when gaseous  $\text{CO}_2$  is  
 added to solutions of  $\text{S}_7\text{N}^-$ , a white solid immediately precipitates.  
 Because we found that  $\text{CO}_2$  was evolved upon addition of 6 M HCl to the  
 white solid, the compound is thought to be  $\text{K}^+\text{S}_7\text{NCO}_2^-$ . However, this  
 compound decomposed upon warming to  $0^\circ$ , and was not characterized  
 further. Because of the formation of  $\text{S}_7\text{NCO}_2^-$ , we thought that stable  
 derivatives of the formula  $\text{S}_7\text{NCO}_2\text{R}$  might be prepared. This was indeed  
 found to be true for the compounds  $\text{S}_7\text{NCO}_2\text{C}_2\text{H}_5$  and  $\text{S}_7\text{NCO}_2\text{CH}_2\text{C}_6\text{H}_5$  which  
 were stable in air for at least two weeks. The structures for these  
 two derivatives have been assigned on the basis of chemical analysis,  
 IR and  $^1\text{H}$  nmr spectra, and in the case of  $\text{S}_7\text{NCO}_2\text{C}_2\text{H}_5$ , a mass spectrum.

We believe that these two derivatives are examples of a generally applicable reaction, i.e.:



The yellow liquid isolated from the reaction of  $S_7N^-$  with  $ClSi(CH_3)_3$  in THF was assigned the structure  $S_7NSi(CH_3)_3$  based on the observed infrared,  $^1H$  nmr, and mass spectra. A comparison of the infrared frequencies for  $(CH_3)_2NSi(CH_3)_3$ ,  $HCH_3NSi(CH_3)_3$ , along with their assignments, and our compound is shown in Table I. We note from Table I that except for the peaks attributable to a  $CH_3N$  or an  $NH$  group, there is a very close correspondence of the spectra. The only definitely non-corresponding peak is found at  $793\text{ cm}^{-1}$ , which is typical for a  $S-N$  stretching frequency. The  $^1H$  nmr chemical shift for the compound  $S_7NSi(CH_3)_3$  occurs in the same region as that of known  $Si(CH_3)_3$  resonances.<sup>6</sup> The similarity of the fragmentation patterns of  $S_7NCO_2C_2H_5$  and the yellow liquid along with the observed parent peak at  $m/e = 311$  confirm the identification of the yellow liquid as  $S_7NSi(CH_3)_3$ . The chemical analysis can be explained by assuming a mixture with 11% of a compound whose empirical formula is  $C_{39}H_{63}S_{26}N_3$  (C, 13.94; H, 3.07; N, 4.33; S, 70.67). Most of the unassigned peaks in the mass spectrum could be attributed to a compound of empirical formula  $Si_2C_9H_{24}O_2$  or  $Si_2C_9H_{24}S$ . The impurity may also be from decomposition of the product. We noted in one of our samples a small proton resonance at 1.18 ppm. This peak was observed to increase significantly (~4-fold) after the sample had been washed with undried acetone. Some  $S_7NH$  was then found

TABLE I

Comparison of IR frequencies observed for  
 $S_7NSi(CH_3)_3$ ,  $(CH_3)_2NSi(CH_3)_3$ , and  $CH_3HNSi(CH_3)_3$

$S_7NSi(CH_3)_3$ ( $cm^{-1}$ )	$(CH_3)_2NSi(CH_3)_3^5$ ( $cm^{-1}$ )	$CH_3HNSi(CH_3)_3^5$ ( $cm^{-1}$ )	Assignment <sup>5</sup>
		3422(w)	$\nu_{N-H}$
2959 (w-m)	2959 (s)	2956 (s)	$\nu_{as} CH_3(Si)(N)$
2899 (sh)	2895 (sh)	2896 (m)	$\nu_s CH_3(Si)$
	2845 (m)	2809 (m)	$\nu_s CH_3(N)$
	2790 (m)		
	1452 (w)		$\delta_{as} CH_3(N)$
1401 (w)	1408 (vw)	1430 (w)	$\delta_{as} CH_3(Si)$
1364(sh)		1374 (m)	
	1282 (s)		$\rho_s CH_3(Si)$
1248 (m-s)	1253 (s)	1251 (s)	
	1173 (m)		$\rho_s CH_3(N)$
	1070 (w)	1101 (s)	$\nu_{N-C} \text{ or } N-C_2$
	989 (s)		
870 (vs)	851 (ssh)	866 (s)	$\nu_{N-Si-C_3}$
842 (s)	832 (vs)	836 (vs)	$\rho_{CH_3(Si)}$
793 (m)			$\nu_{S-N}^a$
756 (w-m)	746 (m)	758 (m)	$\rho_{CH_3(Si)}$
685 (w)	672 (s)	679 (w)	$\nu_{as} Si-C_3$

<sup>a</sup> assigned in this work

in the acetone wash, which is consistent with a decomposition reaction. It is difficult, however, to speculate further on the nature or origin of the impurities.

