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Marshall Harvey Mendelsohn
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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 ($-60°$) 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, $S_7NBH_2 \cdot$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 $S_7NBH_2 \cdot$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;[1] however, the correct formulation of the compound as S_7NH was not made until 1942 by Arnold.[2] Many reactions involving heptasulfur imide have been carried out; however, only one group of workers[3] 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[4,5] 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°).[5] 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-dimethyl-naphthalene were each recrystallized twice from ethanol and were found

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

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
$-62°$ 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 deter-
mined 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.[7] 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. $-60°$. 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 ($\sim -62°$), 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 $-40°$. 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 ob-

tained in the preceding manner were warmed to -22, 0, or ~ 23°. At

various times, an aliquot (5.0 ml) was pipetted into an excess of CH_3I

(0.5-0.6 ml) at 0°. The amount of S_7NCH_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 S_7NH passed through

a column of anhydrous LiOH. The apparatus had a sidearm used for

flushing and maintaining a N_2 atmosphere. The column was loaded with

LiOH to a total height of 5-7 cm, and the cooling jacket was brought

to a temperature of -55 to -68° by adding dry ice to acetone. A known

amount (about .25 g) of S_7NH 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 N_2 tank. The eluate was col-

lected in a flask, which was attached to the column with a standard

19/38 ground-glass joint. The flask was cooled to -78°, 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 S_7NH was determined by

titration as described previously.

Preparation of K^+fluorenyl$^-$.- An apparatus similar to that

referred to previously was used.[7] Solutions of K^+fluorenyl$^-$ were made

by adding a known amount of fluorene to 50.0 ml of diglyme and stir-

ring under a N_2 atmosphere with 3-5 g of powdered 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_7NH + liquid NH_3.- When a small amount of S_7NH is added to dry liquid ammonia at -78°, a bright yellow colored solution is formed. These dilute solutions ($\sim 10^{-4}$ $\underline{M}$) were found to be highly conducting (two measurements gave molar conductances of 210 and 280 cm^2/ohm-mole; for comparison to a known ionic compound, the value for $Na(N(C_6H_5)_2)$ is 235 cm^2/ohm-mole[8]). When methyl iodide was added to these solutions, it was found that S_7NCH_3 could be isolated. However, because of the limited solubility of S_7NH in liquid ammonia and the reactivity of ammonia itself, this solvent system was not investigated further.

S_7NH + CH_3Li.- When methyl lithium is allowed to react with excess S_7NH 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_7NH + LiOH.- When S_7NH reacts with LiOH at $-63°$ to $-45°$, a yellow solution is formed. The number of equivalents of base in solution per mole of S_7NH 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_7N^-, the number of equivalents of base in solution per mole of S_7NH 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_7NH increased with time to values larger than 1.00. We then checked the yields of S_7NCH_3 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_7NH and LiOH, we determined the yield of S_7NCH_3 and the number of equivalents of base in solution per mole of S_7NH from the same solution. The results were as follows:

Yield of S_7NCH_3 (%/100%)	No. of equivalents of base in solution / S_7NH (mole)
0.59 ± .02	0.83 ± .01
0.27 ± .02	0.30 ± .01

S_7NH + K^+fluorenyl$^-$.- Four runs were carried out with an excess of S_7NH, and as can be noted from Table II, the maximum yield of S_7NCH_3 was found to be 80%.

S_7NH + KOH.- When S_7NH 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_7NH + LiOH

Temp.(°C)	stirring time (hr)	equivalents of base in solution/ S_7NH (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_7NH + LiOH

Temp.(°C)	total time through column (min)	equivalents of base in solution/ S_7NH (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

$$S_7NH + K^+ fluorenyl^-$$
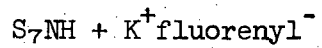
Temp.(°C)	stirring time (hr)	yield of S_7NCH_3 (% ± 3%)
-78	0.5	58
-78	0.7	59
-78	4.0	80
-78	24.0	79

solution is warmed to 0°, 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° to an excess of CH_3I at 0°. The results were as follows (± 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 ~-62° for 15 min ± 5 min. A yield of 99% ± 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° 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 ± 2% (average of 3 runs). Additional runs were made by allowing the filtered solution of S_7N^- to warm to -22 and 0°. 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 ~ 50° to 0°. The results are shown in Table IV. The results of the runs performed on going from -63 to 0° and from 50 to 0° show that the yield leveled off in both instances at 34% ± 1%.

