num and a mixture of an alkyl iodide and iodine with or without aluminum chloride. Sodium borohydride, lithium borohydride, and a mercury–mercury(II) chloride mixture proved ineffective as activators.

Preparation of Silane from a Fluorosilicate, Hydrogen, Aluminum, and Aluminum Chloride.—The aluminum chloride–sodium chloride eutectic melt also was effective as an activating medium for the hydrogenation of salts of fluorosilicic acid to silane. Treatment of a mixture of 33 g. (0.149 mole) of potassium fluorosilicate, 30 g. (1.11 moles) of powdered aluminum, 113 g. (0.847 mole) of anhydrous aluminum chloride, and 30 g. (0.514 mole) of sodium chloride with hydrogen at 750–830 atm. pressure at 200° for 11.5 hr. gave a 92% conversion to silane. Mass spectrographic analysis showed the silane to have a purity 99.9%.

Acknowledgment.—We wish to acknowledge the assistance of Mr. M. C. Nelson in the development of the high-pressure techniques used with the molten salt systems.

Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

The Mass Spectra of Volatile Hydrides. I. The Monoelemental Hydrides of the Group IVB and VB Elements[1]

By Fred E. Saalfeld and Harry J. Svec

Received March 15, 1962

The mass spectra of SiH_4, GeH_4, SnH_4, PbH_4, PH_3, AsH_3, SbH_3, and BiH_3 have been obtained. Fragment ions, after careful test, have been found to have negligible excess kinetic energy. The average M–H bond energies and the ΔH_f^0 obtained from appearance potential data agree well with other values when they exist.

Introduction

The mass spectra of silane, germane, stannane, phosphine, and arsine have been reported by various workers.[2–5] These reports include fragmentation patterns for the compounds but appearance potential (a.p.) data are cited only for the positive fragment ions from germane,[3] stannane,[5] and phosphine.[3a] While there is generally good agreement among the fragmentation patterns, where more than one study is reported, there is not good agreement among the a.p. data. In some cases authors have not attempted to identify particular processes with their data and in two instances[3a,3c] misinterpretation of the data is evident in the published accounts. In none of the studies have attempts been made to determine whether or not the a.p. data contain excess kinetic energy. This paper reports an extension of the scope of mass spectrometric studies of the volatile hydrides as well as careful determinations of whether or not the fragment ions have excess kinetic energy.

Experimental

Silane was prepared in an all-glass vacuum apparatus by the reduction of silicon tetrachloride with lithium aluminum hydride according to the method of Finholt, *et al.*[6] Purification of the product was achieved by distilling through a trap at −117° (m.p. of absolute ethanol), condensing at the temperature of boiling liquid nitrogen, evacuating, and repeating the procedure three times. No higher homologs were observed in the mass spectrum.

Germane was prepared from $^{74}GeO_2$ according to the method of Jolly and Drake.[7] Purification of the product was as described above for silane except that a trap cooled to −111.6° (m.p. of carbon disulfide) instead of −117° was used.

Stannane was prepared from ^{120}Sn according to the procedure outlined by Saalfeld and Svec.[5]

Plumbane was prepared by the reaction of 50 ml. of 0.8 *N* HCl with 117 g. of a metallic mixture corresponding to the composition Mg_2Pb. The acid was added dropwise to the metal mixture under vacuum. Products were swept directly into a paraffin-lined trap cooled with boiling liquid nitrogen. When the reaction was complete, this trap was isolated from the reaction vessel, allowed to warm to −111.6°, and then thoroughly evacuated. The trap again was isolated and slowly warmed to −22.9° (m.p. of carbon tetrachloride). It was opened to a Toepler pump and the gases quickly were transferred to a specially designed sample bulb which was cooled to −111.6°. The plumbane was isolated in the bulb and quickly transferred to the mass spectrometer. After the bulb had been attached to the evacuated inlet system of this instrument it was warmed slowly to −22.9° and the plumbane allowed to distil into the ion source of the mass spectrometer. In spite of these precautions, the yields were low and rapid decomposition took place. Each preparation allowed only 10 to 15 min. of observation time in the instrument and thus several preparations were needed to complete the mass spectrometric studies.