Besides the above reactions, reactions of  $S_7N^-$  were also tried with  $BF_3 \cdot \text{ether}$ ,  $SbCl_3$ ,  $B(CH_3)_3$ ,  $(C_6H_5)_3SnCl$ , and  $(C_5H_5)_2TiCl_2$ . Reaction occurred with  $BF_3 \cdot \text{ether}$  and  $SbCl_3$ , as evidenced by the disappearance of the deep green color of the solutions; however, in neither case were we able to isolate a stable product. In the reaction with  $BF_3 \cdot \text{ether}$ , we were able to identify  $K^+BF_4^-$  as one of the products. It was found that reaction did not occur with  $B(CH_3)_3$ ,  $(C_6H_5)_3SnCl$ , or  $(C_5H_5)_2TiCl_2$  to any appreciable extent, possibly because of steric hindrance in the latter two cases. However, steric hindrance is not a completely satisfactory explanation for the non-reaction observed with  $B(CH_3)_3$ , and further study of the reactions of  $S_7N^-$  with  $BX_3$  compounds would be helpful.

Appendix

Details of the reactions mentioned in section II are presented here.

$S_7N^- + CO_2$ . - The solution of  $S_7N^-$  was made by passing 25 ml of THF, containing 0.3 g  $S_7NH$ , through a column of KOH at  $-63^\circ$ . The apparatus used was the same as that described in section II. An atmosphere of gaseous  $CO_2$  was then admitted into the system, and a white precipitate was immediately noted. The solid was filtered at low temperature in a tube which was sealed at the bottom and was immersed in a cold bath. This tube could be closed at the top by stopping it with a sleeve joint connected to a stopcock. The tube contained a fritted disc and a sidearm below the disc which was connected to a vacuum line. After filtration, the solid was transferred in a dry box to a tube which was stoppered with a standard sleeve joint connected to a stopcock. The tube was evacuated on a vacuum line, and 6 M HCl (1-2 ml) was condensed in. The  $CO_2$  evolved was separated from HCl by passing the mixture through a trap containing yellow HgO. The amount of  $CO_2$  was then determined by pvt measurement and the gas identified by its mass spectrum. Sulfur was determined by a standard gravimetric method.<sup>7</sup> In one run the ratio of S/ $CO_2$  was found to be 7.4. The white solid turned blue when warmed to  $0^\circ$  and was not studied further.

$S_7N^- + (C_5H_5)_2TiCl_2$ . - For this reaction and the remainder of the reactions described in this appendix, the solution of  $S_7N^-$  was made

and the reactant added as described in section II.  $\text{CS}_2$  was added to the crude product, and the mixture was filtered. After the  $\text{CS}_2$  was evaporated, the residue was mixed with a hot 9:1 hexane: $\text{CS}_2$  solvent. The solvent was decanted and slowly evaporated. After evaporation to a small volume (1-2 ml), a solid was collected by filtration and identified as  $\text{S}_7\text{NH}$  by its infrared spectrum.

$\text{S}_7\text{N}^-$  +  $(\text{C}_6\text{H}_5)_3\text{SnCl}$ . -  $\text{CS}_2$  was added to the crude product, and the mixture was filtered. After the  $\text{CS}_2$  was evaporated, methanol was added to the residue. The solid which was not soluble in the methanol was identified as  $\text{S}_7\text{NH}$  by its infrared spectrum. The white solid which crystallized from the methanol was identified as  $(\text{C}_6\text{H}_5)_3\text{SnCl}$  by comparison of its infrared spectrum with that of a known sample of  $(\text{C}_6\text{H}_5)_3\text{SnCl}$ . A very small amount of a yellow oil was noted after evaporation of the methanol. Its infrared spectrum showed two new peaks in the region  $750\text{-}800\text{ cm}^{-1}$ ; however, the yield was so small that the unknown could not be purified.

$\text{S}_7\text{N}^-$  +  $\text{SbCl}_3$ . - When the crude product was exposed to the air, the color of the residue immediately changed, and this reaction was not studied further.

$\text{S}_7\text{N}^-$  +  $\text{B}(\text{CH}_3)_3$ . - After allowing the reactants to sit at room temperature for 15 minutes, the solvent (THF) and any unreacted  $\text{B}(\text{CH}_3)_3$  were pumped through a  $-78^\circ$  trap into a  $-196^\circ$  trap. The THF was held in the  $-78^\circ$  trap. After repeating this separation, the amount of unreacted  $\text{B}(\text{CH}_3)_3$  was determined by pvt measurements. The amount recovered (.94 mmol) was 98% of the amount started with (.96 mmol).

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### III. THE REACTION OF HEPTASULFUR IMIDE WITH DIBORANE

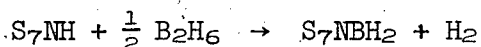
(A paper by M. H. Mendelsohn and W. L. Jolly, submitted to Inorganic Chemistry)

#### A. Introduction

It is known that heptasulfur imide reacts with boron trichloride and boron tribromide to give  $S_7NBCl_2$ <sup>1</sup> and  $S_7NBBr_2$ <sup>2</sup>, respectively. In this note we report the results of our study of the reaction of heptasulfur imide with diborane. This study was undertaken to determine whether the reaction gives an analogous product ( $S_7NBH_2$ ), a borane adduct ( $S_7NBH_3$ ), or a diborane derivative such as  $S_7NB_2H_5$ .

