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Mass Spectra of Volatile Hydrides. III. Silylphosphine

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The mass spectra of silylphosphine and the related hydrides phosphine, diphosphine, silane, and disilane have been measured. From the appearance potentials of selected ions of these compounds the following thermochemical values have been calculated: $D(H_3Si\text{–}PH_2)$ = 88.2 kcal./mole; $D(H_3Si\text{–}SiH_3)$ = 83.7 kcal./mole; $D(H_2P\text{–}PH_2)$ = 74.1 kcal./mole; $\Delta H_f°(SiPH_5)$ = 1.9 kcal./mole; $\Delta H_f°(PH_2)$ = 39.6 kcal./mole; $\Delta H_f°(SiH_3)$ = 50.4 kcal./mole; e.a.(PH_3) = 0.5 e.v.; e.a.(SiH_3) = -1.5 e.v.

Introduction

The preparation and some of the properties of silylphosphine have been reported by Drake and Jolly.[1] The compound was identified from its mass spectrum, but neither the spectrum nor any thermochemical properties were reported. It is the purpose of this paper to supply this information.

Experimental

The method used to prepare and purify silylphosphine including the discharge reaction conditions has been described.[1,2] The compounds used in the preparation which were light-sensitive were shielded from light to retard their rate of decomposition. The mass spectrometer employed was a CEC 21-103c modified for appearance potential studies. An Applied Physics Corp. Model 36 vibrating reed electrometer was used to amplify the ion currents. Ion accelerating voltage was 2000 v. for the appearance potential studies. The following conditions prevailed in the ion source during the measurements: ionizing current 10.5 μa.; the repeller potentials were adjusted to give maximum intensity, flat-topped peaks for the fragmentation patterns and were shorted together and held at 2.5 v. for the appearance potential studies. The ion source temperature was 250° and the instrument was operated in the focused mode. The ionizing voltage was varied by 0.2-v. increments for the appearance potential measurements, and the fragmentation patterns were measured at an electron accelerating voltage of 70 v. The method of taking and plotting the appearance potential data has been described.[3] The results by this method were compared with other methods of interpretation.[4] Values obtained from semilog plots and by the extrapolated difference method agreed within the experimental error. An exception to this statement was the result obtained by the conventional linear extrapolation method, which yielded high results for fragment ions. The method of Flesch and Svec was preferred because of its simplicity and the way in which it emphasizes different ion source reactions.

Results and Discussion

Fragmentation Patterns.—The anisotopic fragmentation pattern of the positive ions of silylphosphine is shown in Table I. Electrostatic scanning was employed to observe the ftagmentation pattern. The pattern was calculated using the following isotope abundances: ^{28}Si, 92.2%; ^{29}Si, 4.7%; and ^{30}Si, 3.1%.[5]

Appearance Potentials.—The appearance potentials, a.p., postulated ion source reactions, and thermochemical calculations are given in Table II. Krypton was used as an internal standard to calibrate the electron voltage scale. As an accuracy check, argon was always introduced with the krypton and the hydride sample. The ionization potential of argon was then determined with the voltage scale correction found from the krypton measurement. By this method a possible error of ±0.2 v. was estimated in the absolute accuracy; however, the precision of the measurement was better than ±0.1 v. The relationship between appearance potentials and the thermochemical equation and the errors in these measurements has been discussed elsewhere.[4,6] The electron affinities of PH_2 and SiH_3, presented in Table II, were calculated by the method of Neale.[7] It has been assumed that no excess kinetic energy is contained in the measured appearance potentials. Since this assumption could not be adequately tested in the present measurements, the values for appearance potentials presented in Table II may be greater than the true ones. However, on the basis of previous work, the excess kinetic energy is probably zero or at least negligible. The ancillary values used in the calculations of Table II which were taken from the data of Gunn and Green[8] are (in kcal./mole): $\Delta H_f°(H)$ = 52.1, $\Delta H_f°(SiH_4)$ = 7.3, $\Delta H_f°(Si_2H_6)$ = 17.1, $\Delta H_f°(PH_3)$ = 1.3, and $\Delta H_f°(P_2H_4)$ = 5.0

There are three notable disagreements between the data presented in Table II and previously published values of $I(SiH_3)$, $\Delta H_f°(SiH_3)$, and a.p.(PH_2^+) from PH_3. The first two differ from the results cited by Steele, *et al.*[9] These authors do not mention the ion source conditions under which their measurements were made. It has been found here that variations in source conditions can drastically affect the values obtained for the appearance potentials of fragment ions. This effect is especially dependent upon the repeller voltage settings. The values presented here are lower than Steele's, and so it is possible that his values include some excess kinetic energy. Since both sets of data were obtained with the same type mass spectrometer,

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[1] J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962).

[2] J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962).

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

[4] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957, pp. 26–31.

[5] J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p. 556.

[6] F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **2**, 46 (1963).

[7] R. S. Neale, *J. Phys. Chem.*, **68**, 143 (1964).

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

[9] W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.* **84**, 4441 (1962).

