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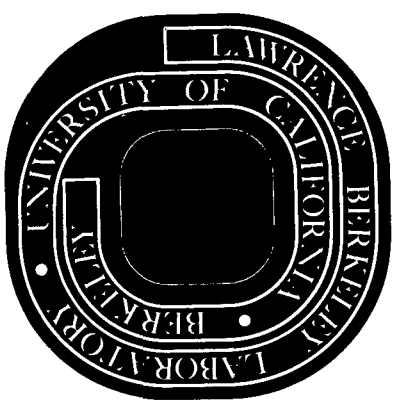

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REACTIONS OF THE HEPTASULFUR IMIDE ANION

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Abstract - Heptasulfur imide can be completely deprotonated by treatment of its solution in tetrahydrofuran with powdered KOH at -62° for 15 min; the resulting solution of $K^+S_7N^-$ reacts with CH_3I to give an essentially quantitative yield of the N-methyl derivative of heptasulfur imide. Extended treatment of a $K^+S_7N^-$ solution with KOH causes irreversible decomposition. In solution, the S_7N^- ion undergoes spontaneous isomerization, probably to an open chain form; at temperatures above about -40°, the rate of isomerization is sufficient to permit equilibrium between the two forms to be readily achieved. The compounds benzyl heptasulfurimidoformate, ethyl heptasulfurimidoformate, and heptasulfurimidotrimethylsilane are formed by the action of the ring form of S_7N^- on the corresponding chloro compounds.

INTRODUCTION

Various N-substituted derivatives of heptasulfur imide have been prepared by reaction of the imide with strong Lewis acids and with strongly electrophilic reagents [1-3]. A much wider range of derivatives is potentially available from reactions of the deprotonated imide, S_7N^-. Olsen et al. [2,3] were the first to report the use of S_7N^- in

the synthesis of alkyl derivatives. They concluded, partly because they were unable to deprotonate S_7NH quantitatively, that the treatment of S_7NH with bases causes an irreversible ring-cleavage reaction in addition to deprotonation. They also suggested that the S_7N^- ion is in equilibrium with an open chain isomer. In this paper, we describe a method for the quantitative deprotonation of S_7NH, present data which help clarify the nature of the ring-cleavage and isomerization, and report the synthesis of several new organo derivatives of S_7NH.

EXPERIMENTAL

Reagents and General Procedures.- Heptasulfur imide was prepared by published methods [4,5] and purified by recrystallization from methanol followed by repeated recrystallization from carbon tetrachloride until the solutions were colorless and the S_7NH melted at 113-114° (lit. 113.5°) [5]. Methyl iodide, trifluoroacetic acid, potassium hydroxide, ethyl chloroformate, benzyl chloroformate, trimethylchlorosilane, boron trifluoride diethyl etherate, and triphenyl tin chloride were all reagent grade chemicals and were used without further purification. Standard methods were used for the preparation of $B(CH_3)_3$ [6] and $(C_5H_5)_2TiCl_2$ [7]. Pyridine was dried with KOH and distilled. Reagent grade carbon disulfide and carbon tetrachloride were used. Spectroquality hexane was used without further purification. Diglyme was distilled first from potassium hydroxide and then from lithium aluminum at reduced pressure. Tetrahydrofuran was distilled from lithium aluminum hydride. Para-

dibromobenzene was recrystallized from ethanol and was found to melt at 86.5-88° (lit. 87°) [8].

To prepare solutions of $K^+S_7N^-$ for synthetic purposes, a solution of S_7NH in tetrahydrofuran was treated with powdered KOH using an apparatus and general technique described previously [9]. The reaction flask was connected to a receiving flask by a tube containing a fritted disc. All operations were carried out with the apparatus flushed with nitrogen gas. Freshly powdered KOH (2-4 g) and 25 ml of tetrahydrofuran were added to the reaction flask, cooled to about -62°, and magnetically stirred for a few minutes; then 0.2-0.5 g of S_7NH was added. The reaction mixture was stirred for 15 min and then filtered by removing the apparatus from the cold bath, inverting it, and applying a partial vacuum to the receiver flask. (During the filtration, which was complete in 5-10 seconds, the solution temperature did not exceed -35°.) The filtered solution was cooled to -78° and then treated with the reagent.

