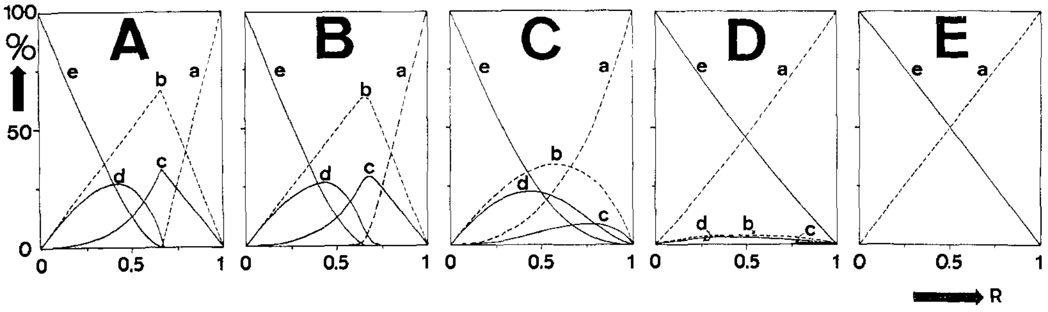

Figure 1.—Theoretically calculated equilibrium curves for systems QT_2 *vs.* MZ in which two kinds of monofunctional substituents, T and Z, are scrambled between a bifunctional central moiety, Q, and a monofunctional central moiety, M. The calculations correspond to $K_1 = 0.250$ (ideal randomness) and varying K_I: A, $K_I = 10^{-20}$; B, $K_I = 10^{-5}$; C, $K_I = 1.00$ (ideal randomness); D, $K_I = 10^{+5}$; E, $K_I = 10^{+20}$. Curve a corresponds to the concentration of the MZ molecule, b to the MT, c to the QZ_2, d to the QZT, and e to the QT_2 molecule, with the over-all composition being given by the parameter $R \equiv Z/(Q + M)$, $R' \equiv M/(Q + M)$.

methyl groups. Halogens also prefer the silicon moiety bearing the larger number of organic substituents when equilibrated with silanic hydrogen.[11]

Estimations of the enthalpy of the reaction of eq 1 based on the bond-energy approach[2] show that the values of ΔH, assuming only σ-bond contributions, differ considerably from ΔH values that were calculated from the intersystem constants K_I according to the approximation

$$\Delta H \approx \Delta F = -RT \ln [K_I/(K_I)_{\text{rand}}]$$

We attribute these differences to π-bonding effects which, therefore, appear to be the major driving force for the nonrandom equilibrations of eq 1. Quantum mechanical calculations[12] support the concept of the major influence of π contributions in these reactions.

Acknowledgment.—We wish to thank Ray E. Miller for obtaining the nmr spectra and for assistance in the data reduction.

[11] D. R. Weyenberg, A. Bey, and P. J. Ellison, *J. Organometal. Chem.* (Amsterdam), **3**, 489 (1965).

[12] J. H. Letcher and J. R. Van Wazer, in preparation.

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The Mass Spectra of Volatile Hydrides. V. Silylarsine[1,2]

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The mass spectra of silylarsine, H_2AsSiH_3, arsine, AsH_3, and diarsine, H_2AsAsH_2, have been studied. From appearance potential data, the heat of formation of several silylarsine positive ions and the following thermochemical values have been calculated (in kcal/mole): $\Delta H_f°(H_2AsSiH_3) = 37$; $D(H_2As\text{–}SiH_3) = 73$; $I(\cdot AsH_2) = 213$; $\Delta H_f°(\cdot AsH_2) = 60$; and $\Delta H_f°(\cdot SiH_2) = 81$.

Introduction

Silylarsine has been prepared by several investigators,[3,4] and although a mass spectrometer was employed in one of the studies[3] for the identification of this hydride, neither the fragmentation pattern nor any appearance potential measurements were reported. It is the purpose of this paper to report these data, the heat of formation of several of the positive ions of silylarsine, the silicon–arsenic bond dissociation energy, and the standard heat of formation of silylarsine.

Experimental Section

Silylarsine was prepared by the method of Drake and Jolly[3] in a vacuum system which contained no grease. Equimolar amounts of silane and arsine were circulated by an automatic Toepler pump through a silent electric discharge, operated at 6 kv ac, and a U trap cooled with an ethanol slush (−125°) for 6 hr. At 1-hr intervals, the discharge was stopped, the U trap was cooled with liquid nitrogen, and any volatile substances remaining in the system were quickly removed by evacuation. Silylarsine and tetrasilane, Si_4H_{10}, were separated from the other compounds formed in the discharge reaction by fractional distillation using conventional vacuum techniques.[5] It was not possible to separate completely silylarsine from tetrasilane by either distillation or with a gas–liquid chromatographic column (12 ft × 0.25-in. i.d.), packed with 10% Silicone 702 on Celite.