Phosphine was prepared by the procedure of Gunn and Green.[8] Purification of the product was as described above for silane except that the trap was cooled to −63.5° (m.p. of chloroform) instead of −117°.

Arsine was prepared by the reduction of an acidic solution of

---

[1] This report is based in part on a Ph.D. dissertation by F. E. Saalfeld and submitted to Iowa State University, Ames, Iowa. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1124.

[2] D. Frost, Univ. of British Columbia, Vancouver, British Columbia, private communication; Callery Chemical Company, Callery, Penna., "Uncertified Mass Spectra," ASTM Committee E-14 on Mass Spectrometry.

[3] (a) H. Neurt and H. Clasen, *Z. Naturforsch.*, **7A**, 410 (1952); (b) M. N. de Mévergnies, *Ann. soc. sci. Bruxelles, Ser. I*, **64**, 188 (1950); (c) G. P. van der Kelen and D. F. van de Vondel, *Bull. soc. chim. Belges*, **69**, 504 (1960).

[4] (a) American Petroleum Institute, Mass Spectral Data, No. 1219; (b) Lawrence Radiation Laboratory, Berkeley, Calif., 1959, private communication.

[5] F. E. Saalfeld and H. J. Svec, *J. Inorg. Nucl. Chem.*, **18**, 98 (1961).

[6] A. E. Finholt, A. C. Bond, K. K. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

[7] W. L. Jolly and J. E. Drake, U.S.A.E.C. Rept. UCLA-9615, University of California, Los Angeles, Calif., 1961.

[8] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

arsenic trichloride with aqueous sodium hydroborate. Fifty ml. of a solution containing 2.5 ml. of concentrated hydrochloric acid and 0.5 ml. of arsenic trichloride was added dropwise to 3.5 g. of sodium hydroborate in 31.5 ml. of water. A stream of nitrogen was used to sweep the products through a trap at −63.5° and then into a second trap cooled with liquid nitrogen. The procedure used for purification of the product was the same as employed for phosphine.

Stibine was prepared by the reduction of 1.0 g. of antimony trichloride dissolved in 50 ml. of 0.8 *N* hydrochloric acid with 10% aqueous sodium hydroborate in a manner similar to that employed to produce arsine. The product was passed through a trap at −16° (m.p. of 24% by weight methyl alcohol in water) and condensed in a second trap cooled with liquid nitrogen. Further purification was achieved as with phosphine except the trap was at −22.4° (m.p. of carbon tetrachloride) instead of −63.5°.

The preparation of bismuthine followed exactly the procedure described above for plumbane except that a mixture of magnesium and bismuth corresponding to Mg_3Bi_2 was used. Again the yield was low and decomposition so rapid that only 10 to 15 min. of observation time in the mass spectrometer was possible from a single preparation. Several preparations thus were required to complete the studies.

Two different mass spectrometers were employed. One was a 60° sector, single deflection instrument of 15 cm. radius with a vibrating reed electrometer as an ion current detector. The other was a 180° instrument of 12.5 cm. radius with a vacuum tube electrometer and d.c. amplifier as the ion current detector. In both instruments the analyzer and sample inlet were all-metal systems. Mass scanning was done by varying the magnetic fields.

In the first instrument a repeller electrode was included in the ion source. Variation of the potential on this electrode enabled semiquantitative information to be obtained about the excess kinetic energy of the fragment ions by Taubert's method.[9] The second instrument had no repeller electrode but employed a drawing out field to extract ions from the electron beam. Ion transmission in the source of this instrument was very much greater than in the first instrument because of geometrical construction, thereby affording greater ion collection sensitivity. The first instrument was used to study phosphine, arsine, stibine, silane, germane, and stannane, while the second instrument was used only with bismuthine and plumbane. Results from the 60° instrument all showed that if the fragment ions contained excess kinetic energy it was negligible but this could not be ascertained directly for the results from the 180° instrument.

