has been studied briefly and found to behave kinetically like the *n*-alkyl lactates. Therefore, the major reactions are again probably the hydronium ion-catalyzed hydrolyses of ester linkages, the hydronium ions being provided by the organic acids formed during the hydrolysis. Thus reactions 7 and 8 are doubtless concerned in the "neutral" hydrolysis in the same way that they are in the acid hydrolysis.

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Infrared Spectra and Structure of Crystalline Ammonia Hydrates

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Recent very careful studies of the heat capacity and thermodynamic properties of $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$,[1] as well as earlier studies of the solid phases of the ammonia–water system,[2] have demonstrated that the two ammonia hydrates are well-defined compounds of exact composition.

The structure of these compounds is of some interest since they might exist either as simple hydrates or as ionic crystals. Although considerable experimental evidence exists to indicate that aqueous solutions of ammonia are only slightly ionized,[3] Hildenbrand and Giauque regard the crystalline hydrates as ammonium salts, *i.e.*, $(NH_4)OH$ and $(NH_4)_2O$.

No previous spectroscopic studies of the solid phases of the NH_3–H_2O system were uncovered in a survey of the literature although the infrared and Raman spectra of aqueous ammonia[4,5] have been obtained.

In the present study mixtures of NH_3 and H_2O vapor were admitted to a low temperature infrared cell[6] and condensed on NaCl or KBr plates cooled with liquid nitrogen. The spectra obtained were consistent with an ammonia hydrate structure and definitely exclude an ionic structure.

Results

Figure 1 shows the spectra obtained for mixtures of NH_3 and H_2O at −195°, together with those of pure NH_3, H_2O and NH_4X for comparison. It is immediately clear that the spectra bear little resemblance to that of the NH_4^+ ion, and the absence of the NH_4^+ ion bending vibration at about 1400 cm.$^{-1}$ is conclusive. On the other hand, they closely parallel the spectra of crystalline NH_3 and H_2O, although there are some clear differences.

The interpretation of the low frequency region of the spectrum is most obvious. The strong ice band at 812 cm.$^{-1}$[7] appears in the spectrum with excess H_2O (A) but not in (B) or (C), so that the H_2O in the compounds is included in a lattice different from ice. If the 812 cm.$^{-1}$ band is a lattice vibration connected with the torsional oscillations of the H_2O molecules, the H_2O molecules cannot be as tightly bound in the hydrates as in ice; *i.e.*, one of the O–H · · · O bonds must have been replaced by an O–H · · · N bond. The symmetrical bending vibration of ammonia, which occurs at 1060 cm.$^{-1}$ in the pure crystal,[8] appears at 1102 cm.$^{-1}$ in $NH_3 \cdot H_2O$ (B) and as a doublet, 1020 and 1091 cm.$^{-1}$, in $2NH_3 \cdot H_2O$ (C). The doubling probably indicates that the environment of the two NH_3 molecules is not identical. Excess NH_3 (D) produces an additional shoulder at 1069 cm.$^{-1}$ which may be identified as free NH_3.

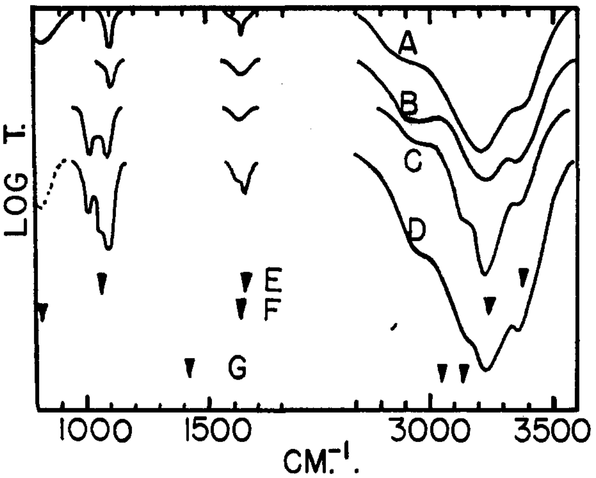

Fig. 1.—Infrared spectra of crystals of the NH_3–H_2O system at −195° together with comparison spectra: A, $NH_3 \cdot H_2O + H_2O$; B, $NH_3 \cdot H_2O$; C, $2NH_3 \cdot H_2O$; D, $NH_3 + 2NH_3 \cdot H_2O$ (some frost formation entailed by a small vacuum leak); E, crystalline NH_3; F, Ice; G, ammonium ion.