In an exploratory study of the reaction of heptasulfur imide with potassium hydroxide, a weighed amount of S_7NH (0.2-0.5 g) was added to a stirred slurry of KOH (2-4 g) in tetrahydrofuran (25.0 ml) at -62°. At various times an aliquot was pipetted from the supernatant solution and added to an excess of standardized trifluoracetic acid in diglyme at room temperature. The excess acid was titrated with standardized 0.100 M NaOH to an endpoint corresponding to the first persistent blue color. (The accuracy of this endpoint was checked by several titrations using a known amount of acid in the presence of some S_7NH.) In a similar study, aliquots of the solution from the KOH slurry at -62°

were pipetted into excesses of CH_3I (0.5-0.6 ml), and after evaporation the amounts of S_7NCH_3 formed were determined by proton nmr spectroscopy using p-$Br_2C_6H_4$ as an internal standard.

A Varian T-60 was used for the proton nmr spectra. Samples were dissolved in CS_2, and the quoted chemical shifts are to low field of internal TMS. A Cary 14 spectrophotometer was used to record the uv-vis spectrum, a Perkin-Elmer Model 137B Infracord Spectrometer was used to record the infrared spectra, and a Consolidated Electrodynamics Corporation Type 21-103C mass spectrometer (operated at 70 eV) was used to obtain the mass spectra.

$S_7NCO_2CH_2C_6H_5$.- Two grams of $ClCO_2CH_2C_6H_5$ was added to a solution of S_7N^- prepared from 0.28 g of S_7NH. The mixture was agitated, held at room temperature for about 10 min, and then evacuated to remove the solvent and excess $ClCO_2CH_2C_6H_5$. The crude product was treated with 20 ml of CS_2; the mixture was filtered, and the filtrate was evaporated. The residue from the evaporation was twice recrystallized from 10 ml of a 9:1 CS_2:hexane mixture to give 0.10 g (25% yield) of a white solid, melting at 98-99° (uncorr.). 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 following infrared bands (cm^{-1}) were observed for a CS_2 solution (except for the 839 cm^{-1} peak, which was seen in a Nujol mull): 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). The nmr spectrum showed two singlets, at 7.27 and 5.16 ppm, with relative

intensities of 5:2, corresponding to the phenyl protons and the CH_2 protons, respectively.

$S_7NCO_2C_2H_5$.- Ethyl chloroformate (1.7 g) was added to a solution of S_7N^- prepared from 0.37 g of S_7NH. A procedure analogous to that used for the $S_7NCO_2CH_2C_6H_5$ was followed to the point of evaporating the CS_2 solution. The residue was extracted with a boiling 9:1 hexane-CS_2 mixture; upon evaporation of the extract to about 1 ml, a dense yellow liquid separated from the solution. The solvent was decanted, and the extraction process was repeated until the infrared spectrum of the yellow liquid showed no peak at 3330 cm^{-1}. Yield: 0.20 g (45%). Anal. Calcd for $S_7NCO_2C_2H_5$: 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 infrared spectrum of a neat sample, pressed between NaCl plates, showed the following bands (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 nmr spectrum showed a triplet at 1.33 ppm and a quartet at 4.22 ppm, with relative intensities of 3:2 and J = 8 Hz. The mass spectrum showed the follwoing peaks (m/e, relative peak height, and assignment respectively; peaks with less than 4% of the intensity of the most intense peak omitted) [10]: 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, , $^{32}SC_2H_5^+$; 58, 8, NCO_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, $C_2H_3^+$.