Several times during the course of this investigation, an explo-

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[1] Paper IV: F. E. Saalfeld and H. J. Svec, *J. Phys. Chem.*, **70**, 1753 (1966).

[2] Presented at the 14th Annual ASTM E-14 Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 22–27, 1966.

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

[4] B. J. Aylett, H. J. Emeléus, and A. G. Maddock, *J. Inorg. Nucl. Chem.* **1**, 187 (1955).

[5] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

sion occurred in the sample bulb. Mass spectral analysis of the volatile compounds remaining in the sample bulb after the explosion showed only the silylarsine had decomposed; the amount of tetrasilane was the same before and after the explosion. Further, none of the constituents of air was observed in the analysis, and the metallic mirror formed on the bulb in the explosion gave a positive spot test for arsenic. It was found that the explosion could be prevented if the samples were shielded from light; thus, all of the sample bulbs were painted black and stored in a light-tight photographic sleeve, and the experiments were conducted in a darkened room. A more intensive investigation of this apparent photolysis reaction of silylarsine is planned.

The data reported here were obtained on a 12-107 Bendix Time-of-Flight mass spectrometer, operated in the pulsed ion mode, which has been modified[6] for appearance potential measurements. This modification, which takes advantage of the multiple analog output systems of the Bendix instrument, permits the chart drive of a two-pen recorder to be synchronized with the continuously decreasing voltage of the linear electron energy control. A start–stop timer was used to energize simultaneously the chart drive and the electron energy control drive motor. The electron energy control potentiometer was rotated by a synchronous 60-c motor, mechanically coupled to the potentiometer through a gear rack. It was possible to obtain the appearance potential curves for two ions (an ion from the hydride and argon, the internal standard used to calibrate the voltage scale) simultaneously in less than 2 min with this modification. The fragmentation pattern was obtained using 70-v electrons and an ionizing current of 0.125 μa.

Results and Discussion

Mass spectral data for silylarsine, arsine, and diarsine are shown in Table I. No mass spectral properties of the SiH_x^+ (x = 0–3) fragment ions of silylarsine are reported because the presence of tetrasilane makes the precursor of these ions ambiguous.

In order to calculate the dissociation energy and standard heat of formation for silylarsine from the data given in Table I, the following ancillary data are required (in kcal/mole): $\Delta H_f°(\cdot H) = 52.1$;[7] $\Delta H_f°(AsH_3) = 15.9$;[8] $\Delta H_f°(H_3SiSiH_3) = 17.1$;[9] $\Delta H_f°(SiH_4) = 7.3$;[9] $\Delta H_f°(H_2AsAsH_2) = 35.2$;[10] $\Delta H_f°(\cdot SiH_3) = 50.4$.[11] Although the relative abundances of all of the arsine ions and the appearance potentials for As^+ and AsH^+ agree well with the data previously published,[12] the appearance potentials for AsH_2^+ and AsH_3^+ in the two studies are in discord. It has been pointed out by Svec[13] that the appearance potentials for AsH_3^+ and AsH_2^+ cited in the earlier work[12] may have been for an excited state. This seems to be the case as the value for the ionization potential of AsH_3 reported here agrees well with the value of 10.6 ev cited by Kiser.[14]

The relationship between appearance potentials and heats of formation and bond energies is well known, as