#### B. Results and Discussion

The reaction of heptasulfur imide with diborane was carried out in various ether solvents, at either room temperature or at 0°. The experimental results, summarized in Table I, show that, with diborane in excess, one-half mole of diborane reacts per mole of  $S_7NH$  and that one mole of hydrogen is formed per mole of  $S_7NH$ . This stoichiometry corresponds to the following reaction:



When the reaction is carried out in diethyl ether at 0°, some of the product precipitates as a white, crystalline ether adduct,  $S_7NBH_2 \cdot Et_2O$ . Similar adducts can be obtained from the other ethers

TABLE I

Stoichiometry of the Reaction of S<sub>7</sub>NH with B<sub>2</sub>H<sub>6</sub>

Solvent	Temperature, °C	S <sub>7</sub> NH, mmol	B <sub>2</sub> H <sub>6</sub> , mmol	measured H <sub>2</sub> /S <sub>7</sub> NH	time of meas., hrs	B <sub>2</sub> H <sub>6</sub> consumed S <sub>7</sub> NH
monoglyme <sup>a</sup>	23	0.288	0.41	1.11 <sup>b</sup>	17	0.49
monoglyme	23	0.992	0.72	1.35 <sup>b</sup>	64.5	--
monoglyme	0	0.574	0.516	1.0 <sup>c</sup>	66	0.495
	23			1.15 <sup>b</sup>	24	
THF <sup>a</sup>	23	0.386	0.356	0.99	67	0.505
THF	23	0.616	0.50	1.13 <sup>b</sup>	65.5	--
THF	23	0.567	0.264	1.09 <sup>b,d</sup>	145	--
THF	0	0.611	0.593	1.02	497	0.52
THF	0	0.302	0.0716	1.31 <sup>b,d</sup>	978	--
dioxane	23	0.505	0.633	2.20 <sup>b</sup>	319	--
diethyl ether <sup>a</sup>	0	0.575	0.292	0.98	260	--

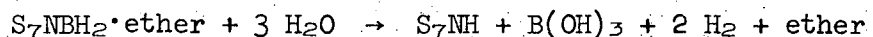
<sup>a</sup> reaction mixture not stirred

<sup>b</sup> traces of H<sub>2</sub> still being evolved, due to slow decomposition

<sup>c</sup> stopped purposely to pump out excess B<sub>2</sub>H<sub>6</sub>

<sup>d</sup> listed as H<sub>2</sub>/B<sub>2</sub>H<sub>6</sub>

by vacuum evaporation of the solvent and removal of excess diborane. The compounds undergo rapid hydrolysis with excess water at room temperature, as follows:



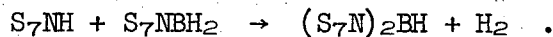
The  $^{11}B$  nmr spectrum of  $S_7NBH_2$  in diethyl ether solution consists of a 1:2:1 triplet due to coupling with the two protons of the  $BH_2$  group. The Raman spectrum of the diethyl ether adduct has lines at 2419 and 2409  $cm^{-1}$ , characteristic of terminal  $BH_2$  groups, and lines at 766 and 750  $cm^{-1}$ , typical S-N stretching frequencies.

As can be noted from Table I, the only products that were stable (as determined by hydrogen evolution) were those obtained from diethyl ether and tetrahydrofuran. The diethyl ether adduct is stable at room temperature in the absence of air and moisture, and the product from tetrahydrofuran is stable at 0°. Hydrogen, hydrogen sulfide, and ether were identified as decomposition products of the tetrahydrofuran and monoglyme adducts at room temperature.

A white solid pyridine adduct,  $S_7NBH_2 \cdot C_5H_5N$  was isolated from the reaction of  $S_7NBH_2 \cdot Et_2O$  with pyridine. Pure samples of this compound were stable indefinitely in vacuo at 0° and could be kept in an ordinary closed bottle at room temperature for as long as 5 days without decomposition. However, impure samples decomposed within a day or two.

When the reaction of heptasulfur imide and diborane is carried out with an excess of  $S_7NH$  in tetrahydrofuran at 0°, the reaction does not stop with the formation of  $S_7NBH_2$ , as evidenced by the continued slow

evolution of hydrogen. Presumably the following subsequent reaction occurs:



however, the reaction was incomplete after 1 month and was not further studied.

### C. Experimental Section

Reagents and procedure.- Heptasulfur imide was prepared by the usual method<sup>3</sup> and was purified by one recrystallization from methanol followed by repeated recrystallizations from carbon tetrachloride until the solutions were colorless and the solid melted at 113-114° (lit. 113.5°).<sup>4</sup> The infrared spectrum agreed with that reported in the literature.<sup>4</sup> Diborane was made by the reaction of potassium borohydride with phosphoric acid<sup>5</sup> and purified by vacuum distillation through a -112° trap. Tetrahydrofuran, diethyl ether, and dioxane were distilled from lithium aluminum hydride immediately before use. Monoglyme (1,2-dimethoxyethane) was distilled first from calcium hydride and then from lithium aluminum hydride. Pyridine was distilled from potassium hydroxide, and carbon tetrachloride was distilled from phosphorus pentoxide.

Approximately 10 ml of solvent was vacuum-distilled into a 50-ml flask containing a known weight of heptasulfur imide. A known amount of diborane was condensed into the reaction vessel, and the vessel was allowed to warm to either room temperature or 0°. At various times the

evolved hydrogen was collected using a Toepler pump, measured in a gas buret, and identified by mass spectroscopy. To isolate the crystalline product  $S_7NBH_2 \cdot Et_2O$ , an all-glass system was employed. The apparatus was sealed off after addition of the reactants and was provided with a break-seal for removal of hydrogen and a side arm for washing the product by decantation. The product was then removed in a dry box. Anal. Calcd for  $S_7NBH_2 \cdot C_4H_{10}O$  : C, 14.76; H, 3.69; N, 4.30; S, 69.01. Found: C, 14.86; H, 3.69; N, 4.45; S, 68.68.