All spectra obtained with the first instrument were made with the following conditions prevailing in the ion source: ionizing current, 95 μa.; ion accelerating voltage, 1625 v.; repeller voltage, +1.0 v.; electron accelerating voltage (e.a.v.), 60 to 10 v. In the second instrument the ion source conditions were: ionizing current, 400 μa.; ion accelerating voltage, 800 v.; draw-out potential, sufficient to produce maximum ion currents; e.a.v., 70 to 10 v. All ionization efficiency curves with the first instrument were made at 0.1-v. increments, while those made for bismuthine and plumbane had to be made at 1.0-v. increments because of the ephemeral existence of the compounds. Argon and krypton were used as calibrating gases. The methods of obtaining and plotting the ionization efficiency curves have been described.[10] Extrapolation of straight line portions of the curves was the method[11] used for obtaining the appearance potentials. While this method has certain disadvantages, experimental problems with some of these compounds make it adequate[12]; therefore no attempt was made to obtain a.p. values by more refined techniques. This method also was used on the more stable hydrides in order to have internal consistency in the study. Indeed more refined methods of obtaining the a.p. values did not significantly change or improve the results.

Results and Discussion

Fragmentation Patterns.—The positive ion fragmentation patterns for all the monohydrides studied are given in Table I. The results for silane and germane disagree with those published by Neurt and Clasen[3a] in the observation of a negligible ion current for the parent ions, SiH_4^+ and GeH_4^+, and an appreciable current for the Si^+ and Ge^+ ions. The discrepancy can be explained on the basis of an erroneous mass assignment by these authors. However, a simple shift in mass scale for their data, while it produces reasonable agreement between the two sets of data, still leaves the question of the identity of the appreciable ion currents they designated as Si^+ and Ge^+. There is little doubt that Neurt and Clasen had erroneously identified their mass scale, since the results of Frost[2] with silane and de Mévergnies[3b] and van der Kelen and van de Vondel[3c] with germane are in excellent agreement with the results obtained here. Careful calibration of the mass scales with well characterized standards was used throughout this work.

The fragmentation patterns from phosphine, arsine, and stannane are in good agreement with those previously published.[4a,4b,5] Minor differences are attributable to the different instrumental conditions and instruments used to obtain the patterns.

Appearance Potentials.—The appearance potentials of the positive ion fragments of the group IVB and VB elements and their associated processes are given in Tables II and III. With the exception of the fragment ions from bismuthine and plumbane these values represent the results of triplicate measurements on each ion. In the cases of germane and stannane, the hydrides were prepared from the separated isotopes ^{74}Ge and ^{120}Sn (obtained from the Stable Isotopes Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.), thereby eliminating problems due to the polyisotopic nature of the natural elements.

These results are in agreement with those reported by Neurt and Clasen for phosphine for all ions except PH_3^+. Here a discrepancy of −1.5 v. exists. No reason is apparent.

The results obtained here for the ions from germane do not agree well with those of de Mévergnies, Neurt and Clasen (corrected where feasible for the error in mass scale), and van der Kelen and van de Vondel. With the exception of the values for the process

$$GeH_4 \longrightarrow Ge^+ + H_2 + 2H + e$$

our values are from 1.5 to 2.2 e.v. lower than those of these authors. A parallel comparison between the present results for stannane and those reported earlier from these Laboratories[5] indicates the presence of approximately 2.4 e.v. of excess kinetic energy in the earlier measurements. Both sets of data show the

---

[9] R. Taubert, "Kinetic Energy of Fragment Ions" in "Advances in Mass Spectrometry," J. P. Waldron, Ed., Pergamon Press, London, 1959, pp. 489–503.

[10] G. D. Flesch and H. J. Svec, *J. Am. Chem. Soc.*, **81**, 1787 (1959).

[11] R. H. Vought, *Phys. Rev.*, **71**, 93 (1947).

[12] R. I. Reed, "Ion Production by Electron Impact," Academic Press, London and New York, N. Y., 1962, pp. 22–23.

Table I

Relative Abundance of Positive Ion Fragments from the Monohydrides of the Group IVB and VB Elements[a]

Ion	Si	Ge	Sn	Pb	P	As	Sb	BiH_3
MH_4^+	$\leqslant 1$	$\leqslant 0.5$	$\leqslant 0.1$	$\leqslant 0.01$	...	...	...	...
MH_3^+	78.1	93.7	100.0	60.5	68.0	66.5	73.9	66.5
MH_2^+	100.0	100.0	52.8	100.0	25.4	22.3	31.8	49.1
MH^+	20.3	28.3	22.7	5.0	100.0	100.0	100.0	100.0
M^+	20.7	47.5	71.2	25.0	40.2	40.4	63.8	50.4

[a] E.a.v. = 67.5 v. for PbH_4 and BiH_3; 60.0 v. for all other hydrides.

