Discussion

It seems certain that chemical equilibrium was achieved in our studies of reactions 1 and 3. For systems in which the amide concentration was held constant, the concentration of electrons (whether determined optically or by esr) was proportional to the square root of the hydrogen pressure.

Equilibrium quotients calculated from data for reaction 1 were found to increase markedly with increasing concentration of amide ion. However when these quotients were corrected to "constants" by use of estimated activity coefficients, the values were reasonably constant with changing amide concentration. The equilibrium constant at 25° corresponding to the most dilute solutions, $K = 5 \times 10^4$, is in fair agreement with that calculated indirectly from the known free energies of formation[2] of the species in reaction 1, $K = 1.2 \times 10^6$. Our experimental value of the heat for reaction 1, $\Delta H° = -15.7$ kcal/mole, is probably in reasonable agreement with that calculated indirectly from calorimetric data,[2] $\Delta H° = -11.5$ kcal/mole, particularly in view of the inaccuracies associated with heats determined from temperature coefficients. An equilibrium constant of 3×10^9 was calculated from data for reaction 3, using estimated activity coefficients. This value may be compared with the value 1.3×10^{10} calculated indirectly from the known free energies of formation of the species in reaction 3.[2,4] In view of the fact that our experimental value of the heat for reaction 3, $\Delta H° = -12.3$ kcal/mole, was obtained from data in a very narrow temperature interval, it is in remarkably good agreement with the heat calculated indirectly from calorimetric data, $\Delta H° = -11.7$ kcal/mole.[2,4]

Of the various species in reactions 1 and 3, that for which the free energy of formation is least accurately known is the electron, e_{am}^-. Using the tabulated[2,4] free energies for the other species and our directly determined equilibrium constants for reactions 1 and 3, we calculate the values 44.1 and 45.1 kcal/mole, respectively, for $\Delta F_f°(e_{am}^-)$ at 25°. We recommend use of the average value, 44.6 kcal/mole.

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Liquid Ammonia Solutions. V. Solutions of Hydrogen Sulfide

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The results of spectrophotometric experiments and potentiometric titrations on anhydrous liquid ammonia solutions of H_2S and the alkali metal sulfides suggest that the former undergoes ionization to give a hydrogen-bonded species, $SH^- \cdots NH_3$ or $S^{2-} \cdots HNH_3^+$. The ionization constant for the process $H_2S + 2NH_3 \rightleftarrows SH^- \cdots NH_3 + NH_4^+$ has been estimated as $(1.04 \pm 0.19) \times 10^{-2}$. The hydrogen-bonded product formed in this ionization does not have the same characteristics as sulfide ions arising from the dissolution of alkali metal sulfides in liquid ammonia.

Introduction

The band at 230 mμ in the electronic spectrum of aqueous solutions containing hydrosulfide ion (HS^-),[1] which has been attributed[2] to a charge-transfer-to-solvent electronic transition and shows the environmental dependence associated with this type of transition,[3] has been used to estimate the first and second dissociation constants of hydrogen sulfide in this medium.[1c] The band at 360 mμ in the spectrum of solutions containing the sulfide ion (S^{2-})[3,4] has also been characterized[3] as arising from a charge-transfer-to-solvent transition.

We present here the results of a study on the nature of the species present in anhydrous liquid ammonia solutions of hydrogen sulfide, which bear on the questions of (a) the relative acidity of substances in liquid ammonia and (b) the constitution of solutions of sulfur in liquid ammonia.[5]

Experimental Section

The spectra of liquid ammonia solutions were determined with the equipment and using the rinsing techniques described in previous publications from this laboratory.[6] Assuming that the vapor pressure lowering for the very dilute solutions studied ($\sim 10^{-4}$ *m*) was negligible, the temperatures of the solutions were conveniently estimated from their vapor pressures; initial experiments using a calibrated thermistor probe indicated that the

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(1) (a) H. Ley and B. Arends, *Z. Physik. Chem.*, **6B**, 240 (1929); (b) H. Ley and B. Arends, *ibid.*, **15B**, 311 (1932); (c) A. J. Ellis and R. M. Golding, *J. Chem. Soc.*, 127 (1959).

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(5) J. T. Nelson, Ph.D. Dissertation, The University of Texas, 1966.

