appropriate Taft σ^* values[15] and give $\rho^* = -0.93$. This relationship was established over only 0.3 logarithmic unit for these alkyl substituents, however, and an attempt to relate kinetic data from the ethylenediamine bisborane study would involve extrapolation to over 0.6 log unit. Data for other N-substituted primary amine boranes are required, therefore, before any reasonable correlation of these data in terms of the σ^* parameter is possible.

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[15] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 3120 (1952); **75**, 4231 (1953).

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Relative Acidities of Some Hydrides of Groups IV and V in Liquid Ammonia. Nuclear Magnetic Resonance Spectra of the Hydrides and Their Anions

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Proton magnetic resonance was used to determine the relative acidities in liquid ammonia of germane, phosphine, arsine, and some of the alkyl derivatives of these hydrides. Special features of the nmr spectra of the hydrides and their anions are discussed.

Introduction

Trends in acidity of the simple hydrides MH_x have been discussed in relation to the position of M in the periodic table,[1,2] but there are essentially no quantitative data regarding the acidities of silane, germane, stannane, arsine, and stibine. Alkali metal derivatives of these hydrides are known,[3-6] and there is evidence that AsH_3, SbH_3, and SnH_4 form disodium derivatives when they react with sodium in liquid ammonia.[4,5] There has been some recent work on the relative acidities of organophosphines and -arsines by Issleib and Kümmel.[7]

We have recently determined the relative acidities of a series of substituted anilines in liquid ammonia by using proton nmr to measure the relative concentrations of anilines and anilide ions in equilibrated systems.[8] In this study, we have applied the same method to some hydrides of groups IV and V and to some of their organic derivatives. Not only has information been obtained regarding the relative acidities of the hydrides, but also some interesting features of the nmr spectra have been observed.

Experimental Section

Chemicals.—The methyl- and ethylgermanes were prepared from commercially available halides by reduction with sodium hydroborate in acid solution.[9] Triphenylgermane was obtained by reduction of triphenylgermanium bromide with $LiAlH_4$ in ether solution.[10] Ethylmethylgermane was prepared by treatment of the sodium salt of ethylgermane with methyl chloride in liquid ammonia. Germane, arsine, and stibine were prepared according to the method of Jolly and Drake.[11] Phosphine was prepared by heating phosphorous acid to 200° and collecting the phosphine evolved.[12]

Methyl- and dimethylarsines were prepared by essentially the same method as used by Burg[13] for the corresponding phosphines. Excess arsine was distilled into a solution of sodium in liquid ammonia and the reaction between the electron and arsine allowed to go to completion at $-63°$, as evidenced by the complete discharge of the deep blue electron color. The hydrogen, excess arsine, and ammonia were then removed under vacuum at $-45°$, leaving $NaAsH_2$. Excess methyl chloride was then distilled into the reaction vessel, where reaction occurred to produce methylarsine. The product was subsequently purified by trap to trap fractionation. Dimethylarsine was prepared in a similar way from methylarsine.

The purity of all hydrides used was checked by vapor pressure measurements, infrared spectroscopy, nmr spectroscopy, and, in some cases, mass spectrometry. All volatile samples were stored in glass bulbs either as the vapor or frozen down with liquid nitrogen.

Synthetic ammonia was dried and stored over sodium in a glass vessel attached to the vacuum line until required.

Sample Preparation.—All of the hydrides were handled by standard vacuum-line techniques and distilled directly into nmr tubes containing ammonia or suspensions of sodium amide in ammonia. The sodium amide suspensions were prepared by allowing the reaction of sodium (*i.e.*, the electron) with ammonia to take place in the nmr tube in the presence of trace quantities of platinum, which accelerates the reaction.

$$Na^+ + e^- + NH_3 \longrightarrow NaNH_2 + {}^1/_2H_2$$

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[1] M. C. Day, Jr., and J. Selbin, "Theoretical Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1962, p 254.

[2] B. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry," Blaisdell Publishing Co., New York, N. Y., 1965, p 188.