TABLE I: SUMMARY OF RESULTS

Postulated ion source reaction	Rel abundance	ap,[a,b] ev	ap,[a,b] kcal/mole	Thermochemistry,[b] kcal/mole
$e^- + H_2As^{28}SiH_3 \longrightarrow As^{28}SiH_5^+ + 2e^-$	59.0	10.1 ± 0.1[c]	233	$\Delta H_f°(AsSiH_5^+) = ap + \Delta H_f°(H_2AsSiH_3) = 270$
$e^- + H_2As^{28}SiH_3 \longrightarrow As^{28}SiH_4^+ + H + 2e^-$	18.1	11.0 ± 0.3	254	$\Delta H_f°(AsSiH_4^+) = ap + \Delta H_f°(H_2AsSiH_3) - \Delta H_f°(\cdot H) = 239$
$e^- + H_2As^{28}SiH_3 \longrightarrow As^{28}SiH_3^+ + H_2 + 2e^-$	100	9.7 ± 0.1	224	$\Delta H_f°(AsSiH_3^+) = ap + \Delta H_f°(H_2AsSiH_3) - \Delta H_f°(H_2) = 261$
$e^- + H_2As^{28}SiH_3 \longrightarrow As^{28}SiH_2^+ + H_2 + H + 2e^-$	22.5	13.7 ± 0.2	316	$\Delta H_f°(AsSiH_2^+) = ap + \Delta H_f°(H_2AsSiH_3) - \Delta H_f°(H_2) - \Delta H_f°(\cdot H) = 301$
$e^- + H_2As^{28}SiH_3 \longrightarrow As^{28}SiH^+ + 2H_2 + 2e^-$	90.1	13.4 ± 0.1	309	$\Delta H_f°(AsSiH^+) = ap + \Delta H_f°(H_2AsSiH_3) - 2\Delta H_f°(H_2) = 346$
$e^- + H_2As^{28}SiH_3 \longrightarrow As^{28}Si^+ + 2H_2 + H + 2e^-$	41.6	16.8 ± 0.3	387	$\Delta H_f°(AsSi^+) = ap + \Delta H_f°(H_2AsSiH_3) - 2\Delta H_f°(H_2) - \Delta H_f°(\cdot H) = 372$
$e^- + H_2As^{28}SiH_3 \longrightarrow AsH_3^+ + {}^{28}SiH_2 + 2e^-$	0.1	13.1 ± 0.6	302	$\Delta H_f°(\cdot SiH_2) = ap + \Delta H_f°(H_2AsSiH_3) - \Delta H_f°(AsH_3^+) = 81$
$e^- + H_2As^{28}SiH_3 \longrightarrow AsH_2^+ + {}^{28}SiH_3 + 2e^-$	42.6	12.4 ± 0.2	286	$\Delta H_f°(H_2AsSiH_3) = \Delta H_f°(AsH_2^+) + \Delta H_f°(\cdot SiH_3) - ap = 37$ $D(H_2As\text{–}SiH_3) = ap - I(\cdot AsH_2) = 73$
$e^- + H_2As^{28}SiH_3 \longrightarrow AsH^+ + ? + 2e^-$	42.3	...	...	...
$e^- + H_2As^{28}SiH_3 \longrightarrow As^+ + ? + 2e^-$	56.1	...	...	...
$e^- + AsH_3 \longrightarrow AsH_3^+ + 2e^-$	70.2	10.5 ± 0.1	242	$\Delta H_f°(AsH_3^+) = ap + \Delta H_f°(AsH_3) = 258$
$e^- + AsH_3 \longrightarrow AsH_2^+ + H + 2e^-$	22.8	13.4 ± 0.2	309	$\Delta H_f°(AsH_2^+) = ap + \Delta H_f°(AsH_3) - \Delta H_f°(\cdot H) = 273$
$e^- + AsH_3 \longrightarrow AsH^+ + H_2 + 2e^-$	100	12.5 ± 0.2	288	$\Delta H_f°(AsH^+) = ap + \Delta H_f°(AsH_3) - \Delta H_f°(H_2) = 304$
$e^- + AsH_3 \longrightarrow As^+ + H_2 + H + 2e^-$	36.5	15.0 ± 0.3	346	$\Delta H_f°(As^+) = ap + \Delta H_f°(AsH_3) - \Delta H_f°(H_2) - \Delta H_f°(\cdot H) = 310$
$e^- + AsH_3 \longrightarrow AsH_3^{2+} + 3e^-$	0.04	...	...	...
$e^- + AsH_3 \longrightarrow AsH_2^{2+} + H + 3e^-$	0.3	...	...	...
$e^- + AsH_3 \longrightarrow AsH^{2+} + H_2 + 3e^-$	2.2	...	...	...
$e^- + AsH_3 \longrightarrow As^{2+} + H_2 + H + 3e^-$	1.5	...	...	...
$e^- + H_2AsAsH_6 \longrightarrow AsH_2^+ + AsH_2 + 2e^-$	...	12.9 ± 0.4	298	$\Delta H_f°(\cdot AsH_2) = ap + \Delta H_f°(H_2AsAsH_2) - \Delta H_f°(AsH_2^+) = 60$ $I(\cdot AsH_2) = \Delta H_f°(AsH_2^+) - \Delta H_f°(\cdot AsH_2) = 213$; $D(H_2As\text{–}AsH_2) = ap - I(\cdot AsH_2) = 85$

[a] Average of at least seven independent measurements determined by Warren's method of extrapolated differences: J. W. Warren, *Nature*, **165**, 811 (1950). [b] ap = appearance potential; $\Delta H_f°$ = standard heat of formation; I = ionization potential; D = dissociation energy; 1 ev = 23.06 kcal/mole. [c] Standard deviation.

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(6) R. S. Olfky and F. E. Saalfeld, "Report of NRL Progress," June 1965, p 56.

(7) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd., London, 1958, p 153.

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

(10) F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **2**, 50 (1963).

