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Liquid Ammonia Solutions. VI. Sulfur and Tetrasulfur Tetranitride (S_4N_4)

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Spectrophotometric data on liquid ammonia solutions containing S, S_4N_4, and $S_4N_4 + H_2S$ indicate that the equilibrium $10S + 4NH_3 \rightleftarrows S_4N_4 + 6H_2S$ does not exist to an appreciable extent. The spectrum of liquid ammonia solutions of S_4N_4 changes with time, which has been interpreted in terms of a reaction of the type $S_4N_4 + \text{am} \rightleftarrows 2S_2N_2\cdot\text{am}$. Sulfur–ammonia solutions have a spectrum which is different from that of sulfur in several other solvents, and the nature of the temperature dependencies of the spectrum of the S–NH_3 solutions suggests that at least two species are present.

Among the unusual properties of liquid ammonia is its ability to dissolve several types of elemental substances. The solubility of the alkali and alkaline earth metals is well known, and the nature of the species present in these solutions has been extensively investigated.[1] The group VI elements are also soluble in liquid ammonia, but the nature of these solutions has been less extensively studied. Of the elements in group VI, sulfur is by far the most soluble in liquid ammonia (38.85% at −84.6°) giving green solutions which become red on cooling to −84.6°; the solubility is almost constant in the temperature range −84.6 to −20.5°. The freezing point curve for the S-NH_3 system indicates the presence of the thermally unstable compounds $S(NH_3)_6$ (mp −78.5°) and $S(NH_3)_3$.[2] Selenium[3] and tellurium[4] are markedly less soluble.

We present the results of an investigation of the spectra of sulfur–ammonia solutions under various conditions in an attempt to establish the identity of the species present.

Results

The spectra of liquid ammonia solutions of sulfur (10^{-3} to 10^{-4} *M*) determined at −35° exhibit absorption maxima at 580, 430, and 297 mμ; the apparent molar extinction coefficients of the bands based on the analytical concentration (in gram-atoms) of sulfur are 7.6, 27, and 130, respectively. The band at 580 mμ decreases in intensity, while the other two bands increase, with a decrease in temperature (Figure 1). Freshly prepared liquid ammonia solutions of S_4N_4 exhibit a band at 254 mμ (ϵ 9.27 ± 0.42 × 10^3) which decreases with time, giving rise to a new band at 360 mμ (ϵ 6.0 ± 0.28 × 10^3). This change in the spectrum was usually complete within 10 min after the solution had been prepared; the rate at which the spectral change occurred increased with increasing temperature. Solutions containing S_4N_4 and H_2S exhibit band maxima at 270 and 360 mμ; however, there were occasional indications of weak bands at 600, 430, and 297 mμ in some solutions, depending upon the method of preparation, which probably arose from traces of sulfur in the reagents.

Discussion

Sulfur–ammonia solutions are spectroscopically different from solutions of sulfur in ethanol,[5–7] hexane,[5–8] chloroform,[5,9] methanol,[5] and benzene,[10] all of which exhibit essentially identical spectra with bands at 275 (ϵ ∼900), 265 (ϵ ∼900), and 230 mμ (ϵ ∼1400). In these solvents, the positions of the bands and their extinction coefficients vary only slightly with the index of refraction of the solvent.[5] The spectrum of sulfur in benzene has been assigned to the S_8 species,[10] and presumably these are the species present in the organic solvents studied. In contrast to these observations, the spectra of sulfur–ammonia solutions indicate that species of a different nature are present. Indeed, the fact that the 580 mμ band increases in intensity with an increase in temperature while the bands at 430 and 297 mμ decrease (Figure 1) suggests that at least two different species are in equilibrium in sulfur–ammonia solutions.

The addition of silver salts to sulfur–ammonia solutions yields insoluble Ag_2S and, after evaporation of the solvent, S_4N_4; on the basis of these results it was suggested that the species shown in eq 1 are in equilibrium in solution, the addition of Ag^+ being necessary to drive the point of equilibrium toward the reactants.[3,11] It was pointed out that the process described by eq 1 did not occur if all traces of water were eliminated from the system.[12] The spectroscopic results reported here, together with the observations on liquid ammonia solutions of hydrogen sulfide,[13] indicate (a) that S_4N_4 does not exist as such in sulfur–ammonia solutions and (b) that if the equilibrium defined by eq 1 is established the concentration of H_2S must be below 10^{-5} *M*. Neither the

