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.[6]

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]

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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

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[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.

TABLE I

RELATIVE ABUNDANCES OF THE POSITIVE ION FRAGMENTS FROM SOME HIGHER HYDRIDES OF THE GROUP IVB AND VB ELEMENTS
(Electron accelerating voltage = 67.5 v.)

Ion	C_2H_6[6a]	Si_2H_6	$^{74}Ge_2H_6$[a]	$^{74}Ge_3H_8$[a]	$^{120}Sn_2H_6$[b]	N_2H_4[6b]	P_2H_4	As_2H_4	Sb_2H_4
$M_3H_8^+$				0.3					
$M_3H_7^+$				22.6					
$M_3H_6^+$				12.9					
$M_3H_5^+$				13.3					
$M_3H_4^+$				9.1					
$M_3H_3^+$				9.1					
$M_3H_2^+$				6.5					
M_3H^+				90.1					
M_3^+				100.0					0.01
$M_2H_6^+$	26.2	45.6	45.8	0.9[c]	1.5				
$M_2H_5^+$	21.5	18.0	29.1	8.3	3.0				
$M_2H_4^+$	100.0	100.0	74.1	58.0	3.8	100.0	8.4	2.7	0.8
$M_2H_3^+$	33.3	18.5	31.6	21.2	20.1	47.3	1.3	11.5	1.4
$M_2H_2^+$	23.0	69.0	100.0	69.5	100.0	31.3	5.8	34.8	6.2
M_2H^+	4.15	36.0	61.7	28.2	29.9	40.1	5.6	11.2	21.1
M_2^+	0.74	24.6	65.8	30.1	28.6	21.4	100.0	100.0	100.0
MH_4^+	0.8	0.4[c]	4.2[c]	0.3[c]	0.06[c]	...	...	...	...
MH_3^+	4.57	0.6	27.9	16.2	0.3	26.1	0.4[c]	0.3[c]	1.4[c]
MH_2^+	3.35	1.0	29.6	17.2	1.5	29.2	5.1	8.6	4.7
MH^+	1.16	0.6	16.6	4.9	2.0	8.05	0.2	0.4	6.2
M^+	0.54	1.8	36.6	8.2	1.0	4.92	1.2	1.5	1.2

[a] Prepared from the separated isotope ^{74}Ge assayed as 96.1% ^{74}Ge. [b] Prepared from the separated isotope ^{120}Sn assayed as 98.2% ^{120}Sn. [c] Proportional to the square of the pressure, indicating that these ions arise from a secondary gaseous reaction in the ion source.

at −22.8° in the manner described above for the separation of disilane. No higher homologs were observed in the mass spectrometer.

Distibine was obtained as a secondary product from the preparation of stibine.[5] Stibine was first removed and then the residue was further fractionated three times through traps at 0° in the manner described above for disilane. No higher homologs were observed.

In all the preparations described above the compounds were transferred from the vacuum line to glass mass spectrometer sample bulbs fitted with Apiezon-N greased stopcocks, by means of a Toepler pump. For the preparations of distannane and distibine the sample bulbs were held at −111.6° until attached to the mass spectrometer and then warmed to room temperature. The collection of all the other compounds was at room temperature.

The mass spectrometer employed was a 180°, 12.5-cm. radius, single deflection instrument. Mass scanning was done by varying the magnetic field. All spectra were obtained under the following ion source conditions: ionizing current, 400 μa.; ion accelerating voltage, 800 v.; draw-out potential, sufficient to maximize the ion currents; electron accelerating potential, variable from 70 to 10 v. The points for the ionization efficiency curves were taken at 0.5-v. increments. Krypton was used as a calibrating gas. The methods and manner of obtaining and plotting the data have been described.[5] It was not possible to determine whether or not the ion fragments being reported possessed excess kinetic energy so the a.p. data given in this paper could be high. Because of this fact the calculated bond energies may be high and the value of ΔH_f^0 may be too low for the reason discussed in the previous paper.[5]

Results and Discussion

Fragmentation Patterns.—The positive ion fragmentation patterns for the hydrides studied here are given in Table I. The patterns for ethane and hydrazine taken from the American Petroleum Institute compilation[6] have been included for completeness. Except for the already mentioned discrepancy for the monoelemental ion currents from disilane, the spectra reported here for both disilane and digermane agree well with the published spectra[2,3] of these compounds. Minor differences are attributed to the different instrumental conditions and the main discrepancy between the monoelemental ion fragments from disilane may be attributed to slight impurities or to the difference in the ionizing voltages used in the two studies.