(6) (a) E. C. Fohn, R. E. Cuthrell, and J. J. Lagowski, *Inorg. Chem.*, **4**, 1002 (1965); (b) D. F. Burow and J. J. Lagowski, Advances in Chemistry Series, No. 50, American Chemical Society, Washington D. C., 1965, p 125

vapor pressure reflected the temperature of the solution within the experimental error of the measurements with the probe. Spectra were recorded from 230 to 700 mμ in the temperature range −77 to −35° with a Cary Model 14 spectrophotometer.

Titrations of liquid ammonia solutions of hydrogen sulfide with potassium and/or potassium amide were conducted in an apparatus similar to that employed by Watt and Otto.[7] The apparatus was cooled in an 2-propanol–Dry Ice bath, rinsed with liquid ammonia using a procedure similar to that employed for the optical cell,[6] and evacuated; a known quantity of either alkali metal or alkali metal amide was introduced into the buret portion of the apparatus in a helium-filled glove box. The titration assembly was then attached to the vacuum system and evacuated, and a known quantity of hydrogen sulfide condensed into the titration vessel from a calibrated manifold attached to the vacuum system; finally known quantities of ammonia were condensed in both the buret and the titration vessel. The titrant was then slowly added to the H_2S solution by pressuring the buret with dry helium and carefully manipulating the stopcock separating these two vessels. In titrations with metal–ammonia solutions, persistence of the characteristic blue color of the solvated electron was taken as the end point. Hydrogen sulfide was titrated with potassium amide until the addition of titrant produced a permanent precipitate of K_2S; the latter substance is very insoluble in liquid ammonia.

Solutions of alkali metal sulfides were prepared by the reaction between stoichiometric amounts of the metal and an alkali metal polysulfide in liquid ammonia. The sulfides were characterized by analysis using conventional techniques.[5] Potassium (purified, J. T. Baker Chemical Co.) was distilled *in vacuo* prior to use. Hydrogen sulfide (reagent grade, Fisher Scientific Co.) was purified by distillation at −50° to give a product showing no extraneous peaks in its mass spectrum. Potassium amide was prepared by the action of potassium on ammonia in the presence of a catalyst.

Results

Liquid ammonia solutions of the alkali metal sulfides (M_2S) exhibit only one absorption band (Figure 1) in the ultraviolet region at 270 ± 1 mμ (−77°), which possesses characteristics similar to those observed for the iodide absorption in this solvent[8] and which is associated with a charge-transfer-to-solvent transition.[9] The position of the band is temperature dependent (dE_{max}/dT = 77 cal/deg for K_2S; Figure 2), as is the density-corrected extinction coefficient ($\epsilon \sim 6 \times 10^3$ at −77°) for this band; the latter constant was difficult to determine accurately because of the very low solubility (*e.g.*, 5.5×10^{-4} mole of K_2S/l. at −77°) of the alkali metal monosulfides in liquid ammonia.

Liquid ammonia solutions of hydrogen sulfide also exhibit only one absorption band which occurs at essentially the same position at −77° as the band characteristic of the alkali metal sulfides (Figure 1). This band displays the typical charge-transfer-to-solvent temperature dependence (Figure 2). Both bands have the same width at half-height and appear to arise from essentially the same species; however, the position of the band in hydrogen sulfide solutions is less dependent on temperature (dE_{max}/dT = 68 cal/deg) than is the band in solutions of the alkali metals (Figure 2). Although Beer's law is obeyed by the alkali metal sulfide solutions below their solubility limits, a marked negative deviation is observed for solutions of hydrogen sulfide (Figure 3).

