changes from sp^3 in germane to something close to p^3 in GeH_3^-. One would expect that the various contributions to chemical shift in isoelectronic species would be similar, and it is found that the chemical shifts of GeH_3^- and AsH_3 are almost equal.

It is interesting to compare the effect of substitution of methyl groups upon the shift of the X–H protons as the structure of the molecule changes. On going from germane to methylgermane, the germanium hydrogens are deshielded by 0.24 ppm; for arsine the deshielding is 0.92 ppm; for the germyl ion, 1.20 ppm; and for AsH_2^-, 1.65 ppm. Substitution of a second methyl group has a similar though smaller effect. The values are 0.21, 0.44, and 0.79 ppm for CH_3GeH_3, CH_3AsH_2, and $CH_3GeH_2^-$, respectively. Thus, the more crowded the X–H protons, the greater the effect of methyl substitution in shifting the X–H resonance to lower field. This crowding is also apparent in the shifts of the alkyl protons. The methyl resonance of the methylgermanes shifts ~0.3–0.4 ppm to higher field upon ionization, the negative charge on the anion causing an increased shielding. Little change in chemical shift in the CH_3 protons occurs upon ionization of methylarsine, while for dimethylarsine the methyl protons actually experience a lower shielding in the anion. The effect of the negative charge is completely counteracted by an anisotropic contribution arising from the crowding together of the methyl groups. Harvey and Wilson[19] have recently shown that in CH_3AsH_2 the C–As–H angle is 94°.

Spin–Spin Coupling.—The effects upon spin–spin coupling in silanes, germanes, and stannanes produced by substitution of hydrogen atoms by methyl groups have been discussed.[15,20,21] The more methyl-substituted a hydride is, the less s character is diverted to the M orbitals in the M–CH_3 bonds, and the lower the H–M–C–H coupling constant is. We find that substitution by ethyl groups also reduces $J_{\mathrm{H-Ge-C-H}}$, although the effect is much smaller. This same effect is observed in the anions of the germanes, as shown in Table I. While most of the data fit in with the concept of a decrease in coupling following the decrease in s character of the M–H bond, the large increase in coupling H–Ge–C–H on going from a methyl-substituted germane to the corresponding anion does not. In the germanes ionization results in a large change in hybridization of the bonding germanium orbitals, going from sp^3 to something approaching p^3. This should result in a reduction in $J_{\mathrm{H-Ge-C-H}}$ rather than the observed increase. Apparently factors other than s character are playing a considerable part in the coupling, as pointed out by Grant and Litchman.[22] It is interesting to note that while $J_{\mathrm{H-Ge-C-H}}$ increases upon ionization, $J_{\mathrm{H-Ge-C-C-H}}$ decreases. This is consistent with the three-bond coupling constant having a sign opposite to that of the four-bond coupling constant. Coupling constants J_{AX} and J_{BX} in $X(B_2A_3)_n$ compounds have been shown to have opposite signs.[23]

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Strong Hydrogen Bonds. III. Hydrogen Sulfide–Hydrosulfide Anion Interactions[1,2]

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Hydrogen sulfide reacts at low temperatures with triethylammonium hydrosulfide and with tetramethylammonium hydrosulfide to form complexes containing, respectively, 2 and 3 moles of hydrogen sulfide per mole of salt. The energy of the hydrogen bond in $HSHSH^-$ is greater than 7 kcal/mole, and possibly as large as 14 kcal/mole.

Recent studies of dilution shifts in infrared and nuclear magnetic resonance spectra of mercaptan solutions have led to the recognition of hydrogen bonds of the SHS type. These hydrogen bonds are very weak resulting in shifts of the magnitude of 20 cm^{-1} in the infrared[3] or 0.3–0.4 ppm in the nmr[4] spectra. Indeed, an nmr study of hydrogen sulfide in carbon disulfide gave no evidence of hydrogen-bond formation.[5] The purpose of this investigation was

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[1] Based on a dissertation submitted by Wilbur G. Evans in 1964 in partial fulfillment of the requirements for the degree of Doctor of Philosophy; part of a paper presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 5–10, 1964.