A sample of  $S_7NBH_2$  prepared in tetrahydrofuran was treated with a 500-fold excess of distilled water. The evolved hydrogen was collected and measured as described above. The precipitated  $S_7NH$  was collected by filtration, air-dried, and then weighed. It was identified by its infrared spectrum.<sup>4</sup> The boric acid formed was determined by a standard double titration method.<sup>6</sup> Anal. Calcd for  $S_7NBH_2$  prepared from 0.386 mmol of  $S_7NH$  :  $H_2$ , 0.772 mmol;  $B(OH)_3$ , 0.386 mmol;  $S_7NH$ , 0.386 mmol. Found:  $H_2$ , 0.773 mmol;  $B(OH)_3$ , 0.393 mmol;  $S_7NH$ , 0.31 mmol.

Raman spectrum.- The following lines were observed for the diethyl ether adduct ( $cm^{-1} \pm 3 cm^{-1}$ ): 2969(w), 2930(w-m), 2419(w), 2409(sh), 1471(w), 1452(w-m), 1442(sh), 1324(w), 1181(w-m), 1091(w-m), 1005(w), 870(w-m), 851(sh), 832(w), 766(w-m), 750(w-m), 602(m), 476(vs), 458(m), 437(m), 292(s), 251(m), 213(vs), 201(s), 178(m), and 153(s). The Raman spectrometer consisted of a Spectra-Physics 125 helium-neon laser with line-filter (35-mW) and a Spex 1401 monochromator equipped with an ITT FW-130 photomultiplier tube.

Nmr spectra.- The samples for the  $^{11}\text{B}$  nmr spectra were prepared and recorded in 12 mm od tubes containing diethyl ether, in which the compound is only slightly soluble. For this reason the spectra were computer-averaged over 10-150 scans. The spectrum consisted of a 1:2:1 triplet centered 33.5 ppm upfield from an external reference peak of boron trichloride, with  $J_{\text{B-H}} = 136$  Hz. A Varian model V4311 high resolution nmr spectrometer operated at 8.134 MHz was used for the boron spectra. Proton spectra of samples prepared from monoglyme and diethyl ether were recorded in  $\text{CS}_2$  using a Varian A-60 spectrometer. Although the samples decomposed in  $\text{CS}_2$ , the spectra did indicate the presence of the coordinated ether. For the sample from diethyl ether, a triplet at 1.98 ppm and a quartet at 4.75 ppm, relative to TMS, were observed, while from monoglyme two singlets at 4.63 ppm and 4.67 ppm and a complex pattern centered at 4.87 ppm were noted. The complexity of the latter spectrum indicates that only one of the oxygen atoms of monoglyme was coordinated to  $\text{S}_7\text{NBH}_2$ .

X-ray diffraction.- Some preliminary X-ray diffraction data on a single crystal of  $\text{S}_7\text{NBH}_2 \cdot \text{C}_4\text{H}_{10}\text{O}$  correspond to the space group  $\text{Pnma}$  and the unit cell dimensions  $a = 15.80$ ,  $b = 13.16$ , and  $c = 6.75$  Å.

Preparation and characterization of  $\text{S}_7\text{NBH}_2 \cdot \text{C}_5\text{H}_5\text{N}$ .- The pyridine adduct is prepared by addition of excess, dry pyridine to the solid  $\text{S}_7\text{NBH}_2 \cdot \text{Et}_2\text{O}$ . The solution is evaporated to a volume of 0.2-0.3 ml, and dry  $\text{CCl}_4$  is then added. A white solid is precipitated and is washed with a small amount of chilled  $\text{CCl}_4$ . The infrared spectrum of a Nujol

mull recorded with a Perkin-Elmer Model 137B Infracord Spectrophotometer consisted of the following peaks ( $\text{cm}^{-1} \pm 10 \text{ cm}^{-1}$ ): 2415(m), 2353(sh), 1618(m), 1186(m), 1157(w), 1139(sh), 1131(s), 1100(m-s), 1025(w), 1013(w), 977(w), 961(sh), 953(m), 943(s), 929(w), 917(m), 775(m), 768(m), 751(s), 687(s). A sample melting at  $87.5\text{-}88^\circ$  was analyzed. Anal. Calcd for  $\text{S}_7\text{NBH}_2 \cdot \text{C}_5\text{H}_5\text{N}$ : C, 18.17; H, 2.14; N, 8.48; S, 67.92; B, 3.3. Found: C, 18.97; H, 2.08; N, 8.62; S, 67.98; B, 3.2 (as a  $\text{B}_2\text{O}_3$  residue). A proton nmr spectrum showed the protons on the pyridine ring, but we were unable to see the protons attached to boron.

Acknowledgment.- We wish to thank Dr. James Scherrer at the U.S. Department of Agriculture Western Regional Research Laboratory for recording the Raman spectrum, Dr. Allan Zalkin of the Lawrence Berkeley Laboratory for the X-ray diffraction data, and Dr. James Neely and John Illige for recording the  $^{11}\text{B}$  nmr spectra.