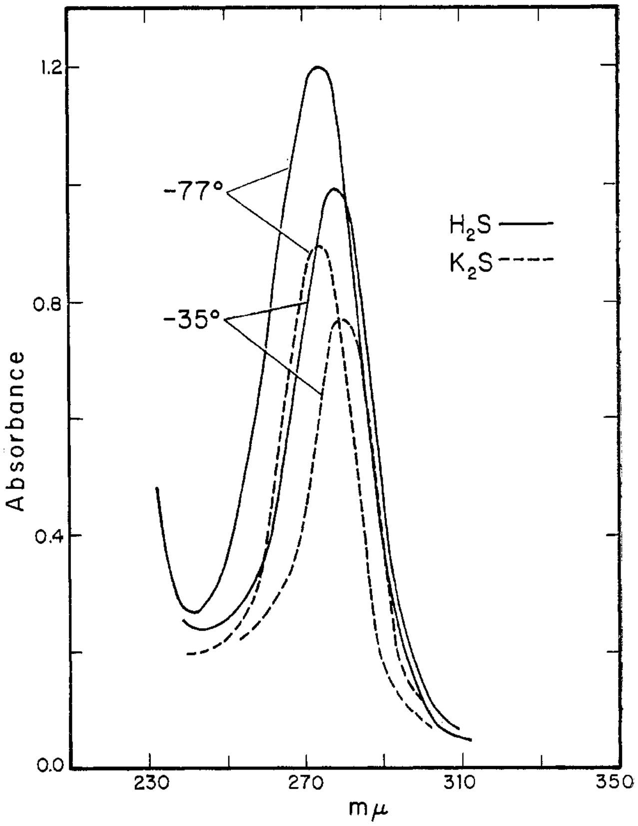

Figure 1.—Absorption spectra of H_2S and K_2S in liquid ammonia at −77 and −35°.

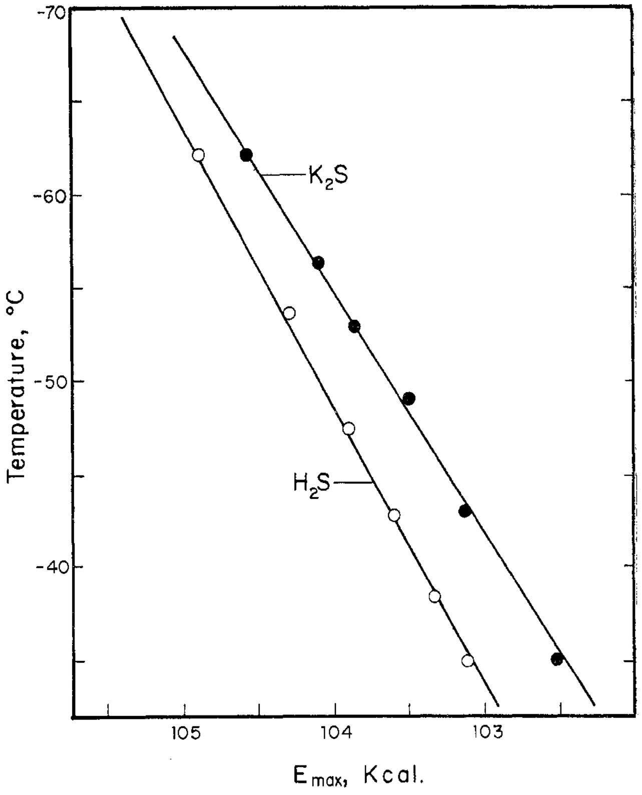

Figure 2.—Temperature dependence of the absorption bands for H_2S and K_2S in liquid ammonia.

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(8) J. T. Nelson and J. J. Lagowski, *J. Phys. Chem.*, **70**, 1492 (1966).
(9) M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, **54**, 338 (1958).

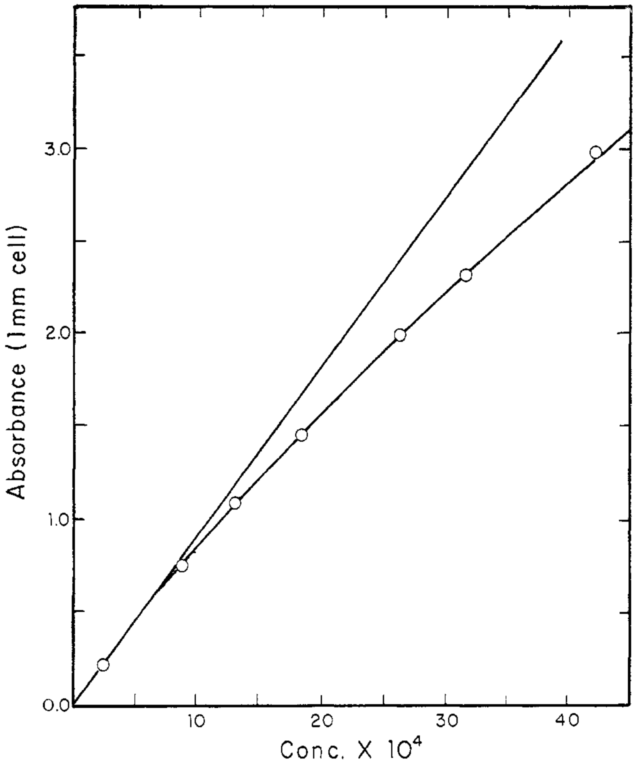

Figure 3.—Beer's law plot for solutions of H_2S in liquid ammonia at 271 mμ (−77°).