Table II

Appearance Potentials and Processes for Forming the Ion Fragments from the Group IVB Hydrides

Ion		Si	Ge	Sn	Pb
MH_4^+	$MH_4 \rightarrow MH_4^+ + e$	11.4[a]	10.5[a]	9.2[a]	9.1[a]
MH_3^+	$MH_4 \rightarrow MH_3^+ + H + e$	11.8 ± 0.2	10.8 ± 0.3	9.4 ± 0.3	9.6
MH_2^+	$MH_4 \rightarrow MH_2^+ + H_2 + e$	12.1 ± 0.2	11.8 ± 0.2	9.5 ± 0.3	...
	$MH_4 \rightarrow MH_2^+ + 2H + e$	16.5 ± 0.3	15.4 ± 0.3	13.9 ± 0.4	10.1
MH^+	$MH_4 \rightarrow MH^+ + H_2 + H + e$	16.1 ± 0.2	11.3 ± 0.3	10.7 ± 0.3	...
	$MH_4 \rightarrow MH^+ + 3H + e$	20.4 ± 0.5	16.8 ± 0.3	14.8 ± 0.5	11.1
M^+	$MH_4 \rightarrow M^+ + 2H_2 + e$	11.7 ± 0.2	10.7 ± 0.2	9.0 ± 0.3	...
	$MH_4 \rightarrow M^+ + H_2 + 2H + e$	16.4 ± 0.2	14.1 ± 0.5	13.4 ± 0.4	11.2
	$MH_4 \rightarrow M^+ + 4H + e$	20.8 ± 0.2	18.3 ± 0.3	18.3 ± 0.4	...

[a] Estimated according to the method described by Saalfeld and Svec[5]; Saalfeld,[13] reported in e.v.

Table III

Appearance Potentials[a] and Processes for Forming the Ion Fragments from the Group VB Hydrides

Ion	Process	P	As	Sb	Bi
MH_3^+	$MH_3 \rightarrow MH_3^+ + e$	11.5 ± 0.3	12.1 ± 0.2	9.9 ± 0.3	10.1
MH_2^+	$MH_3 \rightarrow MH_2^+ + H + e$	14.4 ± 0.2	14.5 ± 0.2	11.8 ± 0.3	12.4
MH^+	$MH_3 \rightarrow MH^+ + H_2 + e$	12.4 ± 0.2	12.4 ± 0.2	9.9 ± 0.2	...
	$MH_3 \rightarrow MH^+ + 2H + e$	16.4 ± 0.4	16.8 ± 0.4	14.2 ± 0.4	12.2
M^+	$MH_3 \rightarrow M^+ + H_2 + H + e$	16.5 ± 0.2	14.8 ± 0.2	12.1 ± 0.2	...
	$MH_3 \rightarrow M^+ + 3H + e$	20.8 ± 0.3	19.4 ± 0.2	16.7 ± 0.3	13.4

[a] Reported in e.v.

same internal consistency, however. This finding suggests that the higher values reported for the fragment ions from germane may be due to the presence of unknown or undetermined excess kinetic energy. There is some evidence for this contention in the paper of van der Kelen and van de Vondel which shows an ionization efficiency curve for Ge^+ from germane. Correct interpretation of this curve[14] shows a difference of 6.5 e.v. between the first and second breaks instead of the 4.55 e.v. quoted by the authors. Thus 2.0 e.v. more energy shows up in the a.p. for the associated processes than can be accounted for by the dissociation energy of H_2. The presence of such energy in the results leads to a low value for ΔH_f^0 and a high value for the bond energies computed from the appearance potential data. Support for the values reported in this paper are presented below in the section on thermochemical properties.