The observation here of ion currents at masses corresponding to Sb_3^+ is noteworthy. This ion species always was associated with the distibine preparations and could not be removed by vacuum fractionation. The ion current intensities varied linearly with pressure, indicating that Sb_3^+ was not formed by a secondary gaseous reaction. The ratios of the peaks observed at masses 363, 365, 367, and 369 agreed excellently with those predicted from the accepted isotopic abundances[7] of antimony. Similar ion species for phosphorus and arsenic have been reported by Drowart and Goldfinger[8] in their work with indium phosphide and gallium arsenide. These authors conclude that M_3^+ arises as a fragment from P_4 or As_4. However, only the Sb_3^+ ions were observed here and no Sb_4^+ ions were seen, thus ruling out Sb_4 as a source of Sb_3^+. It is postulated that the Sb_3^+ ion currents arise from a surface reaction in the ion source and involve Sb_2^+ and some adsorbed species. This is in agreement with the magnitude of the observed Sb_3^+ ion currents given in Table I.

Appearance Potentials.—The a.p. data obtained in this study are shown in Table II. All values given were

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(6) (a) B. J. Zwolenski, A. Danti, J. T. Kerry, and W. T. Berry, "Mass Spectral Data," American Petroleum Institute, Pittsburgh, Penna., p. 2; (b) p. 110.

(7) K. T. Bainbridge and A. O. Nier, Natl. Res. Council Nucl. Sci. Series Prelim. Rept. No. 9, 1950.

(8) J. Drowart and P. Goldfinger, *J. chim. phys.*, **55**, 721 (1958).

TABLE II

THE APPEARANCE POTENTIALS OF THE POSITIVE ION FRAGMENTS FROM SOME HIGHER HYDRIDES, IN ELECTRON VOLTS[a]

Ion	Si_2H_6	$^{74}Ge_2H_6$	$^{74}Ge_3H_8$	$^{120}Sn_2H_6$	P_2H_4	As_2H_4	Sb_2H_4
$M_3H_8^+$			9.6 (i.p.)				
$M_3H_7^+$			9.9				
$M_3H_6^+$			10.0				
$M_3H_5^+$			10.1				
$M_3H_4^+$			10.4				
$M_3H_3^+$			10.6				
$M_3H_2^+$			10.7				
M_3H^+			11.8				
M_3^+			14.6				
$M_2H_6^+$	10.6 (i.p.)	12.5 (i.p.)		9.0 (i.p.)			
$M_2H_5^+$		12.6		10.0			
$M_2H_4^+$		12.7		10.3	10.6 (i.p.)	12.2 (i.p.)	10.2 (i.p.)
$M_2H_3^+$		12.8		10.4	11.3	12.5	10.5
$M_2H_2^+$		12.9		10.5	12.7	12.6	10.7
M_2H^+		13.0		10.6	13.6	12.7	10.9
M_2^+	12.2	13.1	15.8	10.7	13.7	13.0	11.2
M^+	15.2	13.3	16.3	10.8	16.7	14.3	11.5

[a] Krypton was used as an internal standard to calibrate the electron accelerating voltage scale.

experimentally reproducible to ±0.3 e.v. A discrepancy exists between the value reported here for the a.p. of Ge^+ from digermane and the higher value reported by van der Kelen and van de Vondel.[3] This difference may be explained by: (1) the excess kinetic energy of the Ge^+ ions observed by these authors in their instrument could have been greater than the probable excess kinetic energy of the same ion in our mass spectrometer, or (2) these authors may have measured the a.p. of a different ion-source process than was measured here. The second explanation seems more likely since no process is postulated for the formation of Ge^+ in the study of van der Kelen and van de Vondel[3] and the difference between their value of the a.p. and ours is 4.1 e.v., which is very close to the energy of a H–H bond.