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IV. PRELIMINARY INVESTIGATION OF THE REACTION OF  $S_4N_4$   
WITH  $AlCl_3$  IN NITROMETHANE

A. Introduction

The reaction of  $S_4N_4$  with 100%  $H_2SO_4$  has been studied by Lipp and Jolly.<sup>1</sup> Although several products of this reaction were identified and quantitatively determined, one major species remained unidentified. The uv-vis spectrum of the unknown species was observed; however, all attempts to isolate the species from solution failed.

It was decided, therefore, to study the reaction of  $S_4N_4$  with aluminum trichloride in nitromethane. Previous work with  $AlCl_3$  in nitromethane has indicated that this is a strong oxidizing system,<sup>2,3</sup> as is sulfuric acid. If  $S_4N_4$  were to give the same species in a solution of aluminum trichloride in nitromethane as it does in 100%  $H_2SO_4$ , the possibility of isolating the unknown species would be much greater because of the greater volatility and lower viscosity of nitromethane.

B. Experimental

Reagents and procedure.- Reagent grade aluminum trichloride was purified by sublimation. Reagent grade nitromethane was washed with 5%  $H_2SO_4$ , distilled several times from  $CaCl_2$ , and stored over  $CaSO_4$ . Spectroquality nitromethane was used without further purification. Reagent grade ammonium chloride was used without further purification. All manipulations were carried out either in a vacuum line or in a dry box.

Nmr spectra.- Proton spectra were recorded with a Varian T-60 spectrometer. No internal reference was used because of the possibility of reaction.

Uv-vis spectra.- Samples were pipetted into a 0.14-mm quartz cell which was then stoppered. The spectra were recorded from 6400 to 3000 Å using a Cary 14 spectrophotometer. The spectra shown in Fig. 1 are of a  $6 \times 10^{-3}$  M solution of  $S_4N_4$  in nitromethane containing 1-2%  $AlCl_3$  (by weight). The spectra were recorded 0.5, 12, 24, and 48 hours after mixing the reactants. Peaks were observed at the following wavelengths ( $\text{Å} \pm 20 \text{ Å}$ ): 4660, 3900, and 3250.

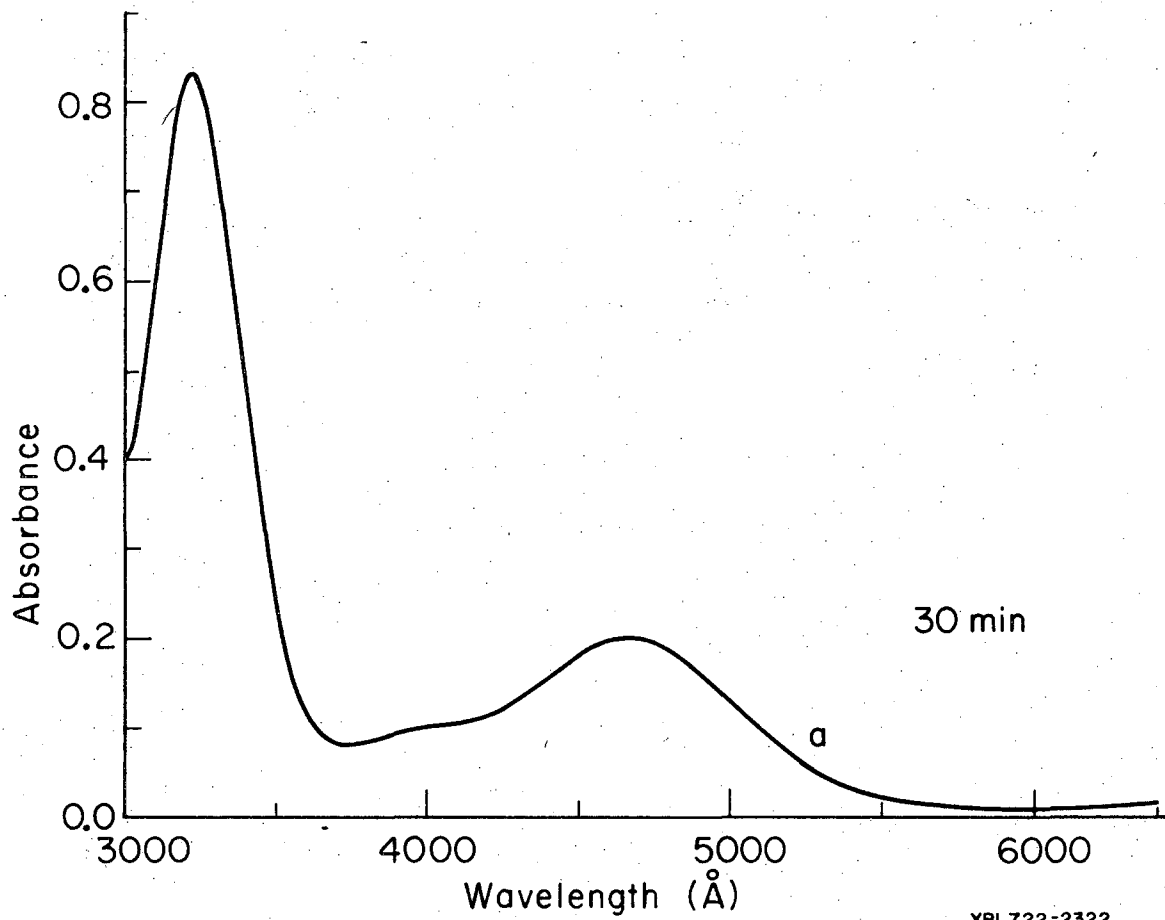
Esr spectra.- Samples were held in capillary tubes, and the spectra were recorded with a Varian 4502 spectrometer. For a 0.01 M solution of  $S_4N_4$  in nitromethane containing 1-2%  $AlCl_3$ , the five-line spectrum shown in Fig. 2 was observed. For this spectrum,  $g = 2.0111 \pm .0001$  and the hyperfine splitting constant is 3.20 gauss.

