AgCl.[3] Strong absorptions from $ClSi_2H_5$,[3] 1,1,2-$Cl_3Si_2H_3$,[3] Cl_3SiH,[17] or $SiCl_4$[18] were absent from the infrared spectrum of the 1,2-Cl_2SiH_4. However, the infrared spectrum demonstrated that some (about 10%) 1,1-$Cl_2Si_2H_4$[3] was present.

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The Acidities of Some Aryl-Substituted Germanes in Liquid Ammonia

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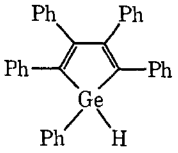
Proton magnetic resonance techniques have been used to determine the acidities of some aryl-substituted germanes in liquid ammonia. It was found that increasing aryl substitution caused a reduction in acidity. Factors such as solvation, ion pairing, and structural effects are used to explain the order of acidities.

Introduction

Although there has been much interest in the acidities of hydrocarbons and the establishment of an acidity scale,[1-3] there is very little information on the analogous hydrides of the other group IV elements. Preliminary work has shown that germane is more acidic than triphenylgermane in liquid ammonia.[4] This is very different behavior from the carbon case where aryl substitution markedly increases acidity by both inductive and resonance effects.[5] The only quantitative study of which we are aware has been carried out by Curtis,[6] who compared the acidity of triphenylgermane with 1,1,3-triphenylpropene in dimethyl sulfoxide. He also showed that pentaphenylgermacyclopentadiene (I) is several orders of magnitude more acidic than triphenylgermane but was unable to obtain an accurate measurement of their relative acidities.



I

We have measured the acidities of some arylgermanes relative to each other and to some hydrocarbon indicators, in liquid ammonia by an nmr method which has already been described.[7] These acidities are discussed in terms of structural and solvation effects upon the acids and their anions.

Experimental Section

Chemicals.—Ammonia was obtained commercially, dried, and stored over sodium metal at −78° until required. Germane, phenylgermane, and di- and triphenylgermanes were prepared and purified as described in the literature.[8-10]

Tri-*p*-tolylgermane (mp 81°, lit.[11] mp 81°) was prepared from *p*-tolylmagnesium bromide by the procedure outlined for triphenylgermane.[11]

Triphenylpropene.—This was prepared by treating phenethylmagnesium bromide with benzophenone to give the alcohol which was subsequently dehydrated with H_2SO_4–CH_3COOH. The product was distilled [210° (0.8 cm)[12]] to yield a mixture of the 1,1,3-triphenylprop-1-ene and 1,3,3-triphenylprop-1-ene isomers. Nmr showed that the 1,1,3 isomer predominated.[13] No attempt was made to separate these isomers since they both yield the same anion upon ionization. Indene was distilled, and fluorene was recrystallized before use.

The purity of all compounds was checked by melting or boiling points and in addition by one or more of nmr, infrared spectroscopy, and mass spectroscopy.

Acidity Measurements.—The method of sample preparation for the acidity measurements has been described previously.[7] For acids and anions of group IV elements, proton exchange is slow on the nmr time scale so that the nmr spectra observed in any one determination consisted of the superimposed spectra of the two acids being compared, their corresponding anions, and the intense ammonia triplet. Fortunately it was possible to choose pairs of acids such that each species present had at least one clearly assignable proton resonance. The relative areas of these absorptions were, in most cases, measured by electronic integration. Occasionally, however, the resonance of interest occurred close to the ammonia triplet preventing electronic integration. In such cases the peak profiles were cut out and the relative areas estimated by accurately weighing the paper profiles. The solutions used were approximately 0.5 *M* in each acid–anion pair.

The nmr samples of lithium, sodium, and potassium germyls were prepared by condensing 2 equiv of germane onto 1 equiv of alkali metal dissolved in ammonia, sealing the nmr tube, and allowing reaction to take place by warming to room temperature. The cesium salt was prepared by treating germane with cesium hydroxide in liquid ammonia. In all cases the excess germane present buffered the solution so that a sharp ammonia triplet was observed. The buffering action controls the [NH_4^+] which has been shown to cause collapse of the ammonia triplet in solutions of water and other acids in liquid ammonia.[14] These solutions were ~0.4 *M* in both GeH_4 and $MGeH_3$.