Both the bending vibration of H_2O and the doubly degenerate bending vibration of NH_3 may contribute to the absorption near 1625 cm.$^{-1}$. However, since the symmetric bending vibration is far more intense than the degenerate one in both gaseous and crystalline NH_3, it does not seem likely that very much of the observed absorption in this region is caused by NH_3.

The stretching region cannot be analyzed so straightforwardly. The peak at 2950 cm.$^{-1}$ occurs in the spectrum of both hydrates but is relatively more intense in that of $NH_3 \cdot H_2O$ (B). It is probably too low in frequency to be ascribed to OH, since only acidic OH in very strong H-bonds absorbs at so low a frequency, and then only rarely. Similarly, NH · · · N bonds would probably not lead to such a low frequency, leaving an NH · · · O bond as the most likely explanation for this band. If this is correct, it seems likely that in $2NH_3 \cdot H_2O$ only one of the ammonia molecules is involved. The peak at 3140 cm.$^{-1}$ (C) belongs to $2NH_3 \cdot H_2O$ and may represent a weaker NH · · · O bond from the second NH_3 molecule.

The remaining peaks at 3220 and 3365 cm.$^{-1}$ are characteristic of hydrogen bonded O–H and N–H vibrations and cannot be assigned in detail. Although some of the 3220 cm.$^{-1}$ absorption in A is

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undoubtedly caused by ice and some of the 3365 cm.$^{-1}$ absorption in D by ammonia, it should be noted that the addition of NH_3 in passing from B to C increases the relative intensity of the 3220 cm.$^{-1}$ peak. It follows therefore that NH_3 also absorbs in this region.

Structural Conclusions

It seems clear that neither hydrate of ammonia contains ammonium ions. In addition to the reasons previously outlined, the presence of NH_4^+ ion would imply OH^- or O^{--} ions. In the former case a frequency higher than any observed would be expected (OH^- absorption occurs at 3638 cm.$^{-1}$ in NaOH[9]); in the latter there is no explanation for the two highest frequencies.

$NH_3 \cdot H_2O$ is a bimolecular crystal. There are five H atoms and only three unshared electron pairs per mole, so at least two H atoms must be either nonbonded or very weakly bonded. If, as in crystalline NH_3, three weak hydrogen bonds are formed to the single electron pair of NH_3, only two strong bonds can be formed. From the spectrum it can be concluded that a strong NH · · · O bond is formed (2.8 Å. or less from the magnitude of the frequency shift observed) and that both hydrogens from H_2O are involved in at least weak hydrogen bonds (since free H_2O absorbs near 3700 cm.$^{-1}$). This implies at least one O–H · · · N bond.

$2NH_3 \cdot H_2O$ is a trimolecular crystal. The two NH_3 molecules appear to be non-equivalent. The structure includes at least one strong NH · · · O bond and all of the hydrogens from H_2O are hydrogen bonded.