Isolation of crystals.- The following procedure was used to obtain crystals from a solution of  $S_4N_4$  and  $AlCl_3$  in nitromethane. The minimum amount of a ca. 2% solution of  $AlCl_3$  in nitromethane was added to dissolve a known quantity of  $S_4N_4$  ( $\sim 20 \text{ ml}/0.5 \text{ g } S_4N_4$ ). The volume of the solution was reduced to ca. 3-4 ml by pumping. The remaining solution was cooled to  $0^\circ$ , and some crystals were noted. An additional 0.5-1.0 ml of solution was then slowly removed by condensation into a  $-78^\circ$  trap, while the evaporating solution was held at  $0^\circ$ . The crystals were then collected by filtration and washed with HCl-saturated chloroform ( $\sim 40 \text{ ml}$ ) to remove the solvent and dried  $CCl_4$  ( $\sim 20 \text{ ml}$ ) to remove any  $AlCl_3$  or

Figure Captions

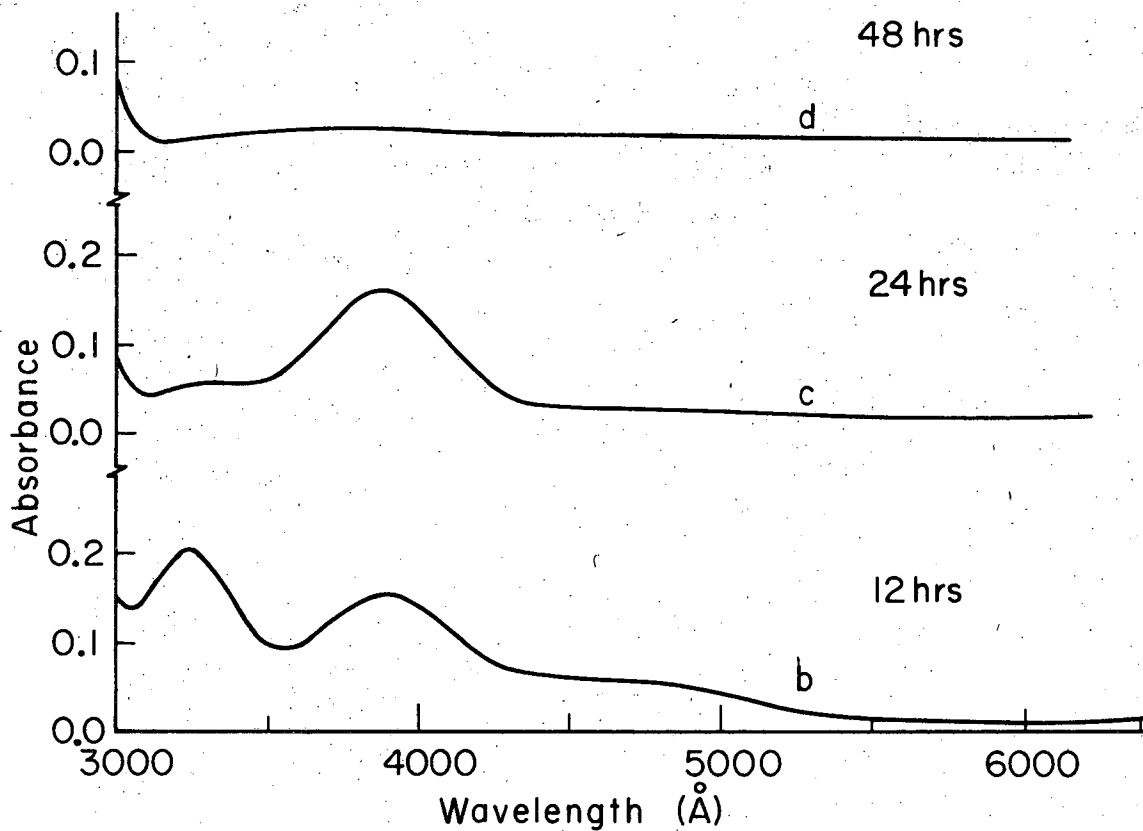
Figure 1 (a-d).  $6 \times 10^{-3} \text{ M } \text{S}_4\text{N}_4$  in nitromethane containing 1-2%  $\text{AlCl}_3$ .

Figure 2. Epr spectrum of  $\text{S}_2\text{N}_2^+$  in nitromethane containing 1-2%  $\text{AlCl}_3$ .