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Results and Discussion

The results of our relative acidity measurements are summarized in Table I. For ease of comparison the results are also shown as "absolute" acidities, assuming fluorene to have a pK_a of 20.6. The hydrocarbon indicators which we have used are those commonly employed in similar determinations in other solvents, such as dimethyl sulfoxide (DMSO)[2,3] and cyclohexylamine.[1] We have adjusted the pK_a's determined in cyclohexylamine to refer to that of 9-phenylfluorene having pK_a = 16.4[3,15] and have also included these values in Table I. One notes that there is quite good agreement between the relative acidities in the various solvents. This serves as a check on the reliability of the nmr method for carrying out measurements of this kind, since the relatively concentrated solutions render suspect the assumptions made concerning the ratios of activity coefficients.[16] Two unusual features are apparent in the acidities of the germanes studied. First, there is a decrease in acidity as the number of phenyl groups is increased, and, second, substitution by only one ethyl group dramatically reduces the acidity by ~10^6.

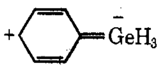
TABLE I

DATA FOR LIQUID NH_3 AT +30°

Acid	+Log {[HB][A^-]/ [HA][B^-]}	pK_a referred to fluorene pK_a = 20.6[a]	pK_a in $C_6H_{11}NH_2$[1] referred to 9-phenylfluorene pK_a = 16.4[3,15]	pK_a in DMSO[2,3]
Indene		17.4	18.1	18.5
	0.3 ± 0.1			
GeH_4		17.7		
	2.1 ± 0.2			
$C_6H_5GeH_3$		19.8		
	0.8 ± 0.1			
Fluorene		(20.6)	20.7	20.5
	0.8 ± 0.1			
$(C_6H_5)_2GeH_2$		21.4		
	1.7 ± 0.2			
1,1,3-Triphenylpropene		23.1	24.3	23.1
	0.1 ± 0.1			
$(C_6H_5)_3GeH$		23.2		23.0[6]
	0.4 ± 0.1			
(p-$CH_3C_6H_4)_3GeH$		23.6		
	0.3 ± 0.1[4]			
$C_2H_5GeH_3$		23.9		

[a] Fluorene pK_a = 20.6 was chosen as our standard because of agreement between DMSO and cyclohexylamine measurements. Direct measurement of 9-phenylfluorene in DMSO[2] was used as the standard for establishing pK_a for fluorene.

A previous investigation of the relative acidities of germane and triphenylgermane by Birchall and Jolly[4] showed triphenylgermane to be the weaker acid, but these workers underestimated the acidity difference by a factor of ~10^4. They suggested that the reduction in acidity was the result of multiple bonding between the aromatic π system and the empty germanium d orbitals. However, proton magnetic resonance studies[17] have shown that perturbation of the π-electron system of the aromatic ring in phenylgermane is very small. The extent of pπ → dπ bonding contributions such as II would have to be large to cause the large reduction in acidity and such perturbations would have been easily detected by nmr. In the case of similar substitution in methane,[18] the acidity increases with increasing number of phenyl groups. This increase in acidity is due to the extensive delocalization of the negative charge in the anion and the inductive effect of the phenyl group. Delocalization does not occur in the phenylgermyl anion[17] and hence no increase in acidity would be expected through resonance, though one might have expected an increase due to the inductive effect.[19,20] No such increase in germane acidities is noted (Table I). Clearly some other factor must be causing the order observed.



II

A recent reevaluation of the Chatt–Williams experiments on the acidity of silyl, germyl, and other substituted benzoic acids[21] has shown[22] that solvation effects are important. These workers found that unless solvation effects are constant, as reflected in the entropy of ionization $\Delta S°$, conclusions concerning electronic effects obtained from $\Delta G°$ of ionization (*i.e.*, the pK_a of the acid) will not be valid. We believe that solvation effects will be important in the systems studied here. One would expect a reduction in the solvation energy of the phenylgermyl anion, compared to the germyl ion, due to the bulky nature of the phenyl group, and a subsequent reduction in acidity as a result of this. Introduction of additional phenyl groups into the germane should further decrease the solvation energy and produce a still weaker acid. However the greatest effect should be produced by the first phenyl group, and subsequent substitution might have been expected to produce successively smaller reductions in acidity. The data in Table II reveal that while this is true for the first two members of the series, triphenylgermane is weaker than would have been expected. It seems reasonable to attribute this further reduction in acidity of triphenylgermane to steric crowding in the triphenylgermyl anion. We have shown[23,24] that the H–Ge–H bond angle is reduced from 109° 28′ in GeH_4 to ~93° in GeH_3^- indicating that the lone pair of the anion has a considerable stereochemical influence. Such a C–Ge–C bond angle in the triphenylgermyl anion would be resisted by the bulky aromatic rings and such crowding could be relieved by protonation.