TABLE III

S_7NH + KOH

Temp. (°C)	stirring time (hr)	equivalents of base in solution/ S_7NH (mole)
-63	0.5	0.97
-63	0.75	1.06
-63	1.0	1.09
-78[a]	0.25	0.98
-78[a]	0.5	1.07
-78[a]	1.0	1.09
-78[b]	0.5	0.81
-78[b]	1.0	0.85
-78[b]	2.3	1.00
-78[b]	4.5	1.19

[a] initially at -63° for 3 min

[b] 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. (°C)	Yield of S_7NCH_3 (% ± 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	~ 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°, and the best straight line ap-
proximated by sight, the following half-times were noted:

Half-time (min)	Temp. (°C)
12	0
84	-22

In a separate experiment, a solution which was warmed to room tempera-
ture for one hour and which gave a yield of S_7NCH_3 of 26% was kept at
approximately -35° 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. (°C)	Yield of S_7NCH_3 (%)
-35	53
-22	46
0	34
20	27

$\underline{S_7NH + KOH \text{ in } DMSO}$.- 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 un-

suitable for the quantitative preparation of solutions of the hepta-

sulfur imide anion. However, we did find that with KOH we could con-

vert greater than 95% of the S_7NH to the heptasulfur imide anion by

carrying out the reaction at low temperature and by carefully con-

trolling the reaction time. This conclusion is based on the assumption

that the yield of S_7NCH_3 upon addition of methyl iodide is a quanti-

tative indicator of the species S_7N^-. We believe that this assumption

is at least partially verified by the fact that under certain conditions

we <u>do</u> get 100% yields of S_7NCH_3. Also, it has been shown that S_7NH

and CH_3I do not react at 35°,[3b] 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.
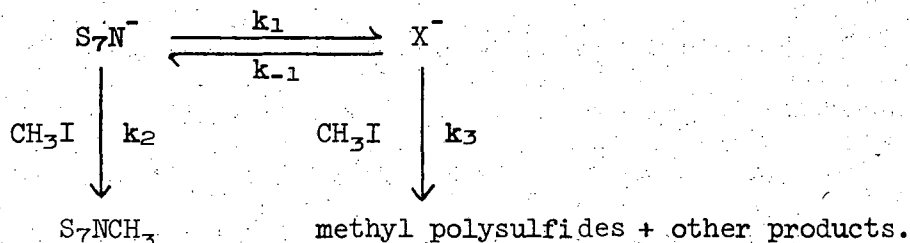
If the decomposition reaction is a base attack on the S_7N^-, then we can consider the following two consecutive reactions to be true:

1) $S_7NH + 2 MOH \rightarrow S_7N^- + M^+ + MOH \cdot H_2O$

2) $S_7N^- + x MOH \rightarrow$ decomposition products,
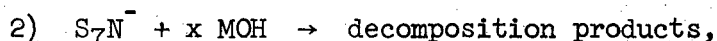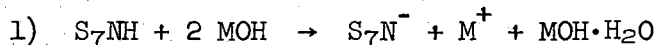
where M = K or Li. In order to detect the intermediate, S_7N^-, reaction 1 must be faster or of about the same speed as reaction 2. We find that with LiOH and KOH, the yield of S_7NCH_3 (i.e. the amount of S_7N^-) does build to a maximum and then slowly declines. Therefore, the deprotonation reaction 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.[3b] 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.[3b] We have found that at 0°, the yield of S_7NCH_3 levels off after the temperature of a solution of the anion has been raised from -62 to 0°. Secondly, we found that a yield of 34% is reached at 0° 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°.