Some comments on the results in Table II are in order. The a.p. values of all the fragment ions from disilane are not given because of overlap due to the three isotopes of silicon. No. a.p. data are presented for any of the monoelemental ion fragments except the M^+ ions because no useful thermochemical information can be obtained readily from these data.

There is an increase in the ionization potential, i.p., of the parent ions progressing from the third row elements to the fourth followed by a decrease to the fifth row elements. This irregularity is analogous to other anomalous properties of the fourth row elements such as the instability of arsenic pentachloride compared to similar compounds of phosphorus and antimony, the greater electronegativity of arsenic on the Rochow scale compared to phosphorus and antimony, and the fact that either phosphorus or antimony will reduce arsenic trichloride to arsenic.

Thermochemical Properties.—The processes by which M^+ and M_2^+ are formed and for which a.p. values have been measured are assumed to differ only by the energy of a $(M–M^+)$ bond. Values for this energy which are obtained from the difference of the a.p. values are summarized in Table III. It is noted that the bond energy decreases as the atomic number of M increases for these elements. The comparatively large values for the $(Si–Si^+)$, $(P–P^+)$, and $(As–As^+)$ bonds are offered as an explanation of the small amounts of monoelemental fragments observed from these dihydrides compared with the remaining dihydrides of this study.

TABLE III

DISSOCIATION ENERGIES OF THE $M–M^+$ BOND (in electron volts)

Metal	Si	Ge	Sn	P	As	Sb
Bond energy	3.0	0.4[a]	0.1	3.0	1.3	0.3

[a] Value obtained by averaging the data from Ge_2H_6 and Ge_3H_8.

The processes which are assumed to lead to the formation of the M^+ ions from the hydrides of this study are

$$M_2H_6(g) \longrightarrow M^+(g) + M^0(g) + 3H_2 \qquad (1)$$

and

$$M_3H_8(g) \longrightarrow M^+(g) + 2M^0(g) + 4H_2 \qquad (2)$$

for the group IVB elements and

$$M_2H_4 \longrightarrow M^+(g) + M^0(g) + 2H_2 \qquad (3)$$

for the group VB elements. Using these equations, the a.p. values for the M^+ ions given in Table II, the spectroscopic ionization potentials from Moore,[9] the heats of formation of $M^+(g)$ and $M^0(g)$ from Latimer,[10] and the M–H bond energies cited by Gunn and Green[11] and Saalfeld and Svec,[5] the standard heats of formation of the compounds and the M–M bond energies for the gaseous hydrides have been calculated. These values along with those reported by Gunn and Green[11] are shown in Table IV. Considering the possible errors present in the mass spectral measurements on compounds of this type,[5] the agreement with the colorimetric values[11] is excellent, indicating that

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

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

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

TABLE IV

STANDARD HEATS OF FORMATION AND M–M BOND ENERGIES OF SOME GASEOUS HIGHER HYDRIDES OF THE GROUP IVB AND VB ELEMENTS

(in kcal./mole)

	Si_2H_6		Ge_2H_6		Ge_3H_8	Sn_2H_6	P_2H_4		As_2H_4	Sb_2H_4
	This work	Gunn and Green	This work	Gunn and Green	This work	This work	This work	Gunn and Green	This work	This work
$\Delta H_f^0(g)$	15.1	17.1	39.1	38.7	48.4	65.6	9.9	5.0	35.2	57.2
B.e.(M–M)	39.7	46.4	33.2	37.9	27.9	29.9	43.7	46.8	44.7	30.7

the assumed ion source reactions are correct. The poorest pair of values are those for $\Delta H_f^0(g)$ diphosphine but even these may be reconciled considering the fact that 1 e.v. is equivalent to 23.0 kcal. and our measuring uncertainties were slightly higher than usual when the work was done with this compound.