[3] S. N. Glarum and C. A. Kraus, *J. Am. Chem. Soc.*, **72**, 5398 (1950).

[4] H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 2444 (1958).

[5] H. J. Emeléus and K. M. Mackay, *ibid.*, 2676 (1961).

[6] M. A. Ring and D. M. Ritter, *J. Am. Chem. Soc.*, **83**, 802 (1961).

[7] K. Issleib and R. Kümmel, *J. Organometal. Chem.* (Amsterdam), **3**, 84 (1965).

[8] T. Birchall and W. L. Jolly, to be published.

[9] J. E. Griffiths, *Inorg. Chem.*, **2**, 375 (1963).

[10] O. H. Johnson and D. M. Harris, *J. Am. Chem. Soc.*, **72**, 5566 (1950).

[11] W. L. Jolly and J. E. Drake, *Inorg. Syn.*, **7**, 34 (1963).

[12] W. L. Jolly and S. Gokhale, University of California, Lawrence Radiation Laboratory, UCRL-11177 (1963).

[13] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3869 (1953).

TABLE I

CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS FOR GERMANIUM HYDRIDES AND THEIR ANIONS

	$-\delta$, ppm, from external TMS				
Compound	Ge–H	Ge–CH_3	Ge–C_2H_5 or Ge–C_6H_5	$J_{H-Ge-C-H}$, cps	$J_{H-Ge-C-C-H}$, cps
GeH_4	2.98	...	...	...	...
GeH_3^-	0.99	...	...	...	...
CH_3GeH_3	3.22	0.19	...	4.22	...
$CH_3GeH_2^-$	2.19	−0.23	...	5.73	...
$(CH_3)_2GeH_2$	3.43	0.12	...	3.82	...
$(CH_3)_2GeH^-$	2.98	−0.16	...	4.90	...
$(C_2H_5)(CH_3)GeH_2$	3.75	0.36	1.21, 1.12	3.85[a]	...
$(C_2H_5)(CH_3)GeH^-$	2.40	−0.06	1.05, 0.94, 0.79	4.04[a]	...
$C_2H_5GeH_3$	3.26	...	0.93	2.8	0.5
$C_2H_5GeH_2^-$	2.33	...	1.16, 1.13, 1.07, 0.90	4.20	0.0
$(C_2H_5)_2GeH_2$	3.47	...	0.95, 0.89	2.73	~0.5
$(C_2H_5)_2GeH^-$	3.10	...	1.02, 0.91, 0.80	3.85	0.0
$(C_6H_5)_3GeH$	5.48	...	7.30	...	...
$(C_6H_5)_3Ge^-$	...	...	7.25, 6.83	...	...

[a] Refers to coupling with the protons of the methyl group.

The nmr tube was fitted with a break-off seal, and when the above reaction was complete, the seal was broken and the hydrogen produced was collected and measured by means of a Toepler pump. In this way the amount of sodium amide in the ammonia was accurately determined. Anion spectra were obtained by distilling into the nmr tube containing the sodium amide–ammonia mixture a quantity of hydride equivalent to that of the amide ion. The tube was sealed, the mixture allowed to come to equilibrium at room temperature, and the nmr spectrum recorded.

$$HA + NaNH_2 \longrightarrow A^- + NH_3 + Na^+$$

In comparing the strengths of two acids HA and HB, approximately equal amounts were distilled into the $NaNH_2$ suspension, the acids were allowed to compete for the amide ion, and the spectrum was recorded at equilibrium. From the spectrum the relative extents of ionization were determined, and hence the relative acidities were estimated.

The spectra were recorded on a Varian A60 nmr spectrometer at 31°. All of the solutions were approximately 0.5 *M* in the compounds being studied.