Discussion

One of the more important features of the spectra of the alkali metal sulfides is the absence of the charge-transfer-to-solvent band associated with the amide ion at 325 mμ,[10] indicating that the sulfide ion does not undergo ammonolysis to an appreciable extent (eq 1),

$$S^{2-} + NH_3 \rightleftarrows HS^- + NH_2^- \qquad (1)$$

in contrast with the extensive hydrolysis of this species in aqueous solutions. These results indicate that the band at 270 mμ arises from the presence of sulfide ion rather than hydrosulfide ion. Under the conditions of these experiments it would be possible to detect the presence of ~2×10^{-5} M amide.

The deviation from Beer's law for solutions of H_2S suggests that the absorbing species is involved in an equilibrium process. It might be expected that H_2S, SH^-, and S^{2-} would be the only sulfur-containing species present in dilute solutions of hydrogen sulfide in ammonia[11] and that these would be related by eq 2 and 3, which represent the stepwise ionization of H_2S.[12]

$$H_2S + NH_3 \rightleftarrows HS^- + NH_4^+ \qquad (2)$$

$$HS^- + NH_3 \rightleftarrows S^{2-} + NH_4^+ \qquad (3)$$

Although the existence of other sulfur-containing species might be possible in this system, the spectroscopic observations are consistent with the presence of only the species indicated in eq 2 and 3. Indeed, other data presented here suggest that a form of eq 2 is sufficient to describe the equilibrium established in these solutions.

If an appreciable fraction of hydrogen sulfide existed in the molecular form in these solutions, it might be expected that some gaseous H_2S would be present in the system in equilibrium with the dissolved molecules. Mass spectroscopic analysis of the gases above the solutions proved the absence of gaseous H_2S, even above the boiling point of this substance (−61.8°), indirectly suggesting that the concentration of dissolved molecular H_2S is small compared to the ionized forms of this substance (*vide infra*).

The reactions of liquid ammonia solutions of H_2S with potassium and/or potassium amide were studied spectrophotometrically using the shoulder of the electron band at ~1500 mμ which gives potassium solutions their blue color,[6b] the band at 325 mμ characteristic of the amide ion,[10] and the band at 270 mμ to follow the concentration of the species in these reactions. The results of these experiments are surprising in that only 1 g-atom of potassium reacts with 1 mole of H_2S, the excess potassium giving the solution the characteristic blue color of solvated electrons; such solutions can be boiled for several hours without discharging the color. The addition of potassium metal to a solution of H_2S leads to a slight increase (~6%) in the intensity of the band at 270 mμ. On the other hand, 2 moles of potassium amide react with 1 g-atom of H_2S with the concomitant formation of a white precipitate (K_2S) during the addition of the second mole of potassium amide. The addition of 1 mole of potassium amide followed by the addition of 1 g-atom of potassium to a solution containing 1 mole of H_2S results only in a blue solution; further addition of 1 mole of potassium amide to this mixture yields a blue solution and a white precipitate (K_2S). However, the addition of 1 g-atom of potassium to 1 mole of H_2S, *followed* by 1 mole of potassium amide, yields a colorless solution containing a white precipitate. It is interesting to note in this respect that the conductometric titration of H_2S with KNH_2 in liquid ammonia shows only one sharp inflection, whereas potentiometric titration data on the same system show the two stages of dissociation of H_2S.[13] The spectrophotometric results were confirmed by titrimetric studies involving the same reagents. Furthermore, it was observed that the addition of a large excess of potassium bromide to a solution of hydrogen sulfide did not precipitate K_2S. These results suggest that one of the two hydrogen atoms associated with sulfur in H_2S is bonded differently from the other. The first hydrogen ion is apparently almost completely ionized and exists as NH_4^+ in solution; however, the second does not appear to be as readily available for reaction. The absence of a precipitate upon the addition of a large excess of potassium ions to solutions of H_2S suggests that there are no free sulfide ions present as such, although the species appears to be related to the sulfide ion, a conclusion which finds support in the similar spectroscopic charac-

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[10] R. E. Cuthrell and J. J. Lagowski, submitted.

[11] L. Scheflan and C. R. McCrosky, *J. Am. Chem. Soc.*, **54**, 193 (1932).

[12] For simplicity, the question of association of ionic species has been excluded from these arguments (see ref 6a).