No limits of accuracy are indicated in the tables for the a.p. values of the ion fragments from plumbane and bismuthine. Although the measurements were reproducible to within ±0.3 e.v., there is no way of determining whether or not these values contain excess kinetic energy. Since the ion source employed with these compounds has been greatly changed from that used in the earlier stannane work, it is not possible to extrapolate the differences discovered in the present work with stannane to the data on plumbane and bismuthine.

Thermochemical Properties.—Thermochemical quantities can be obtained from appearance potential measurements since these correspond directly to ΔE for the reaction occurring in the ion source. However, for the processes taking place in the ion source the magnitude of $\Delta(PV)$ is negligible and thus

$$\text{a.p.} \cong \Delta H_{\text{reaction}}$$

If an ion source reaction is known or can reasonably be assumed, heats of formation can be calculated from a.p. data. For example, the process of forming M^+ from MH_4 requiring the least energy is

$$MH_4 + e \longrightarrow M^+ + 2H_2 + 2e$$

hence for this process

$$\text{a.p.} = \Delta H_{\text{reaction}} = H_f^0(M^+) + 2\Delta H_f^0(H_2) - \Delta H_f^0(MH_4) + \text{k.e.}^{15}$$

If the excess kinetic energy, k.e., can be shown to be negligible, $\Delta H_f^0(MH_4)$ is obtained by combining thermochemical data from other sources with the measured appearance potentials. In the event that it is impossible to ascertain the amount of kinetic energy con-

---

(13) F. E. Saalfeld, "The Mass Spectrum of Stannane," unpublished M.S. Thesis, Iowa State University, Ames, Iowa, 1959.

(14) C. A. McDowell and J. W. Warren, *Discussions Faraday Soc.*, **10**, 53 (1951).

(15) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957, p. 80.

tained in the measured a.p., then the calculated value of ΔH_f^0 must be considered as a lower limit. A summary of the standard heats of formation of the gaseous hydrides calculated in this way using the values for $\Delta H_f^0(M^+)$ from Latimer[16] appear in Table IV. For comparison the recent calorimetric values of Gunn and Green[8] and the earlier values of Rossini[17] are included.

TABLE IV

HEATS OF FORMATION OF THE GROUP IVB AND VB MONOHYDRIDES IN KCAL./MOLE

	This work	Gunn and Green[8]	Rossini, *et al.*[17]
CH_4	...	−17.9	−17.9
SiH_4	7.8	7.3	−14.8
GeH_4	20.8	21.6	...
SnH_4	35.0	38.9	...
PbH_4	59.7	...	...
NH_3	...	−11.0	−11.0
PH_3	2.3	1.4	2.21
AsH_3	15.2	15.9	41.0
SbH_3	34.6	34.7	...
BiH_3	66.4	...	...

Considering the uncertainties associated with the a.p. measurements given in Tables II and III, the agreement between the values of Gunn and Green[8] and this work is excellent. It is obvious that the early values of Rossini for silane and arsine are incorrect. The numbers obtained for plumbane and bismuthine appear to be reasonable ones but since it is not possible to rule out the existence of excess kinetic energy in the appearance potentials, these ΔH_f^0 values must be considered as a lower limit for the actual ones. In the work with plumbane and bismuthine, assumed ion source reactions for the observed a.p. values are based upon the reasonableness of values for ΔH_f^0 calculated on the basis of one possible process or another.

Average numbers for the energies of the M–H bond can be obtained by combining the a.p. data with the spectroscopic ionization potentials of M^+ [18] and the dissociation energy of H_2 in equations given by Franklin and Field.[15] A summary of the calculated results is given in Table V and a comparison of our values with those derived from other sources is given. Again the agreement between the calorimetric values of Gunn and Green and these mass spectrometric values is good. In the cases of Pb–H and Bi–H, the values presented must be considered as upper limits because of the uncertainties in the accuracy of the a.p. data.

The dissociation energies of the successive bond ruptures in the positive ions are given in Table VI. These are obtained from the appearance potential measurements for the same type of ion-source reaction. The low values for the dissociation energy of the MH_3^+–H bond in SiH_4^+, GeH_4^+, SnH_4^+, and PbH_4^+ explains the observation of a negligible amount of parent ions. The large values for the MH_2^+–H and MH^+–H energies corroborate observations in the fragmentation patterns.