Results and Discussion

Acidities.—In our experiments with phosphines and arsines, whenever both a hydride and its anion were present together in appreciable concentrations, we were unable to observe an nmr peak attributable to the acidic proton. Presumably proton exchange between the hydride and its anion was occurring, and the exchange rate was not fast enough to collapse the signal to a line sharp enough to be observed. It is also possible that the time-averaged line was hidden by the strong absorption of the solvent protons. The solvent proton signal (a triplet because of ^{14}N coupling) was always sharp, thus ruling out the participation of ammonia in the exchange. In the case of the germanes, proton exchange between the acid and anion was slow; separate peaks for the acid and anion were visible, and it was a simple matter to determine the relative amounts by electronic integration. However we have observed a broadening of the Ge–H proton peaks in solutions containing mixtures of germane and the anions of either arsines or phosphines, indicating that the germanium protons were involved in an exchange process in these cases. In cases where the group V hydride and the germane had similar acidities so that appreciable quantities of both anions were present at equilibrium, then a combined time-averaged peak for all four species was observed. Such a situation occurred with GeH_4 and CH_3AsH_2. These two acids when added to a suspension of sodium amide in liquid ammonia showed two peaks in addition to the solvent signal. One sharp peak was due to the CH_3 protons; the other broad peak was due to GeH_4, GeH_3^-, $-AsH_2$, and $-AsH^-$ which were exchanging their protons with one another. Knowing the initial quantities of GeH_4, CH_3AsH_2, and $NaNH_2$ and the chemical shifts of the various protons involved (Tables I and II), the extent of ionization of the two acids could be calculated and hence their relative acidities determined.

TABLE II

CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS FOR PHOSPHORUS, ARSENIC, AND ANTIMONY HYDRIDES AND THEIR ANIONS

Compound	$-\delta$, ppm from external TMS			
R_nXH_{3-n}	X–H	X–C–H	J_{X-H}, cps	$J_{H-X-C-H}$, cps
PH_3	1.64	...	188.7	
PH_2^-	−1.64	...	139.3	
AsH_3	0.90[a]	...		...
AsH_2^-	−2.69	...	...	...
CH_3AsH_2	1.82	0.88	...	7.24
CH_3AsH^-	−1.04	0.85	...	6.15
$(CH_3)_2AsH$	2.26	0.93	...	6.89
$(CH_3)_2As^-$	...	1.20	...	...

[a] Obtained from the chemical shift in CCl_4 solution 1.57 ppm after correction for the differences in bulk diamagnetic susceptibility of CCl_4 and NH_3 (0.67 ppm).

The relative acidities of the acids which we have studied are given in Table III. Only for four pairs of acids were we able to obtain quantitative data; the ΔpK values for these pairs are indicated in the table.

One interesting aspect of the order of acidities is the fact that the acidity of germane lies between those of arsine and phosphine. Arsine is a much stronger acid (at least 100-fold) than germane, with no detectable overlap occurring with this pair of acids. We were also unable to obtain any quantitative data for methylarsine and phosphine, because no signal attributable to a combined arsine–phosphine proton could be de-

TABLE III

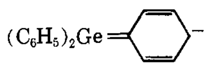
RELATIVE ACIDITIES OF HYDRIDES IN LIQUID AMMONIA

Acids[a]	ΔpK, when known
AsH_3	
GeH_4	
	0.7
CH_3AsH_2	
PH_3	
	0.3
$(C_6H_5)_3GeH$	
	0.7
$C_2H_5GeH_3$	
	0.45
CH_3GeH_3	
$(C_2H_5)_2GeH_2$	
$(CH_3)_2GeH_2$	
CH_3PH_2	

[a] Acids are listed in the order of decreasing acidity.

tected. The relative order was established by the behavior of each acid separately with sodium hydroxide in liquid ammonia. The mixture of CH_3AsH_2 and NaOH in liquid ammonia gave an nmr spectrum with a detectable peak attributable to water, whereas a corresponding solution with PH_3 and NaOH showed no such peak. The sodium hydroxide remained unreacted in the bottom of the nmr tube in this latter case. Phosphine did react to some extent with the NaOH, as evidenced by the solution having a yellow color indicative of the presence of the PH_2^- ion. Furthermore, the characteristic doublet of PH_3 was no longer visible in the nmr spectrum. Probably CH_3AsH_2 and PH_3 differ by about 1 p*K* unit in their acidities. Arsine and germane are completely ionized to AsH_2^- and GeH_3^- by sodium hydroxide in liquid ammonia.