The question arises, however, whether the addition of CH_3I actually quenches the equilibrium. That is, does the yield of S_7NCH_3 represent the true amount of S_7N^- at the time of addition of the CH_3I? The proposed reaction scheme is as follows:

$$S_7N^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^-$$

$$CH_3I \downarrow k_2 \qquad\qquad CH_3I \downarrow k_3$$

$$S_7NCH_3 \qquad\qquad \text{methyl polysulfides + other products.}$$

We first note that over the temperature range -35 to 20° $k_1 \approx k_{-1}$. 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 S_7NCH_3 does indicate the actual S_7N^- 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_{a_2} (activation energy) $> E_{a_1}$, then $k_2 \gg k_1$ would be true at all higher temperatures. From our kinetic data for runs at -22 and 0°, we can estimate that $E_{a_1} = 12$ kcal/mole. The activation energies for the reaction of methyl iodide with $C_2H_5O^-$, Br^-, $S_2O_3^=$, and o, m, and p-$CH_3C_6H_4O^-$ are all known[9] and all fall in the range 18.8 ($S_2O_3^=$) - 21.4 (Br^-) kcal/mole. It is plausible then that $E_{a_2} > E_{a_1}$. It is more difficult to speculate on E_{a_3}, because we do not know what the species 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 $\sim 20°$. 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° 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 success-
ful 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 chloro-
formate, boron trifluoride ether complex, antimony trichloride, tri-
methylchlorosilane, and trimethyl tin chloride were all reagent grade
chemicals and were used without further purification. Standard
methods were used in the preparation of $B(CH_3)_3$[1] and $(C_5H_5)_2TiCl_2$.[2]
Pyridine was dried with KOH and distilled. Reagent grade carbon di-
sulfide 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.[3]
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°. For the volatile reactants, BF_3·

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° with a dry ice-acetone bath. In

all cases, the reaction mixture was held at -78° for 5-15 minutes with

occasional agitation. The vessel was them 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·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.[4] 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 (~ 5 ml), a solid was collected by filtra-

tion 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 de-

canted 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 (~ 20°) 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° (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$_2$ allowed to evaporate. A boiling 9:1 hexane:CS$_2$ 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^{-1}. The yield was 0.20 g (45%) from .37 g S$_7$NH. Anal. Calcd for S$_7$NCO$_2$C$_2$H$_5$: 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$_7$NSi(CH$_3$)$_3$ was dissolved by addition of 20 ml of a 50:50 hexane:CS$_2$ solvent or CCl$_4$ 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$_7$NH by its infared 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$_7$NH, as determined from the disappearance of the peak at 3300 cm^{-1} 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$_7$NH. Anal. Calcd for S$_7$NSi(CH$_3$)$_3$: 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} ± 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} ± 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} ± 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).

^{1}H 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.

$^{32}S_3NSi(CH_3)_3^+$; 177, 5, na; 168, 4, $^{32}S_3NSi(CH_3)_2^+$; 162, 6, $^{34}S^{32}S_4^+$;

160, 23, $^{32}S_5^+$; 153, 9, $^{34}S^{32}SNSi(CH_3)_3^+$; 152, 3, $^{32}S_2N^{29}Si(CH_3)_3^+$;

151, 60, $^{32}S_2NSi(CH_3)_3^+$; 138, 6, $^{34}S^{32}SNSi(CH_3)_2^+$; 137, 4,

$^{32}S_2N^{29}Si(CH_3)_2^+$; 136, 39, $^{32}S_2NSi(CH_3)_2^+$; 130, 5, $^{34}S^{32}S_3^+$; 128,

10, $^{32}S_4^+$; 121, 9, $^{32}SNSiCH_3^+$; 120, 11, $^{32}SN^{29}Si(CH_3)_3^+$; 119, 100,

$^{32}SNSi(CH_3)_3^+$; 109, 4, $^{34}S^{32}SSiCH_3^+$; 107, 19, $^{32}S_2SiCH_3^+$; 105, 5,

$^{32}SSi(CH_3)_3^+$; 96, 5, $^{32}S_3^+$; 90, 10, $^{32}SSi(CH_3)_2^+$; 86, 4, na; 75,

10, $^{32}SSiCH_3^+$; 74, 5, $^{32}SNSi^+$, $^{29}Si(CH_3)_3^+$; 73, 64, $Si(CH_3)_3^+$; 64,

15, $^{32}S_2^+$; 45, 5, na; 43, 5, $SiCH_3^+$. Na means that those peaks so

designated were not assigned. Imp is noted after fragments which are

from S_7NH.

C. Results and Discussion

In exploratory experiments, we found that when gaseous CO_2 is

added to solutions of S_7N^-, a white solid immediately precipitates.