TABLE V

AVERAGE M–H BOND ENERGIES FOR THE GROUP IVB AND VB HYDRIDES IN KCAL./MOLE

	This work	Gunn and Green[8]	Huggins[19]	Cottrell[20]
C–H	...	99.3	...	98.7
Si–H	72.6	76.5	79.0	76.0
Ge–H	68.4	69.0	74.0	...
Sn–H	61.7	60.4	71.0	74.0
Pb–H	49.0	...	...	...
N–H	...	93.4	85	85
P–H	80.5	76.8	77	77
As–H	73.1	66.8	71	66
Sb–H	61.3	60.9	70	...
Bi–H	46.9	...	...	...

TABLE VI

ION FRAGMENT BOND DISSOCIATION ENERGIES[a] OF THE MONOHYDRIDES

Ion	Si	Ge	Sn	Pb	P	As	Sb	Bi
MH_3^+–H	0.4	0.3	0.2	0.5	...	...	...	...
MH_2^+–H	4.7	4.6	4.5	0.5	2.9	2.4	1.9	2.3
MH^+–H	3.9	1.4	0.9	1.0	2.0	2.3	2.4	...
M^+–H	0.4	1.5	2.2	...	4.4	2.6	2.5	1.2

[a] Reported in e.v.

Summary and Conclusions

The relative fragmentation patterns of the hydrides discussed here may be compared if the ions are corrected for their difference in ionization cross sections. Absolute measurement of these cross sections is very difficult, but a convenient method of calculating them is that of Otvos and Stevenson.[21]

The comparisons shown in Tables VII and VIII, respectively, are based on the cross sections calculated for methane and ammonia, whose fragmentation patterns have been taken from the compilation of the

TABLE VII

FRAGMENTATION PATTERNS OF GROUP IVB HYDRIDES ON THE COMMON IONIZATION CROSS SECTION OF 8.16 FOR METHANE

	C	Si	Ge	Sn	Pb
MH_4^+	100.0	0.44	0.18	0.03	0.002
MH_3^+	85.7	34.6	34.1	27.4	14.0
MH_2^+	16.1	44.3	36.4	14.5	23.2
MH^+	8.1	9.0	10.3	6.2	1.6
M^+	2.8	9.2	17.3	19.5	5.8

TABLE VIII

FRAGMENTATION PATTERNS OF GROUP VB HYDRIDES ON THE COMMON IONIZATION CROSS SECTION OF 6.84 FOR AMMONIA

	N	P	As	Sb	Bi
MH_3^+	100.0	27.7	20.9	17.4	13.1
MH_2^+	80.0	10.3	7.0	7.5	9.7
MH^+	7.5	40.7	31.5	23.5	19.7
M^+	2.2	11.4	12.7	15.0	9.9

---

(16) W. Latimer, "Oxidation Potentials," Second Ed., Prentice-Hall Inc., Englewood Cliffs, N. J., 1952.

(17) F. D. Rossini, *et al.*, Natl. Bur. Std. Circular 500, U. S. Government Printing Office, Washington, D. C., 1949, 1952, 1958.

(18) C. E. Moore, Natl. Bur. Std. Circular 467, U. S. Government Printing Office, Washington, D. C., Vol. 1, 2, 3 (1949, 1952, 1958).

(19) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

(20) T. L. Cottrell, "The Strength of Chemical Bonds," Second Ed., Butterworth Scientific Publications, London, England, 1958.

(21) J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.*, **78**, 546 (1956).

American Petroleum Institute. The fragmentation patterns of methane and ammonia have been included for completeness. The fragmentation pattern of stannane is taken from the work of Saalfeld and Svec.[5]

The fact that the number of parent ions MH_4^+ and MH_3^+ decrease regularly from C to Pb and N to Bi concurs with the information on the stability of these molecules obtained from values of the heats of formation. The increasing trend of the amount of the M^+ fragments from C to Sn and N to Sb agrees both with the fact that the M–H bond energy decreases with atomic number and with the atomic ionization potential data of these atoms.

The good agreement between the heats of formation and bond energies based on the appearance potentials reported here and those obtained calorimetrically is considered to be corroborative evidence that the discordant a.p. data of Neurt and Clasen, de Mévergnies, and van der Kelen and van de Vondel for silane and germane and the earlier work of Saalfeld and Svec with stannane contain an unknown amount of excess kinetic energy.