[2] For paper II in this series see S. A. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

[3] M. O. Bulanin, G. S. Denisov, and R. A. Pushkina, *Opt. Spectry.*, **6**, 491 (1959); *Chem. Abstr.*, **53**, 18630*h* (1959).

[4] L. D. Colebrook and D. S. Tarbell, *Proc. Natl. Acad. Sci. U. S.*, **47**, 993 (1961); see also other references cited here on SHS bonds.

[5] H. Schmidbaur and W. Siebert, *Ber.*, **97**, 2090 (1964).

to seek evidence for SHS hydrogen bonds in ion–molecule systems where it was felt that the interactions would be much stronger than those previously reported. In order to obtain an interaction between the SH^- ion and H_2S, the insertion of H_2S in the ionic lattice must not cause too much loss in lattice energy (*i.e.*, the loss in lattice energy must be less than the energy released by the formation of the hydrogen bond). This condition was found to be satisfied in the interaction of hydrogen sulfide with the alkylammonium hydrosulfides.[6]

Experimental Section

Materials.—Hydrogen sulfide, triethylamine, and a solution of tetramethylammonium hydroxide were obtained from Matheson Coleman and Bell. The hydrogen sulfide was purified after passing it through a tube containing glass beads coated with phosphorus(V) oxide by vacuum line fractionation. The triethylamine was equilibrated with phosphorus(V) oxide to remove water and any secondary amines which might have been present.

Tetramethylammonium hydrosulfide[7] was made in a vacuum line from hydrogen sulfide and a 24% solution of tetramethylammonium hydroxide in methanol. The reaction was carried out at −63.5°, at which temperature all chemicals were initially liquids. The excess alcohol and hydrogen sulfide were removed under vacuum, allowing the temperature to rise slowly to room temperature. Heating was continued, raising the temperature in 5° increments until 95° was reached and a pressure of less than 10^{-5} mm attained. Tetramethylammonium hydrosulfide is hygroscopic and sensitive to air oxidation to give sulfur and polysulfides.

Temperature–composition phase diagrams were obtained using techniques similar to those previously described for handling hydrogen bromide and hydrogen iodide[8] except that Apiezon N vacuum grease was used to lubricate the stopcocks.

Results and Conclusions

Triethylammonium hydrosulfide was prepared by the reaction of hydrogen sulfide on triethylamine at 0°. The 0° pressure–composition isotherm is given in Figure 1 and shows that at this temperature only $(C_2H_5)_3NHSH$ forms at H_2S pressures up to 1 atm.[9] At −78.5°, two additional moles of H_2S may be reversibly absorbed. The −78.5° isotherm is also shown in Figure 1. The slight increase in pressure over the composition range of 1:1–2:1 moles of H_2S/mole of $(C_2H_5)_3N$ indicates the formation of a solid solution. The plateau between mole ratios of 2:1 and 3:1 indicates the coexistence of two solid phases in this region. The variation of this plateau pressure with temperature was found to be as follows: −45.5°, 49.119 cm; −50.0°, 33.625 cm; −63.5°, 12.729 cm; and −78.5°, 3.590 cm. From these data an enthalpy change of −7.0 kcal may be calculated for the reaction

$$(C_2H_5)_3NHSH\cdot H_2S(s) + H_2S(g) \longrightarrow (C_2H_5)_3NHSH\cdot 2H_2S(s) \qquad (1)$$

It may be noted here that an enthalpy change of identical magnitude has been observed for the closely similar reaction[8] shown in eq 2.