TABLE I

ANISOTOPIC POSITIVE ION FRAGMENTATION PATTERN OF SILYLPHOSPHINE (70 E.V. ELECTRONS)

Ion type	$SiPH_5^+$	$SiPH_4^+$	$SiPH_3^+$	$SiPH_2^+$	$SiPH^+$	SiP^+	PH_2^+
% total ionization	3.4	6.2	6.0	4.1	58.4	15.2	2.9
Ion type	PH^+	P^+	SiH_3^+	SiH_2^+	SiH^+	Si^+	
% total ionization	1.5	0.6	1.0	0.6	0.2		

TABLE II

SUMMARY OF RESULTS[a]

	Appearance pot.			
Ion source reaction	e.v.	kcal.	Thermochemical result	kcal./mole
$SiH_4 \rightarrow SiH_3^+ + H$	11.8	272.0	$\Delta H_f°(SiH_3^+) = a.p. - \Delta H_f°(H) + \Delta H_f°(SiH_4)$	227.2
			$D(H_3Si–H) = a.p. - I(SiH_3)$	95.2
$Si_2H_6 \rightarrow SiH_3^+ + SiH_3$	11.3	260.5	$\Delta H_f°(SiH_3) = a.p. - \Delta H_f°(SiH_3^+) + \Delta H_f°(Si_2H_6)$	50.4
			$I(SiH_3) = \Delta H_f°(SiH_3^+) - \Delta H_f°(SiH_3)$	176.8
			$D(H_3Si–SiH_3) = a.p. - I(SiH_3)$	83.7
$PH_3 \rightarrow PH_2^+ + H$	13.2	304.3	$\Delta H_f°(PH_2^+) = a.p. - \Delta H_f°(H) + \Delta H_f°(PH_3)$	253.6
			$D(H_2P–H) = a.p. - I(PH_2)$	90.3
$P_2H_4 \rightarrow PH_2^+ + PH_2$	12.5	288.1	$\Delta H_f°(PH_2) = a.p. - \Delta H_f°(PH_2^+) + \Delta H_f°(P_2H_4)$	39.6
			$I(PH_2) = \Delta H_f°(PH_2^+) - \Delta H_f°(PH_2)$	214.0
			$D(H_2P–PH_2) = a.p. - I(PH_2)$	74.1
$SiPH_5 \rightarrow SiPH_5^+$	10.0	230.5	$I(SiPH_5) = a.p.$	230.5
$SiPH_5 \rightarrow SiH_3^+ + PH_2$	11.5	265.1	$\Delta H_f°(SiPH_5) = \Delta H_f°(SiH_3^+) + \Delta H_f°(PH_2) - a.p.$	1.8
			$D(H_3Si–PH_2) = a.p. - I(SiH_3)$	88.3
$SiPH_5 \rightarrow PH_2^+ + SiH_3$	13.1	302.0	$\Delta H_f°(SiPH_5) = \Delta H_f°(PH_2^+) + \Delta H_f°(SiH_3) - a.p.$	2.0
			$D(H_3Si–PH_2) = a.p. - I(PH_2)$	88.0
			$e.a.(SiH_3) = -1.5$ e.v.	−34.6
			$e.a.(PH_2) = 0.5$ e.v.	11.5

[a] $\Delta H_f°$ = standard enthalpy of formation; D = dissociation energy; I = ionization potential; a.p. = appearance potential; e.a. = electron affinity; 1 e.v. = 23.05 kcal./mole.

this is the only reasonable explanation for the discrepancy. The third major difference is that a.p.(PH_2^+) from PH_3 does not agree with the value given previously by Saalfeld and Svec[6] but does agree with a recent result by Wada and Kiser.[10] At first it appeared that a serious systematic error in measurement occurred in the early measurements of Saalfeld and Svec. Subsequent review of the research record brought to light the error and its source. Due to an arithmetic mistake a value of 14.4 e.v. instead of 13.4 was recorded for a.p.(PH_2^+) from PH_3. Thus the three measured values for this quantity are in good agreement.

It is interesting to note the trends in the data. As would be expected considering that SiH_3 and PH_2 have different electronegativities, $D(H_3Si–PH_2)$ is greater than either $D(H_2–PH_2)$ or $D(H_3Si–SiH_3)$. The ionization potential of SiH_3 is lower than that of CH_3 and $I(PH_2)$ is lower than $I(NH_2)$. This agrees with the concept that the ionization potential should decrease in a chemical group as the atomic number increases. Similarly, the ionization potential is expected to increase in value as one goes to the right in a row in the periodic table and this is observed since $I(PH_2)$ is greater than $I(SiH_3)$.

It is gratifying that there is an internal consistency in the values for $\Delta H_f°(SiPH_5)$ and $D(H_3Si–PH_2)$ despite the two different thermochemical equations employed in the computations. Under the circumstances it is unlikely that this should be altogether fortuitous. Thus some corroborative support is obtained for the assumption that the appearance potential values for the fragment ions do not contain appreciable excess kinetic energy if any at all.

It should be noted that the appearance potentials reported here for silicon-containing fragments were measured on the fragment containing the ^{30}Si isotope. This isotope comprises only 3.1% of the silicon isotopes. This means that the ions on which the measurements were made were low in abundance, certainly a less favorable experimental situation than if larger ion currents were used. Also, as stated previously there is no assurance that the ions do not contain excess kinetic energy. However, until silylphosphine can be prepared in quantities sufficient for calorimetric measurements, the values cited here are the best acceptable estimates now available.

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(10) Y. Wada and R. W. Kiser, *Inorg. Chem.*, **3**, 174 (1964).