Because we found that CO_2 was evolved upon addition of 6 M HCl to the

white solid, the compound is thought to be $K^+S_7NCO_2^-$. However, this

compound decomposed upon warming to 0°, and was not characterized

further. Because of the formation of $S_7NCO_2^-$, we thought that stable

derivatives of the formula S_7NCO_2R might be prepared. This was indeed

found to be true for the compounds $S_7NCO_2C_2H_5$ and $S_7NCO_2CH_2C_6H_5$ 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 ^1H nmr spectra, and in the case of $S_7NCO_2C_2H_5$, a mass spectrum.

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

$$S_7N^- + ClCO_2R \rightarrow S_7NCO_2R + Cl^- .$$
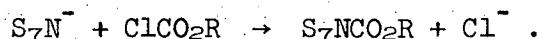
The yellow liquid isolated from the reaction of S_7N^- with $ClSi(CH_3)_3$
in THF was assigned the structure $S_7NSi(CH_3)_3$ based on the observed
infrared, ^{1}H nmr, and mass spectra. A comparison of the infrared
frequencies for $(CH_3)_2NSi(CH_3)_3$, $HCH_3NSi(CH_3)_3$, along with their assign-
ments, 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 cm^{-1}, which is typical for a
S-N stretching frequency. The ^{1}H nmr chemical shift for the compound
$S_7NSi(CH_3)_3$ occurs in the same region as that of known $Si(CH_3)_3$ reso-
nances.[6] 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 ($\sim$ 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[5]
		3422(w)	ν_{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)	$\nu_{N-C\ or\ N-C_2}$
	989 (s)		
870 (vs)	851 (ssh)	866 (s)	ν_{N-Si-C_3}
842 (s)	832 (vs)	836 (vs)	$\rho_{CH_3(Si)}$
793 (m)			ν_{S-N}[a]
756 (w-m)	746 (m)	758 (m)	$\rho_{CH_3(Si)}$
685 (w)	672 (s)	679 (w)	$\nu_{as\ Si-C_3}$

[a] 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
$BF_3 \cdot$ether, $SbCl_3$, $B(CH_3)_3$, $(C_6H_5)_3SnCl$, and $(C_5H_5)_2TiCl_2$. Reaction
occurred with $BF_3 \cdot$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 $BF_3 \cdot$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 satis-
factory 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°. 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.[7] In one run the ratio of S/CO_2 was found to be 7.4. The white solid turned blue when warmed to 0° 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. CS_2 was added to the crude product, and the mixture was filtered. After the CS_2 was evaporated, the residue was mixed with a hot 9:1 hexane: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 S_7NH by its infrared spectrum.

$S_7N^- + (C_6H_5)_3SnCl$.- CS_2 was added to the crude product, and the mixture was filtered. After the CS_2 was evaporated, methanol was added to the residue. The solid which was not soluble in the methanol was identified as S_7NH by its infrared spectrum. The white solid which crystallized from the methanol was identified as $(C_6H_5)_3SnCl$ by comparison of its infrared spectrum with that of a known sample of $(C_6H_5)_3SnCl$. 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 750-800 cm^{-1}; however, the yield was so small that the unknown could not be purified.

$S_7N^- + SbCl_3$.- When the crude product was exposed to the air, the color of the residue immediately changed, and this reaction was not studied further.

$S_7N^- + B(CH_3)_3$.- After allowing the reactants to sit at room temperature for 15 minutes, the solvent (THF) and any unreacted $B(CH_3)_3$ were pumped through a -78° trap into a -196° trap. The THF was held in the -78° trap. After repeating this separation, the amount of unreacted $B(CH_3)_3$ 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[1] and S_7NBBr_2,[2] respectively. In

this note we report the results of our study of the reaction of hepta-

sulfur 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 experi-

mental 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 cor-

responds to the following reaction:

$$S_7NH + \frac{1}{2} B_2H_6 \rightarrow S_7NBH_2 + H_2$$
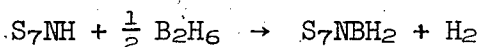
When the reaction is carried out in diethyl ether at 0°, some of