$$10S + 4NH_3 \rightleftarrows S_4N_4 + 6H_2S \qquad (1)$$

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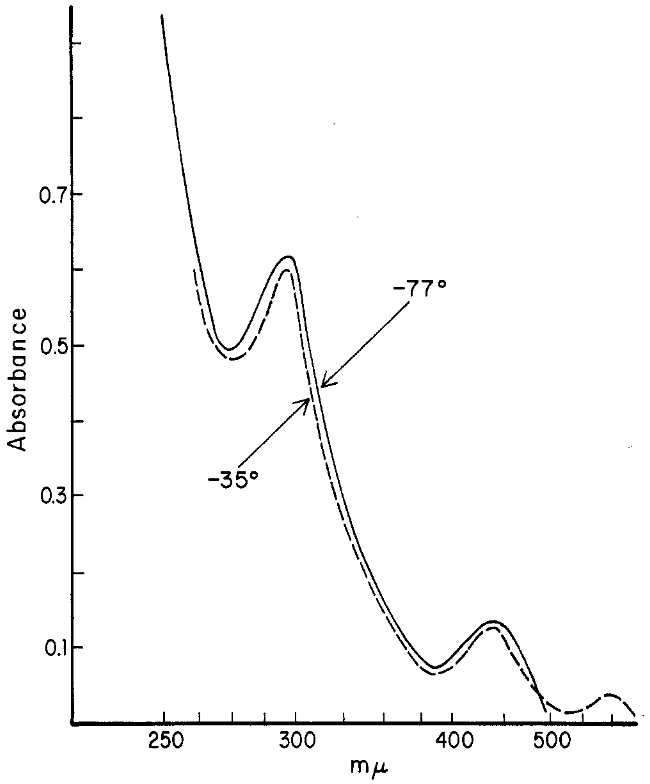

Figure 1.—Absorption spectra of sulfur in liquid ammonia at −77 and −35°.

band at 270 mμ (ε 9.14 × 10^3), which is characteristic of solutions of H_2S,[13] nor the bands at 254 and/or 360 mμ (*vide infra*), which are characteristic of S_4N_4 solutions, are observed for sulfur–ammonia solutions. In addition, ammonia solutions containing mixtures of H_2S and S_4N_4 exhibit only the bands characteristic of these substances. If the point of the equilibrium described by eq 1 were far to the left, it might be expected that a mixture of H_2S and S_4N_4 would generate the species characteristic of elemental sulfur.

Spectral data on ammonia solutions of S_4N_4 indicate that the latter is rapidly converted into a new species, since the disappearance of the band at 254 mμ, which is characteristic of an intramolecular transition of S_4N_4,[14] is accompanied by the appearance of a new band at 360 mμ. Ruff and Geisel[15] have shown that S_4N_4 gives an ammoniate of the composition $S_4N_4\cdot 2NH_3$ which is identical with the ammoniate formed when disulfur dinitride is dissolved in liquid ammonia, *i.e.*, $S_2N_2\cdot NH_3$.[16] The band at 360 mμ is assigned to the species $S_2N_2\cdot NH_3$ or its ionization products; $S_2N_2\cdot NH_3$, formulated as $HNSNSNH_2$,[16] has been reported to give deep red conducting solutions in liquid ammonia.[16-19] Thus, the change in the spectrum of a freshly prepared solution of S_4N_4 in liquid ammonia corresponds to the process in eq 2; the process must go

$$S_4N_4 + 2NH_3 \rightleftarrows 2S_2N_2\cdot NH_3 \qquad (2)$$

essentially to completion since the band at 254 mμ cannot be detected in these solutions after equilibrium has been established.

Since the spectroscopic data for sulfur–ammonia solutions presented here indicate that the species S_8, H_2S, S_4N_4, or $S_2N_2\cdot NH_3$ are not present in appreciable concentrations in solution and since S_4N_4 can be obtained from these solutions, it appears that the bands at 297, 430, and 580 mμ may be associated with species that are precursors of S_2N_2 of the type $S_x(NH_3)_y$, $S_x(NH_2)_y{}^{y-}$, and/or $S_x(NH)_y{}^{2y-}$. The first named species may be either of the ammoniated sulfur species reported by Ruff and Hecht[2] [*i.e.*, $S(NH_3)_6$ or $S(NH_3)_3$]; the other two species could arise from the ammonolysis of the first and would explain the observed conductivity of sulfur–ammonia solutions.[20]

Experimental Section

The spectra of liquid ammonia solutions were determined in the 230–700 mμ region in the temperature range −77 to −35° using the equipment and techniques described previously.[21]

Sulfur (U.S.P., Fisher Scientific Co.) was used without further purification since preliminary experiments indicated that solutions of a sample sublimed *in vacuo* were spectroscopically indistinguishable from those prepared from the unsublimed material. Tetrasulfur tetranitride (S_4N_4) was prepared by the reaction of SCl_2 with NH_3 in carbon tetrachloride solution[22] and purified by fractional sublimation *in vacuo* at 90°, mp 177.5° (lit.[23] 178°). Hydrogen sulfide (reagent grade, Fisher Scientific Co.) was distilled at −50° *in vacuo* before use.

Solutions of sulfur or S_4N_4 were prepared by adding a weighed sample to a measured volume of liquid ammonia in the optical cell assembly. Solutions containing both H_2S and S_4N_4 were prepared by adding a weighed quantity of the latter to a previously prepared solution of H_2S.[13]

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