$S_7NSi(CH_3)_3$.- Excess trimethylchlorosilane was distilled onto a solution of S_7N^- prepared from 0.50 g of S_7NH. The mixture was gradually warmed to room temperature, agitated for about 10 min, and then evacuated to remove the solvent and excess $(CH_3)_3SiCl$. The crude product was dissolved in 29 ml of 50:50 hexane-CS_2 mixture, and, in a dry box, the solution was filtered. Upon evaporation of the filtrate to 2-3 ml, some S_7NH (identified by its ir spectrum) precipitated. After filtration, the solution was evaporated to yield a yellow liquid. Further S_7NH was removed by cooling a hexane solution to -78° and filtration. Evaporation yielded 0.10 g (15% yield) of the yellow liquid. Anal. Calcd for $S_7NSi(CH_3)_3$: 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. The following infrared bands (cm^{-1}) were observed for a neat sample pressed between two NaCl plates: 2959(w-m), 2899(sh), 1401(w), 1364(sh), 1248(m-s), 870(vs), 842(s), 793(m), 756(w-m), and 685(w). The nmr spectrum showed a single line at 0.33 ppm. The mass spectrum showed the following peaks (m/e, relative peak height, and assignment, respectively; peaks with less

than 3% of the intensity of the most intense peak omitted) [10]: 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, $^{32}S_3NSi(CH_3)_3^+$; 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, $SiCH_3^+$.

Miscellaneous Studies.- The reactions of S_7N^- with $(C_5H_5)_2TiCl_2$, $(C_6H_5)_3SnCl$, $B(CH_3)_3$, $BF_3{\cdot}O(C_2H_5)_2$ and CO_2 were investigated by procedures similar to those described above. No evidence of reaction was found except in the case of $BF_3{\cdot}(OC_2H_5)_2$ and CO_2. The crude products from the $BF_3{\cdot}O(C_2H_5)_2$ reaction were washed with pyridine and acetone to yield KBF_4, identified by its ir spectrum [11], in an amount corresponding to 0.93 mol KBF_4/mol S_7N^-. Some S_7NH was isolated from the pyridine extract, but no other product was identified. When CO_2 was added to a cold $K^+S_7N^-$ solution, a white solid (presumably $K^+S_7NCO_2^-$) precipitated.

Addition of 6 M HCl caused evolution of CO_2, but the compound decomposed on warming to 0° and was not further characterized.

RESULTS AND DISCUSSION

The Preparation and Properties of $K^+S_7N^-$ Solutions.- A solution of S_7NH in tetrahydrofuran, when stirred with powdered KOH at -62°, becomes initially yellow, and eventually green. Treatment of this solution with excess methyl iodide at 0° yields S_7NCH_3, and, because it is known that there is no reaction between S_7NH and CH_3I [3], we conclude that the active agent in the solution is the anionic eight-membered ring, S_7N^-, formed by deprotonation of the S_7NH. The percentage yield of S_7NCH_3 is dependent on the time of stirring with the KOH. Data for a run at -62° follow: 2 min, 68%; 10 min, 101%; 15 min, 102%; 20 min, 103%; 30 min, 95%; 40 min, 94%; 90 min, 85%. The fact that the yield goes through a maximum suggests that either the S_7N^- ion undergoes degradation on continued treatment with KOH or the S_7N^- ion is itself unstable at -62°. Separate experiments showed that a filtered solution of $K^+S_7N^-$ (prepared by treatment with KOH for 15 min) gave essentially 100% yield of S_7NCH_3 for periods as long as a day when it was stored at -62° or lower. Thus we conclude that the KOH reacts with S_7N^- to give a species which does not yield S_7NCH_3 upon treatment with CH_3I. Further evidence for degradation of S_7N^- by KOH was obtained by titrating the S_7N^- solutions with acid after various times of stirring with KOH. The equivalents of base found in solution per mole of S_7NH, for a -62°

run, follow: 0.5 hr, 0.97; 0.75 hr, 1.06; 1.0 hr, 1.09. Similar data for two -78° runs follow [12]: (1) 0.25 hr, 0.98; 0.5 hr, 1.07; 1.0 hr, 1.09. (2) 0.5 hr, 0.81; 1.0 hr, 0.85; 2.3 hr, 1.00; 4.5 hr, 1.10. The fact that the theoretical value of 1.00, corresponding to quantitative formation of S_7N^-, is exceeded after prolonged treatment with KOH suggests that the S_7N^- ring is irreversibly cleaved by OH^- to give an open-chain species which consumes two or more moles of acid in the titration. This interpretation is the same as that of Olsen and Olsen [3], who studied the effects of other bases.