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_7NH with B_2H_6

| Solvent	Temperature,°C	S_7NH, mmol	B_2H_6, mmol	measured H_2/S_7NH	time of meas.,hrs	B_2H_6 consumed S_7NH
monoglyme[a]	23	0.288	0.41	1.11[b]	17	0.49
monoglyme	23	0.992	0.72	1.35[b]	64.5	--
monoglyme	0	0.574	0.516	1.0[c]	66	0.495
	23			1.15[b]	24	
THF[a]	23	0.386	0.356	0.99	67	0.505
THF	23	0.616	0.50	1.13[b]	65.5	--
THF	23	0.567	0.264	1.09[b,d]	145	--
THF	0	0.611	0.593	1.02	497	0.52
THF	0	0.302	0.0716	1.31[b,d]	978	--
dioxane	23	0.505	0.633	2.20[b]	319	--
diethyl ether[a]	0	0.575	0.292	0.98	260	--

[a] reaction mixture not stirred

[b] traces of H_2 still being evolved, due to slow decomposition

[c] stopped purposely to pump out excess B_2H_6

[d] listed as H_2/B_2H_6

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

$$S_7NBH_2 \cdot ether + 3\ H_2O \rightarrow S_7NH + B(OH)_3 + 2\ H_2 + ether$$
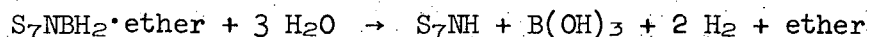
The ^{11}B nmr spectrum of S_7NBH_2 in diethyl ether solution consists
of a 1:2:1 triplet due to coupling with the two protons of the BH_2
group. The Raman spectrum of the diethyl ether adduct has lines at
2419 and 2409 cm^{-1}, characteristic of terminal BH_2 groups, and lines
at 766 and 750 cm^{-1}, 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 decom-
position. 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:

$$S_7NH + S_7NBH_2 \rightarrow (S_7N)_2BH + H_2 \quad .$$
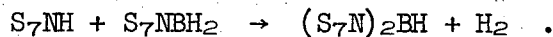
however, the reaction was incomplete after 1 month and was not further studied.

C. Experimental Section

Reagents and procedure.- Heptasulfur imide was prepared by the usual method[3] 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°).[4] The infrared spectrum agreed with that reported in the literature.[4] Diborane was made by the reaction of potassium borohydride with phosphoric acid[5] 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. <u>Anal.</u> 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.[4] The boric acid formed was determined by a standard double titration method.[6] <u>Anal.</u> 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.

<u>Raman spectrum</u>.- 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}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_{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 CS_2 using a Varian A-60 spectrometer. Although the samples decomposed in 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 S_7NBH_2.

X-ray diffraction.- Some preliminary X-ray diffraction data on a single crystal of $S_7NBH_2 \cdot C_4H_{10}O$ correspond to the space group P_{nma} and the unit cell dimensions $\underline{a}$ = 15.80, $\underline{b}$ = 13.16, and $\underline{c}$ = 6.75 Å.

Preparation and characterization of $S_7NBH_2 \cdot C_5H_5N$.- The pyridine adduct is prepared by addition of excess, dry pryidine to the solid $S_7NBH_2 \cdot Et_2O$. The solution is evaporated to a volume of 0.2-0.3 ml, and dry CCl_4 is then added. A white solid is precipitated and is washed with a small amount of chilled CCl_4. The infrared spectrum of a Nujol

mull recorded with a Perkin-Elmer Model 137B Infracord Spectrophotometer consisted of the following peaks (cm^{-1} ± 10 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 87.5-88° was analyzed. <u>Anal</u>. Calcd for $S_7NBH_2 \cdot C_5H_5N$: 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 B_2O_3 residue). A proton nmr spectrum showed the protons on the pyridine ring, but we were unable to see the protons attached to boron.