[13] P. W. Shenk, *Angew. Chem. Intern. Ed. Engl.*, **5**, 557 (1966).

teristics of the sulfur-containing species present in solutions of K_2S and H_2S. The data suggest that the species in H_2S solutions which absorbs at 270 mμ is probably a sulfide ion hydrogen bonded to an ammonium ion, *i.e.*, $S^{2-}\cdots HNH_3^+$. However, this species probably would not be distinguishable from a hydrosulfide ion hydrogen bonded to ammonia, $SH^-\cdots NH_3$, and the species at equilibrium in solutions of hydrogen sulfide are related through equilibrium 4 which is related to eq 2.

$$H_2S + 2NH_3 \rightleftharpoons [SHNH_3]^- + NH_4^+ \qquad (4)$$

In contrast, the sulfur-containing species in solutions of K_2S can only be hydrogen bonded to solvent molecules, since the sulfide ion is apparently not a sufficiently strong base to remove successfully a proton from the solvent (*cf.* the absence of an NH_2^- band in these solutions).

The negative deviation of solutions containing H_2S from Beer's law would be expected if the species in eq 4 are at equilibrium. Under these conditions, an increase in the formal concentration of hydrogen sulfide would cause the point of equilibrium in eq 4 to shift toward the products with a corresponding decrease in the fraction of sulfur in the form of $[SHNH_3]^-$. Using the extrapolated value of the molar extinction coefficient for the sulfide ion at the band maximum (ϵ 9.14×10^3) to estimate the fraction of sulfur in the $[SHNH_3]^-$ form and assuming that concentrations can be substituted for activities in dilute solution, the equilibrium constant for eq 4 at −77°, expressed in the standard manner, can be estimated from the data in Figure 3 as $(1.04 \pm 0.19) \times 10^{-2}$. In aqueous solutions the first and second ionization constants for H_2S are 9.5×10^{-8} (25°) and 1.0×10^{-14} (20°), respectively,[1c] and an increase in the value of K_1 in liquid ammonia would be expected on the basis of an increase in the basicity of the solvent.

The apparent anomaly of solvated electrons being less reactive than amide ions with respect to the "second hydrogen ion" in H_2S is probably related to the fact that the solvated amide ion is more similar structurally to the solvent than is the solvated electron and therefore does not require a reorganization of its solvent sphere before reacting with the species $S^{2-}\cdots HNH_3^+$.

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The Preparation, Isomerization, and Oxidation of Silylhydrazines[1]

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The reaction of 1,2-bis(dimethylchlorosilyl)ethane with hydrazine affords both 3,3,6,6-tetramethyl-1,2-diaza-3,6-disilacyclohexane (III) and 1-amino-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (IV). It has been shown that III and IV are in equilibrium at room temperature in the absence of added catalysts. The thermal equilibration of 1,1- and 1,2-bis(trimethylsilyl)hydrazine has similarly been demonstrated. The oxidations of III and IV, and 1,1- and 1,2-bis(trimethylsilyl)hydrazine, with mercuric oxide and with ethyl azodicarboxylate have been investigated. The various oxidation products have been identified and their formation rationalized by invoking oxidation at both silicon and hydrogen.

Established methods for preparing small-ring compounds containing both carbon and silicon have utilized metal reduction of an appropriate α,ω-dihalide to effect ring closure.[2] Because of the limitations of this approach,[3] a study of alternative methods of ring closure appeared to be desirable. A particularly useful method for obtaining highly strained cyclic hydrocarbons[4,5] has involved the oxidation of cyclic hydrazines followed by mild pyrolytic elimination of the resulting azo group. We have been interested in whether this scheme might be adapted to the preparation of cyclic carbosilanes. The reported[6] oxidation of bis(trimethylsilyl)hydrazine to hexamethyldisilane would indicate that the oxidative elimination of the hydrazo group is applicable to the preparation of acyclic silicon derivatives. Unfortunately, despite the considerable interest in silicon–hydrazine chemistry,[7] there are no suitable examples of monocyclic silylhydrazines which contain the NH–NH function.[8] Thus it became necessary for us to investigate the synthesis of such compounds before proceeding to study their oxidation.

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(8) For the single example of a monocyclic silylhydrazine containing (two) NH–NH groups, see H. Niederprüm and U. Wannagat, *Z. Anorg. Allgem. Chem.*, **311**, 270 (1961).