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A New Reaction of Organogermanium Compounds

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Among organometallic compounds, those of arsenic have long been considered to be unique in that primary and secondary derivatives can be reduced to mono- or dialkylarsines, $RAsH_2$ or R_2AsH, by zinc and hydrochloric acid.[1] We have found that organogermanium compounds can be reduced to the corresponding hydrides under similar conditions. This reaction is interesting since all attempts to reduce organotin or organosilicon compounds to the hydrides in the same way have been unsuccessful. Thus a solution of triphenylgermanium bromide, when treated with amalgamated zinc and aqueous HCl, is readily reduced to triphenylgermane. The product can be identified easily by the strong Ge–H fundamental stretching vibration at 2400 cm.$^{-1}$ in the infrared spectrum.[2] However, under similar conditions triphenyltin chloride or iodide gave no material showing Sn–H absorption (at 1870 cm.$^{-1}$)[3]; and diphenyldichlorosilane and triphenylchlorosilane gave no products showing Si–H absorption (at 2100 cm.$^{-1}$).[4]

The reduction of organogermanium compounds to hydrides in this way parallels the known reaction of inorganic germanium compounds with alkali and aluminum, in which small amounts of GeH_4 are formed.[5] The reason for the anomalous easy formation of Ge–H bonds in reductions of this type is not known, but it is interesting to note that such reduction is consistent with Sanderson's recent conclusion that germanium is actually more electronegative than either silicon or tin.[6] The evidence found by Johnson and Harris for the metalation of triphenylgermane by phenyllithium[7] is another possible indication of abnormally high electronegativity for germanium.

Experimental

Triphenylgermane.—To 15 g. of amalgamated zinc dust was added 2 g. of triphenylgermanium bromide[8] dissolved in 100 ml. of 1:1 ethanol–ethyl ether. Over two hours, 50 ml. of 12 *N* aqueous HCl was added, with occasional stirring. The solution was then decanted and partitioned between water and ether; the organic layer was washed with water, dried and evaporated to give 0.6 to 1.0 g. of oily material, principally triphenylgermane. This crude product contained about 15% of tetraphenylgermane, m.p. 230°, which could be obtained by washing with methanol.

Crude triphenylgermane from two such runs was passed through an alumina chromatographic column in cyclohexane solution; the cyclohexane was then evaporated and the residual oil was crystallized from methanol to give 0.5 g. of triphenylgermane as transparent hexagonal plates of the β-form, m.p. 27°.[7,8] The infrared absorption spectrum in chloroform solution showed bands at 4200, 3030, 2040, 1950, 1880, 1818, 1726, 1610, 1490, 1433, 1382, 1338, 1308, 1260, 1098, 1068, 1027 and 1002 cm.$^{-1}$.

Further elution of the chromatogram with 1:1 benzene-chloroform gave 0.3 g. of solid material, m.p. 130°, probably triphenylgermanol.[8]

Dimethylgermane.—To 20 g. of amalgamated zinc dust was added 4.0 g. of dimethylgermanium sulfide[9] dissolved in 50 ml. of ethanol. Over 1 hour, 50 ml. of 12 *N* HCl was added. The gaseous products were condensed in a trap held at −78°. The contents of the trap (dimethylgermane, ethanol and hydrogen sulfide) were separated by bulb-to-bulb distillation on a vacuum chain to give 0.2 g. of dimethylgermane; mol. wt. calcd. 105, found 97, 99 (vapor density). The gas had strong infrared absorption bands at 2985 (C–H), 2060 (Ge–H) and 844 cm.$^{-1}$ (Ge–C), as well as weaker bands at 898 and 882 cm.$^{-1}$.

A similar reaction was carried out using methylgermanium trichloride instead of dimethylgermanium sulfide. No methylgermane was found in the trap, which was held at −120° during the reaction.

Attempted Reduction of Tin and Silicon Compounds.—These reactions were carried out similarly to the reduction of triphenylgermanium bromide, except that the crude products were not chromatographed. Diphenyldichlorosilane and triphenylchlorosilane were treated with amalgamated zinc and gaseous HCl in absolute ethanol to prevent irreversible hydrolysis. The only compounds found in the products from these reactions were diphenylsilanediol and triphenylsilanol, respectively.

Triphenyltin chloride and iodide were treated in the same way as triphenylgermanium bromide, except that the reactions were carried out under nitrogen to prevent any oxida-

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