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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.[1] 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,[2,3] 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 6×10^{-3} $\underline{M}$ 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 (Å ± 20 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 $\underline{M}$ 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 ± .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 $\underline{ca}$. 2% solution of $AlCl_3$ in nitromethane was added to dissolve a known quantity of S_4N_4 (~ 20 ml/0.5 g S_4N_4). The volume of the solution was reduced to $\underline{ca}$. 3-4 ml by pumping. The remaining solution was cooled to 0°, and some crystals were noted. An additional 0.5-1.0 ml of solution was then slowly removed by condensation into a -78° trap, while the evaporating solution was held at 0°. The crystals were then collected by filtration and washed with HCl-saturated chloroform (~ 40 ml) to remove the solvent and dried CCl_4 (~ 20 ml) to remove any $AlCl_3$ or

Figure Captions

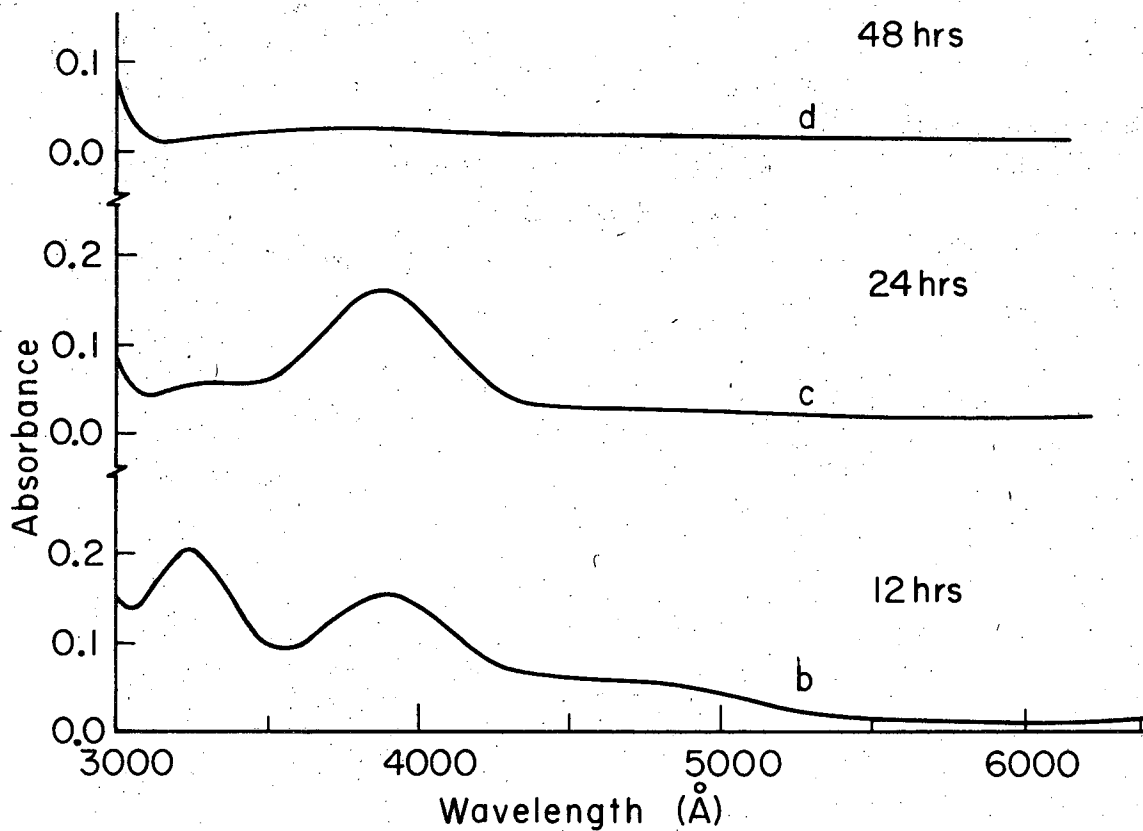Figure 1 (a-d). 6×10^{-3} $\underline{M}$ S_4N_4 in nitromethane containing 1-2% $AlCl_3$.