Filtered solutions of $K^+S_7N^-$, prepared by reaction of S_7NH with KOH for 15 min at -62°, were allowed to stand at various temperatures until the yields of S_7NCH_3, determined by treatment of aliquots with excess methyl iodide, did not change with time. The results are presented in Table I.

Table I

Yields of S_7NCH_3 from S_7N^- Solutions

Temperature, °C	Time at specified temperature, hr.	% yield of S_7NCH_3
-35	264	53
-22	12	46
0	20	34
20	1	27

Sufficient data were collected during the runs at -22 and 0° to determine that the S_7NCH_3 yield followed a first-order decay law, with

half-times of 84 and 12 min, respectively. The same final yield of S_7NH (34%) at 0° was obtained by cooling a solution from 50° as by warming another solution from -62°, thus showing that an equilibrium is reached which can be approached from either side. The data indicate that the 8-membered ring form of the S_7N^- ion (form I) isomerizes reversibly to a form II which gives less than quantitative (perhaps zero) yield of S_7NCH_3 upon treatment with methyl iodide.

The percentage yields in Table I do not necessarily correspond to the equilibrium percentages of the S_7N^- in form I. For example, they would correspond to upper limits to the equilibrium percentages of form I if both the rate of reaction of CH_3I with form I and the rate of conversion of form II to form I were greater than the rate of reaction of CH_3I with form II. We can only conjecture as to the nature of form II. Probably it corresponds to an open-chain structure for S_7N^-, such as $S{=}N{-}S_5{-}S^-$ or $S{=}S^+{-}S{-}N^-{-}S{-}S{-}S{-}S^-$, or to a mixture of such structures.

When S_7NH in tetrahydrofuran is treated with powdered KOH at -78°, deprotonation is exceedingly slow. However, if the reaction mixture is first stirred at -62° for 2 or 3 min and is then cooled to -78°, the reaction proceeds rapidly enough to effect complete deprotonation to a yellow solution of $K^+S_7N^-$ in about 30 min. In fact this procedure is the only one we know of for preparing a solution of $K^+S_7N^-$ which is not green or blue. If a yellow solution of $K^+S_7N^-$ is warmed to -62°, it soon turns green, and if warmed to 0°, it turns blue. Cooling back to -62 or -78° does not reverse the color changes. These results indicate that the S_7N^- ion of form I is yellow, and that the blue color

is due to a decomposition product. Perhaps the blue decomposition product is the same as the form II S_7N^- referred to above; however our data are inadequate to decide the point.

Nucleophilic Reactions of S_7N^-.- Pure samples of ethyl and benzyl heptasulfurimidoformate were obtained from the reaction of S_7N^- (form I) with ethyl and benzyl chloroformates, respectively. The identification of these compounds was achieved by chemical analysis, infrared and nmr spectroscopy, and, in the case of $S_7NCO_2C_2H_5$, mass spectroscopy. We believe that it should be possible to prepare many analogous compounds by the same general synthetic reaction:

$$S_7N^- + ClCO_2R \rightarrow S_7NCO_2R + Cl^-$$

Although the compound $S_7NSi(CH_3)_3$ obtained from the reaction of S_7N^- with $(CH_3)_3SiCl$ was relatively impure, it was unambiguously identified by infrared, nmr, and mass spectroscopy. The infrared spectrum corresponds very closely to those of $(CH_3)_2NSi(CH_3)_3$ and $H(CH_3)NSi(CH_3)_3$ [13], except for the absence of bands due to CH_3N and NH groups and the presence of a band at 793 cm^{-1} due to S-N stretching. The nmr chemical shift is in the same region as that found for known $-Si(CH_3)_3$ compounds [14]. The similarity of the mass spectral fragmentation pattern to that of $S_7NCO_2C_2H_5$ and the observed parent peak at m/e = 311 confirm the formulation $S_7NSi(CH_3)_3$.

The lack of reactivity of $B(CH_3)_3$, $(C_6H_5)_3SnCl$, and $(C_5H_5)_2TiCl_2$ toward S_7N^- can probably be ascribed to steric hindrance.

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