Substitution of hydrogen by an alkyl group has the expected effect of reducing the acidity, though the magnitude of the change might not have been predicted. An ethyl group appears to increase the p*K* value by about 3 units and a methyl group is slightly more effective. Dialkyl hydrides are still weaker acids. Triphenylgermane might have been expected to be a stronger acid than germane because of the ability of the phenyl group to delocalize the charge in the anion (as in structure I). Indeed, the nmr spectrum of sodium triphenylgermane indicates that this delocalization is appreciable; the *ortho* and *para* proton peaks are shifted to higher field. However, triphenylgermane is found to be a much weaker acid than germane. One possible explanation of this unusual behavior is that there is interaction of the π electrons of the aromatic systems with the empty d orbitals of the germanium, atom, as in structure II. Such interaction would place a partial negative charge on the germanium, making the proton more difficult to remove. Electron spin resonance data of Carrington and co-workers[14] support the idea of interaction between aromatic π systems and the d orbitals of germanium. On the other hand, Issleib and Kümmel have found that phenyl substitution *increases* the acidity of phosphine and arsine. We have no explanation for the different behavior.



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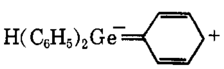

II

Nmr Data.—The results of the nmr measurements are given in Tables I and II, and the data for the parent hydrides agree well with the literature values that are available.[15–17] There are some differences in the chemical shifts, but these undoubtedly arise from differences in bulk diamagnetic susceptibility of the various solvents used. The ethyl portions of the ethylgermane spectra are A_3B_2-type spectra, with the added complication of spin–spin coupling with the Ge–H protons. We were unable to analyze these spectra, and the chemical shift data in Table I refer to the most prominent peaks. We were unable to observe any ^{13}C–H coupling in the spectra of solutions of the alkyl compounds because of the low concentrations used and because some parts of the spectra were obscured by the ammonia solvent peaks.

The coupling constants for the ethylgermanes appear to be new, as are the data for the anions of these hydrides. Solutions of the hydride anions in liquid ammonia were reasonably stable at room temperature, but on standing for several weeks, ammonolysis was appreciable. This was especially true of the anions of the weaker acids such as dimethylgermane and methylphosphine. The anion of this latter compound showed so much ammonolysis that we were prevented from obtaining its nmr spectrum. Burg and Wagner[13] have observed that ammonolysis of the PH bonds occurs in the preparation of alkyl-substituted phosphines in liquid ammonia.

Chemical Shifts.—Substitution of alkyl groups for hydrogen in these hydrides causes a deshielding at the hydrogens remaining, ethyl groups being slightly more effective in this respect than methyl groups. The Ge–H proton of triphenylgermane is at lowest field because of the large ring-current effects of the phenyl groups. Removal of a proton to give the anion results in a shielding of the remaining protons and a shift to higher magnetic field. This is most pronounced for the unsubstituted hydrides, where shifts of 1.99, 3.28, and 3.59 ppm are observed in GeH_4, PH_3, and AsH_3, respectively, in going from the acid to the anion. It seems likely that the neighbor-anisotropy effect would increase on going from the parent acid to the anion, the result being a greater diamagnetic susceptibility along the X–H bond than perpendicular to it and hence a greater shielding at the proton.[18] There would also be an increased paramagnetic contribution, and hence increased shielding, as the hybridization

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(14) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).

(15) G. P. Van der Kelen, L. Verdonck, and D. Van der Vondel, *Bull. Soc. Chim. Belges*, **73**, 733 (1964).

(16) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(17) H. S. Gutowsky and C. J. Hoffman, *ibid.*, **19**, 1259 (1951).

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.