Figure 2.   Epr spectrum of $S_2N_2^+$ in nitromethane containing 1-2% $AlCl_3$.
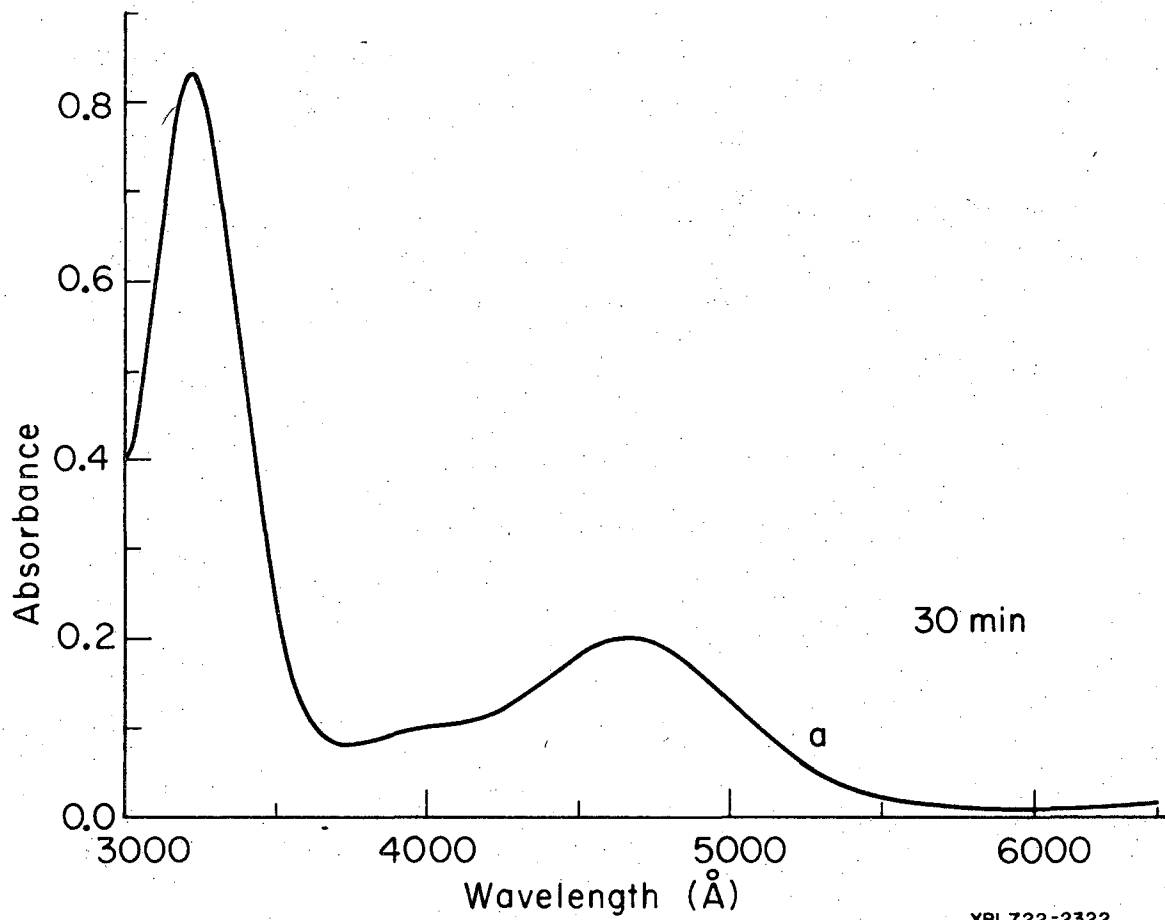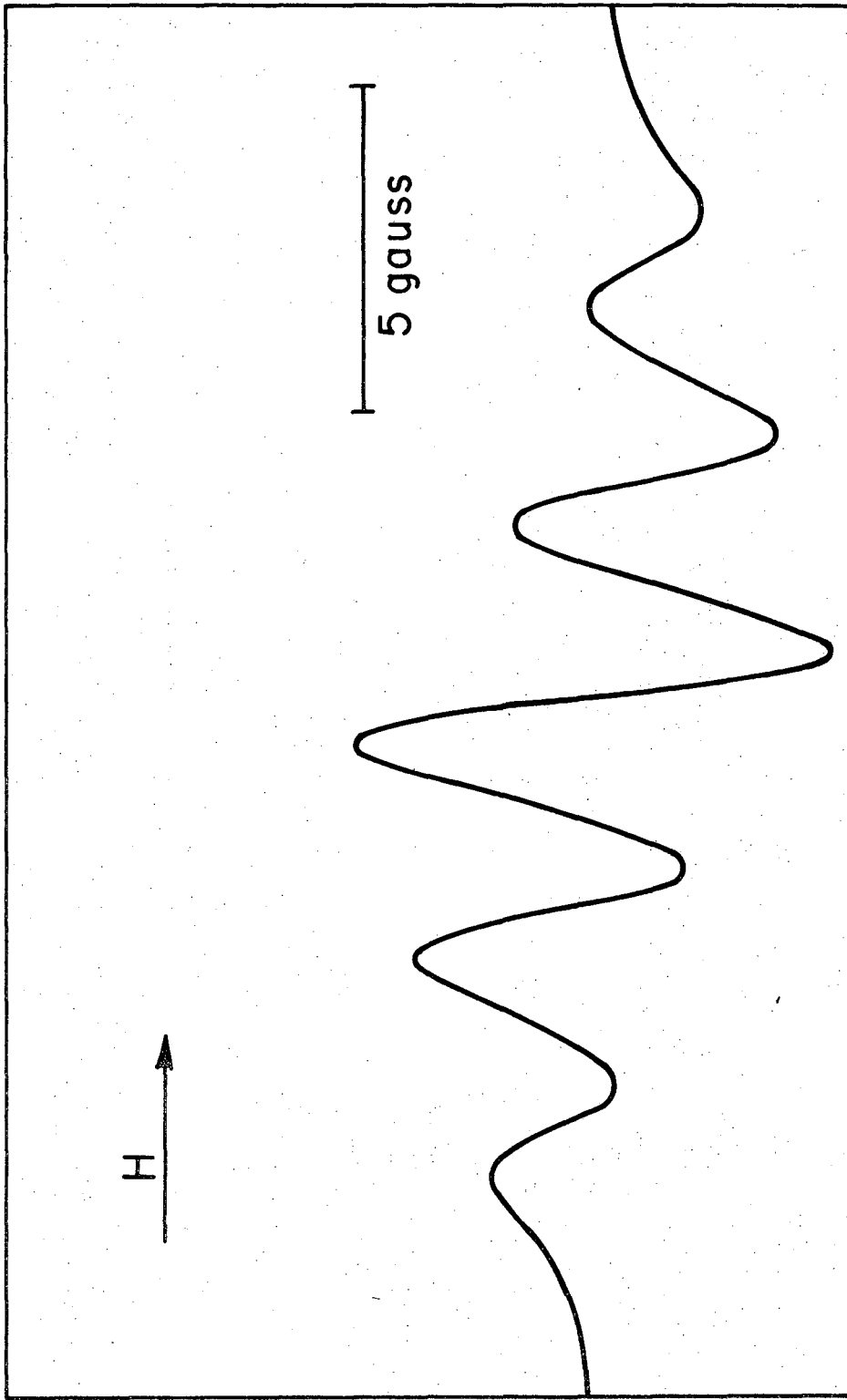
Fig. 1.(a)