Acknowledgment.—The authors wish to thank G. D. Flesch for his generous assistance during the course of this work.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Mass Spectra of Volatile Hydrides. II. Some Higher Hydrides of the Group IVB and VB Elements[1]

BY FRED E. SAALFELD AND HARRY J. SVEC

Received September 6, 1962

The mass spectra of Si_2H_6, $^{74}Ge_2H_6$, $^{74}Ge_3H_8$, $^{120}Sn_2H_6$, P_2H_4, As_2H_4, and Sb_2H_4 have been obtained. The average M–M bond energies and the ΔH_f^0 have been calculated from appearance potential data.

Introduction

The mass spectra of disilane and digermane have been reported previously.[2,3] Pupezin and Zmbov report only the fragmentation pattern of disilane but van der Kelen and van de Vondel give both the fragmentation pattern and the appearance potentials (a.p.) of the monoelemental fragments of digermane. The results reported here agree essentially with the fragmentation pattern reported for digermane[3] and the dielemental fragments from disilane.[3] However, much larger monoelemental ion currents are reported for disilane than those observed in this study. This discrepancy may be explained if the previous observations on disilane included some trisilane and silane as impurities. However, since the published disilane spectra were obtained in a 60° sector instrument using 90 v. ionizing elections compared to the 180° instrument and 67.5 v. electrons used here, the usually observed differences in spectra from these two types of instruments may account in part for the discrepancies.

Experimental

Disilane was prepared by hydrolyzing 10 g. of magnesium silicide with 50 ml. of 0.8 *N* hydrochloric acid in an all-glass vacuum line. The gaseous products were passed through a trap at −22.8° (m.p. of carbon tetrachloride) and condensed in a trap cooled with liquid nitrogen. Purification of the product was accomplished by isolating and evacuating the liquid nitrogen cooled trap and then warming it to −111.6° (m.p. of carbon disulfide). Monosilane distilled at this temperature and was condensed in another liquid nitrogen cooled trap. The procedure was repeated three times and the residues were retained. Disilane was obtained from the combined residues by using the same procedure except a trap at −22.8° was used instead of the one at −111.6°. Mass spectrometric assay indicated the absence of higher homologs.

Digermane and trigermane were prepared and separated according to the method of Jolly and Drake.[4] The only variation used here was that the 3 *M* sulfuric acid was added to a reaction solution consisting of 30 ml. of water, 1 g. of potassium hydroxide, 0.1 g. of $^{74}GeO_2$, and 3.5 g. of potassium hydroborate.

Distannane also was prepared and separated according to the method of Jolly and Drake[4] except that the composition of the reaction solution was changed in order to use a separated isotope, ^{120}Sn, in the preparation. The change consisted of dissolving 0.1 g. of ^{120}Sn in 50 ml. of 0.8 *N* hydrochloric acid and adding the solution to 50 ml. of a solution containing 6 g. of potassium hydroxide and 6 g. of potassium hydroborate held at 0°.

Diphosphine was prepared by the disproportionation of phosphorous acid prepared by hydrolyzing 11 ml. of phosphorus trichloride with 7 ml. of water. The resulting sirupy solution was heated under vacuum and the disproportionation products were condensed in a liquid nitrogen cooled trap. Diphosphine was obtained by a fractionation process similar to that described for disilane except that the traps were held at −63.5° (m.p. of chloroform) and −22.8° instead of −111.6 and −22.8°.

Diarsine was obtained as a secondary product from the preparation of arsine.[5] Arsine was first removed and then the residue was further fractionated by distilling three times through traps

---

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1208.

[2] J. D. Pupezin and K. F. Zmbov, *Bull. Inst. Nucl. Sci. "Borish Kidrick"* (Belgrade), **8**, 89 (1959).

[3] G. P. van der Kelen and D. F. van de Vondel, *Bull. soc. chim. Belges*, **69**, 504 (1960).

[4] W. L. Jolly and J. E. Drake, USAEC Rept. UCLA-9615, University of California, Los Angeles, Calif., 1961.