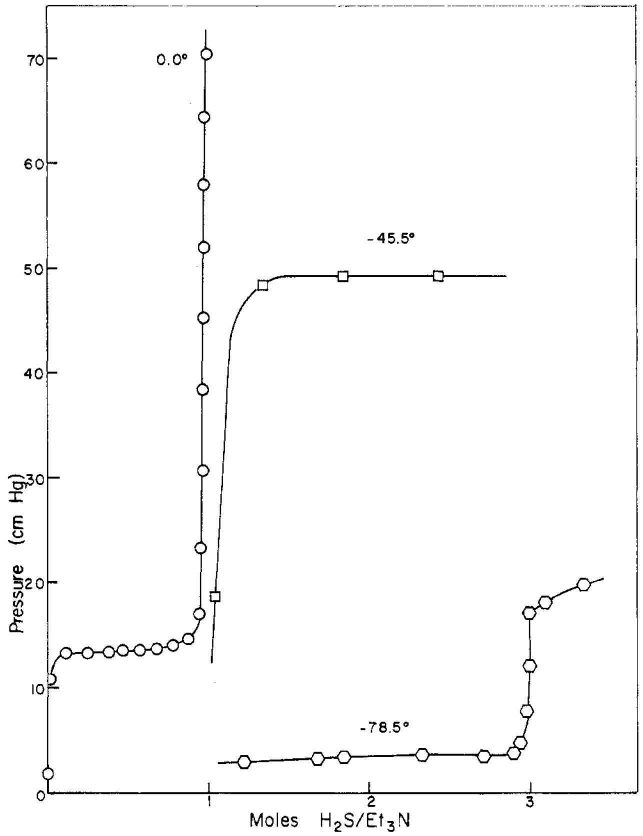

Figure 1.—Pressure–composition isotherms for the system triethylamine–hydrogen sulfide.

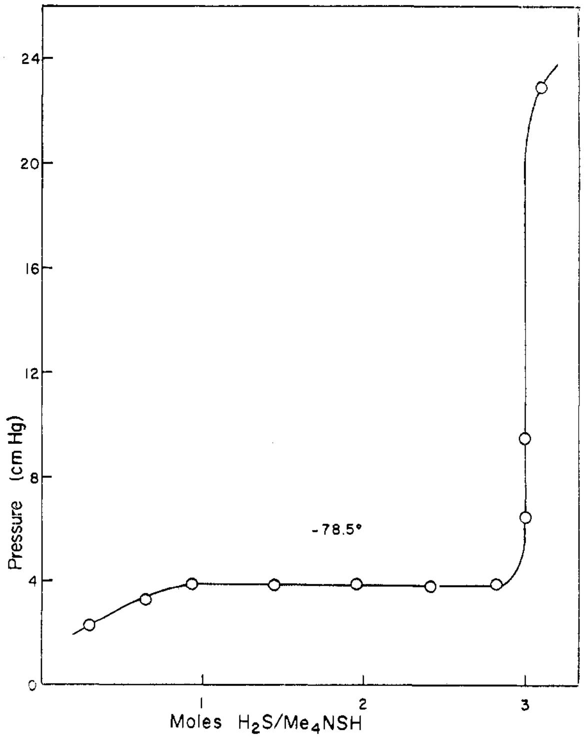

Figure 2.—Pressure–composition isotherm for the system tetramethylammonium hydrosulfide–hydrogen sulfide.

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[6] J. D. Cotton and T. C. Waddington have very recently reported the preparation of a series of tetraalkylammonium hydrosulfides and noted the low-temperature formation of hydrogen sulfide adducts; the hydrogen energy was estimated to be 5 kcal/mole: *J. Chem. Soc., Sect. A*, 785 (1966).

[7] This compound was reported to have been prepared in 1888, but was probably not prepared in anhydrous form: A. T. Lawson and N. Collie. *J. Chem. Soc.*, **53**, 634 (1888).

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[9] This is consistent with an earlier study of the equilibria between H_2S and $(CH_3)_2NH$ and/or $C_2H_5NH_2$ reported by J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **71**, 428 (1897).