TABLE II

Compd	GeH_4		$C_6H_5GeH_3$		$(C_6H_5)_2GeH_2$		$(C_6H_5)_3GeH$
ΔpK		2.1		1.6		1.8	

The much lower acidity of ethylgermane compared to that of phenylgermane can be attributed to the inductive effects of the phenyl and ethyl groups. In the case of phenylgermane the inductive effect opposes the acidity-reducing solvation effects discussed above,

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while in the case of ethylgermane these two effects reinforce one another.

All of our measurements have been carried out using sodium salts of the acids. Streitwieser, *et al.*, have noted[25] that the counterion affects the acidity of certain compounds in cyclohexylamine solution. Burley and coworkers[26] have used nmr methods to obtain information about ion pairing in solution of alkali metal salts. Table III presents some nmr data which we have obtained for solutions of germane and its alkali metal salts. The chemical shifts are reported relative to the solvent ammonia, and one notes that while the shift of the germane peak is constant, that for the germyl ion is dependent upon the cation. The lithium, sodium, and potassium salts have the same shift relative to germane whereas the cesium salt has a chemical shift to lower field. We conclude that this is because $Cs^+GeH_3^-$ exists as a contact ion pair in ammonia solution but that the other salts exist as solvent-separated ion pairs. By analogy to Streitwieser's systems[25] we expect that the use of the cesium instead of the sodium salt would cause the acidity of the germanes, in which the anions have a localized charge, to increase relative to the hydrocarbons. However we would not expect to change the acidity of the germanes relative to each other.

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TABLE III[a]

Alkali metal cation	$\delta(GeH_3^-)$, ppm	$\delta(GeH_4)$, ppm	Alkali metal cation	$\delta(GeH_3^-)$, ppm	$\delta(GeH_4)$, ppm
Li^+	−0.38	−2.40	K^+	−0.42	−2.43
Na^+	−0.42	−2.43	Cs^+	−0.50	−2.40

[a] Values ±0.02 ppm relative to center peak of NH_3 triplet. Solutions ~0.4 *M* in both GeH_4 and salt.

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Reactions of Borane (BH_3). IV. The Absolute Rate of Reaction with Acetone

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The reaction of free borane (BH_3) with acetone to produce an adduct having a mass corresponding to BC_3H_9O has been shown to occur in the gas phase. At 450°K, 4.6 Torr total pressure of helium, and low partial pressures of reagents, the absolute bimolecular rate constant for this reaction is 3×10^8 l./mol sec. It is likely that the observed product of the reaction between BH_3 and acetone is a Lewis acid–base adduct rather than an alkoxyborane.

It has been suggested that the reactivity of tricoordinate boron compounds is controlled by two factors: the acceptor strength of the boron species and the ease of ligand displacement or rearrangement.[1] These principles follow if the reactions expected for a tricoordinate boron species, BX_3, may be written in general as

$$X_3B + :YL_p \longrightarrow X_3B:YL_p \qquad (1)$$

$$X_3B:YL_p \longrightarrow X_2BYL_{p-1} + XL \qquad (2)$$

$$X_3B:YL_p \longrightarrow X_2BYXL_p \qquad (3)$$

where boron is attached to three, not necessarily identical, ligands X and where Y is a central atom attached to *p*, not necessarily identical, ligands L. Reaction 1 is a Lewis acid–base addition reaction; (2) is an elimination reaction which may occur when Y is saturated and at least one ligand L is hydrogen; and (3) is a rearrangement reaction which may occur when Y is unsaturated and at least one ligand X is hydrogen. These postulates certainly allow the rationalization of many of the reactions of tricoordinate boron compounds. However, to understand the factors that control the reactivity of these compounds it is necessary to probe in detail the reactions of carefully selected systems containing tricoordinate boron. We are engaged in a program of examining the reactions of the simplest tricoordinate boron species, borane (BH_3). By identifying the reactions of this species and measuring the rates, we hope more fully to document the concepts of reactivity presented above.

Our methods for producing kinetically useful quantities of BH_3 and for examining the reactions of BH_3 in the gas phase have been reported previously.[2–6] Thus far we have examined the reactions of BH_3 with BH_3,[3] PF_3,[4] $N(CH_3)_3$,[4] C_2H_4,[5] B_2H_6,[6] and B_5H_9.[6] In this report, an examination of the reaction of BH_3 with acetone, $(CH_3)_2CO$, is presented. This molecule possesses both a basic site and unsaturation. Consequently, we wished to contrast the identity and absolute rate of its reaction or reactions with BH_3 with those of the other species mentioned above.

The uses of boron hydrides in the reduction of various organic functional groups has been extensively discussed by Brown.[7] Although the reaction of BH_3

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