XBL722-2322

Fig. 1(b-d)

XBL722-2323

Fig. 2.

XBL 722 - 2324

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 $\underline{M}$ 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.[4]

The proton nmr spectrum of a sample, one-half hour after initial mixing of the reactants, showed three peaks to low field of the nitro-methane 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 6×10^{-3} $\underline{M}$ 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 $\underline{ca}$. 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 CO_2 or N_2O, while in another run, the main peak was at $m/e = 76$, corresponding to CS_2. However, in both cases, the characteristic pattern for the fragment CCl_3^+ was observed at $m/e = 117$, 119, and 121. We have also observed that when diethyl ether is added to solutions of S_4N_4 in $AlCl_3$/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 S_4N_4, precipitates from the solution.

D. Discussion

The esr spectrum shows that the species $S_2N_2^+$ is present in solutions of S_4N_4 in $AlCl_3$/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 Å correlates with our esr and nmr data if we assume that this peak is due to the species $S_2N_2^+$. The 3900 Å 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.[2] 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.[5] 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 qth level, q is a quantum number, h is Planck's constant, m is the mass of an electron, and ℓ 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 $\ell = 12.8$ Å which is the circumference of a circle escribed about a regular octagon with one side = 1.55 Å (the known average S-N bond length for $S_4N_3^+$ is 1.55 Å [6,7]). For a 10-electron pi system, the first transition is from the $q = 2$ to the $q = 3$ level. With the preceeding assumptions, we have calculated the first transition for $S_4N_4^{2+}$ to be 2700 Å. In our system, we observe a peak at 4660 Å and in 100% H_2SO_4 a peak is observed at 4560 Å.[1] 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 Å 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 questions 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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Acknowledgments