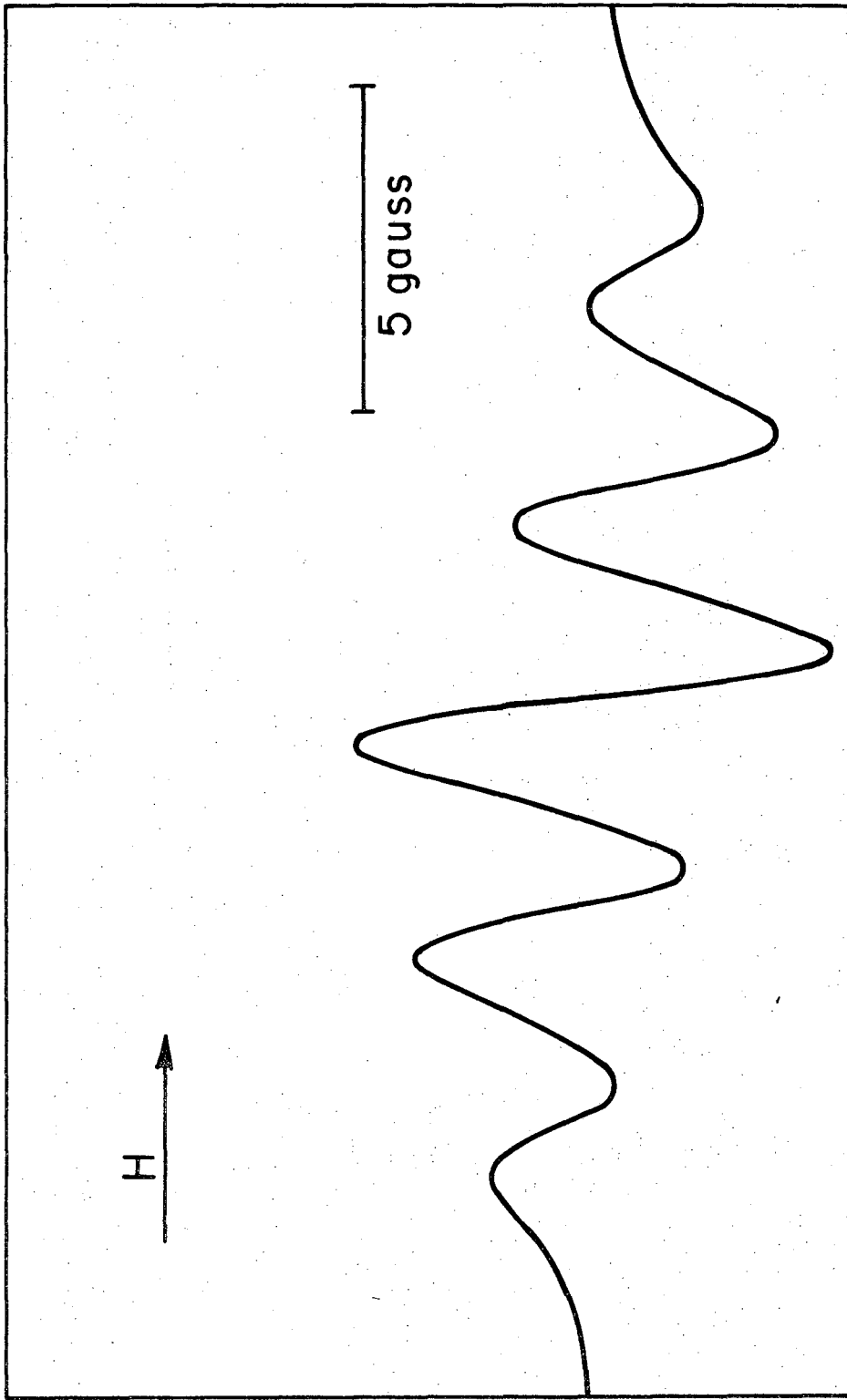
XBL722-2322

Fig. 1.(a)



XBL722-2323

Fig. 1(b-d)



XBL722 - 2324

Fig. 2.

$S_4N_4$ . The crystals were then stored in an evacuated glass container at room temperature.

### C. Results

The esr spectra for a 0.01 M solution of  $S_4N_4$  in  $AlCl_3/CH_3NO_2$  were recorded 2, 5, and 30 days after initial mixing of the reactants. There was no noticeable change in the signal intensity in the first two cases; however, after 30 days the signal had practically disappeared. The five-line spectrum had the same *g* value and hyperfine coupling constant as that reported for  $S_2N_2$ .<sup>4</sup>

The proton nmr spectrum of a sample, one-half hour after initial mixing of the reactants, showed three peaks to low field of the nitromethane resonance. There was no appreciable broadening of the peaks observed in this spectrum. In spectra recorded 1 and 3 days later, considerable broadening of all the resonances had occurred and one of the three new peaks had disappeared. Ammonium chloride was then added to the solution. Of the three resonances attributable to the ammonium ion, one appeared as a shoulder on the solvent peak and the other two were coincident with the two remaining resonances in the spectrum.

The initial uv-vis spectrum of a  $6 \times 10^{-3}$  M solution of  $S_4N_4$  in  $AlCl_3/CH_3NO_2$  was taken 30 minutes after mixing, and peaks were observed at 3250 and 4660 Å. Over a period of ca. 24 hours, a peak at 3900 Å grew in, and the peaks at 3250 and 4660 Å declined. The color of the solution was originally bright orange, but this changed to yellow-orange and then to a bright yellow. The final spectrum was recorded

48 hours after initial mixing of the reactants. It showed that all three peaks had disappeared, and the color of this solution was a light, straw-yellow.