The trend of increasing ΔH_f^0 with increasing atomic number should be noted. A reverse trend is true for the M–M bond energies except for the (P–P) and (As–As) bonds, which are of equal strength. This is not entirely unexpected due to the other anomalous properties of the fourth row elements.

It is hoped that the problems pointed out in this paper indicate the need for improved methods of synthesizing some of these compounds so their thermochemical properties can be measured more accurately. At present, synthetic methods for all the compounds of this study are not adequate to allow for direct calorimetric measurements. However, any improvements in the syntheses will make it expedient that more refined mass spectrometric techniques be applied in the future. For the present, however, the results given in this paper can stand well alongside existing, comparable calorimetric results.

Acknowledgment.—The authors wish to acknowledge the helpful discussions of Gerald D. Flesch and Harold A. Belsheim.

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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The Kinetics of the Disproportionation of Americium(V)[1]

BY JAMES S. COLEMAN

Received June 8, 1962

Use of the isotope Am^{243} ($T_{1/2}$ = 7951 years) has made possible the first observations of the disproportionation of Am(V) unobscured by the effects of radiolysis. The net reaction is: $3AmO_2^+ + 4H^+ \rightarrow 2AmO_2^{++} + Am^{+3} + 2H_2O$. The rate at 75.7° in perchlorate solutions of ionic strength 2 M is given by $-d(AmO_2^+)/dt = k_2(H^+)^2(AmO_2^+)^2 + k_3(H^+)^3(AmO_2^+)^2$, with k_2 and k_3 equal to $7.0 \times 10^{-4}\ M^{-3}\ sec.^{-1}$ and $4.6 \times 10^{-4}\ M^{-4}\ sec.^{-1}$, respectively. Estimation of the difference in the entropies of activation for the parallel paths suggested by this rate law combined with rate measurements at 60–85° gives $\Delta H_2^* = 16.5$ kcal./mole, $\Delta S_2^* = -26$ e.u., $\Delta H_3^* = 10.5$ kcal./mole, $\Delta S_3^* = -44$ e.u. At 75.7°, the rates in 2 N HNO_3, HCl, and H_2SO_4 are 4.0, 4.6, and 24 times as great as that in 2 N $HClO_4$. At room temperature, the reaction rate increases by a factor of 450 in going from 3 to 8 M perchloric acid. Observation of the oxidation of Am(III) by Am(VI), the reverse of the disproportionation reaction, is reported for the first time.

Introduction

The disproportionation of Am(V) has been observed in hydrochloric,[2] sulfuric,[3] nitric,[3] and perchloric[3–5] acids using the isotope Am^{241}. The α-decay of the Am^{241} led to radiolytic reduction of Am(VI) to Am(V) at a rate which, during most of the previous experiments, was roughly equal to that of the disproportionation reaction. This has resulted in disagreement regarding even the stoichiometry of the reaction. Hall and Markin[4b] and Stephanou, *et al.*,[4a] concluded that the reaction $2Am(V) \rightarrow Am(VI) + Am(IV)$ is followed by immediate reduction of Am(IV) by water so that the apparent reaction is $2Am(V) \rightarrow Am(VI) + Am(III)$. On the other hand, Zaitsev, *et al.*,[3] and Gunn and Cunningham[5] suggest the stoichiometry $3Am(V) \rightarrow 2Am(VI) + Am(III)$ during which the average oxidation number of the americium is conserved.

Each study has confirmed that the rate of disproportionation is directly proportional to the square of the Am(V) concentration. Zaitsev, *et al.*,[3] reported specific rate constants in 4, 6, and 9 M perchloric acid and suggested that the rate is directly proportional to the fourth power of the hydrogen ion concentration. Similar results are reported in the earlier work of

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission.

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