Mass spectral examination of the trace volatile products has given non-reproducible results. In one case, the main peak was at  $m/e = 44$ , corresponding to  $\text{CO}_2$  or  $\text{N}_2\text{O}$ , while in another run, the main peak was at  $m/e = 76$ , corresponding to  $\text{CS}_2$ . However, in both cases, the characteristic pattern for the fragment  $\text{CCl}_3^+$  was observed at  $m/e = 117, 119,$  and  $121$ . We have also observed that when diethyl ether is added to solutions of  $\text{S}_4\text{N}_4$  in  $\text{AlCl}_3/\text{nitromethane}$  an exothermic reaction takes place; the color of the solution rapidly changes from red-orange to yellow, and a yellow solid, which was identified as  $\text{S}_4\text{N}_4$ , precipitates from the solution.

#### D. Discussion

The esr spectrum shows that the species  $\text{S}_2\text{N}_2^+$  is present in solutions of  $\text{S}_4\text{N}_4$  in  $\text{AlCl}_3/\text{nitromethane}$ . Since this was the only radical detected, we believe that the broadened nmr spectra were due to the presence of this species. The time dependence of the adsorbance peak at  $3900 \text{ \AA}$  correlates with our esr and nmr data if we assume that this peak is due to the species  $\text{S}_2\text{N}_2^+$ . The  $3900 \text{ \AA}$  peak has a relatively constant adsorbance during the color change orange-yellow to yellow (Figs. 1b and 1c) and this corresponds to the esr spectra taken 2 days (orange-yellow) and 5 days (yellow) after mixing, which showed approximately the same signal

intensity. The color change yellow to straw-yellow (Figs. 1c and 1d) corresponds to the disappearance of the peak at 3900 Å and to the disappearance of the five-line esr spectrum, and the lack of the peak at 3900 Å (Fig. 1a) corresponds to the initial non-broadened nmr spectrum observed.

Our data also indicate that there is a precursor to the species  $S_2N_2^+$ . The lack of broadening in the initial nmr spectrum suggest that there is no appreciable concentration of  $S_2N_2^+$  in the first 1/2 hour of reaction, yet the uv-vis spectrum shows two strong peaks at 3250 Å and 4660 Å within the first 30 minutes of reaction. Then as the peak at 3900 Å grows in, the peaks at 3250 and 4660 Å decline.

#### E. Summary

We can only guess what the precursor to the  $S_2N_2^+$  might be; however, it is not unreasonable to suggest that this species is  $S_4N_4^{2+}$ . The reaction of  $S_4N_4$  with aluminum trichloride in nitromethane to give  $S_4N_4^{2+}$  would be similar to other reactions observed in this solvent system.<sup>2</sup> Also an indication that the ring remains intact, at least initially, is our ability to regenerate  $S_4N_4$  by addition of diethyl ether to the solution. Our ability to recover  $S_4N_4$  was not investigated for solutions which had sat for long periods of time.

The possibility of the existence of the species  $S_4N_4^{2+}$  raises two other questions. First, would this be a planar molecule? Planarity might be predicted since one could consider a model with a 10-electron

pi system which fits the Hückel  $4n + 2$  rule for aromatic compounds. To test this model, we have made free-electron type calculations analogous to Platt's application of the free-electron model to aromatic ring systems.<sup>5</sup> The equation applicable to these systems is as follows:

$$E_q = q^2 h^2 / 2m\ell^2,$$

where  $E_q$  is the energy of the  $q^{\text{th}}$  level,  $q$  is a quantum number,  $h$  is Planck's constant,  $m$  is the mass of an electron, and  $\ell$  is the circumference of the circularized molecule. In Platt's treatment, the ring must be distorted to a circle. In our calculations, we have chosen  $\ell = 12.8 \text{ \AA}$  which is the circumference of a circle escribed about a regular octagon with one side =  $1.55 \text{ \AA}$  (the known average S-N bond length for  $S_4N_3^+$  is  $1.55 \text{ \AA}$ <sup>6,7</sup>). For a 10-electron pi system, the first transition is from the  $q = 2$  to the  $q = 3$  level. With the preceding assumptions, we have calculated the first transition for  $S_4N_4^{2+}$  to be  $2700 \text{ \AA}$ . In our system, we observe a peak at  $4660 \text{ \AA}$  and in 100%  $H_2SO_4$  a peak is observed at  $4560 \text{ \AA}$ .<sup>1</sup> Several possible reasons can explain the discrepancy; however, the most likely are that either Platt's method is too imprecise for the molecule  $S_4N_4^{2+}$ , or that the peak at  $4660 \text{ \AA}$  does not represent the species  $S_4N_4^{2+}$ .

The second question is whether an equilibrium exists between  $S_4N_4^{2+}$  and  $S_2N_2^+$ . Presently we have no evidence that such an equilibrium does exist, but this possibility has not yet been excluded.

The only species we have identified in this system other than  $S_2N_2^+$  is the ammonium ion. The question arises as to where the ammonium ion

comes from. Even though it most likely comes from the  $S_4N_4$ , it is possible that it comes from the nitromethane. This question is important because in order to balance an equation for this reaction, we must know what the reduced species is. If the ammonium ion does come from the  $S_4N_4$ , then we have not yet found the reduced species in this system.

In conclusion, although we were unable to find the same unknown species in the  $AlCl_3$ /nitromethane system as in 100%  $H_2SO_4$ , we believe that the reaction of  $S_4N_4$  with aluminum trichloride in nitromethane has several interesting possibilities, and further experiments should be performed in order to answer the questions raised above.

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