(11) F. E. Saalfeld and H. J. Svec, *ibid.*, **3**, 1442 (1964).

(12) F. E. Saalfeld and H. J. Svec, *ibid.*, **2**, 46 (1963).

(13) H. J. Svec in "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1966, p 245.

(14) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 308.

are the errors in this type of measurement.[12, 15] In using the data presented in Table I to calculate the heat of formation and bond dissociation, it has been assumed that the measured appearance potentials do not include excess kinetic or excitation energy. Since this assumption could not be tested experimentally, values cited here should be taken as a lower limit for the heat of formation and an upper limit for the bond dissociation energy. These values are 37 and 73 kcal/mole, respectively. The heat of formation of the $\cdot SiH_2$ radical, 81 kcal/mole, agrees within experimental error with the value of 72 kcal/mole cited by Vedeneyev, *et al.*[16] A comparison of the thermal properties of silylarsine and the $\cdot AsH_2$ radical with those reported earlier for silylphosphine and the $\cdot PH_2$ radical[11] shows that $D(H_2P–SiH_3)$ is more positive than $D(H_2As–SiH_3)$, agreeing with the concept that the bond energy decreases in a chemical group as the atomic number increases. The data also show that the ionization potential of silylarsine equals that of silylphosphine and the ionization potentials of the radicals $\cdot PH_2$ and $\cdot AsH_2$ are equal. The heat of formation of the ions of arsine, like those of ammonia and phosphine, become more positive with the stepwise removal of hydrogen. In the series of ions formed from silylarsine, the loss of one hydrogen atom from the molecular ion yields the ion with the least positive heat of formation; then the heat of formation of the ions becomes more positive with each succeeding loss of hydrogen. The same trend can be noted for the ions produced from the related compound, methylamine.[15]

[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.

[16] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Mednedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Publishers Ltd., London, 1966, p 135; C. J. O'Brien and J. R. Perrine, "Kinetics, Equilibria and Performance of High Temperature Systems," London, 1960.

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A Proton Magnetic Resonance Study of Some Alkylalkoxysilanes

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Proton magnetic resonance data for several series of alkylalkoxysilanes, $R_{n-4}Si(OR)_n$, together with Si^{29} data from the literature, indicate that inductive electron withdrawal and $(p-d)\pi$ bonding of oxygen to silicon both contribute to electron densities in the molecules. The inductive effect *per alkoxy group* decreases as the number of alkoxy groups increases while the π-bonding effect *per alkoxy group* is either unchanged or diminished to only a slight extent as the number of alkoxy groups increases. Replacement of one alkyl group in a tetraalkylsilane by an alkoxy group results in a *net* decrease but replacement of the second and remaining alkyl groups results in a *net* increase in electron density on silicon with corresponding changes in the electron densities on the alkyl and alkoxy protons. The importance of π-bonding effects in alkylalkoxysilanes is further indicated by a comparison of the chemical shifts of the methoxy protons in trimethylmethoxysilane and *t*-butyl methyl ether. Data on some alkylchlorosilanes indicate that inductive effects in alkylchlorosilanes dominate over any π-bonding effects.

In the course of an investigation of alkoxy–alkoxy exchange[2] in some alkylalkoxyboranes by proton magnetic resonance methods, the chemical shifts of the α protons of the alkoxy groups were taken as evidence of extensive π bonding between oxygen and boron in alkylalkoxyboranes.

The present study of four series of alkylalkoxysilanes was initiated in order to determine whether evidence for π bonding between oxygen and silicon in alkylalkoxysilanes could be obtained.

Experimental Section

Reagents.—Methyltrimethoxy-, methyltriethoxy-, dimethyldiethoxy-, trimethylethoxy-, tetramethyl-, and ethyltriethoxysilane, and the alkylchlorosilanes, were obtained in pure grade from Anderson Laboratories, Inc., Weston, Mich. Tetraethoxysilane was supplied by E. H. Sargent & Co., Chicago, Ill., and tetraethylsilane was obtained from K & K Laboratories, Jamaica, N. Y. The remaining alkylalkoxysilanes were prepared by the method of Emeléus and Robinson.[3] All compounds were purified by fractional distillation to give products with a boiling range of less than 0.2°.

Proton Magnetic Resonance Procedures.—Proton magnetic resonance spectra were obtained using a Varian Associates Model H-60, high-resolution, 60-Mc nmr spectrometer. Samples were sealed under dry nitrogen in 5×160 mm glass tubes. Chemical shifts were determined using the side-band technique with tetramethylsilane as an internal standard and were reproducible to 0.008 ppm.

Results

Intermolecular interactions were found to have no detectable influence on the chemical shifts of the protons in alkylalkoxysilanes. The spectra of the compounds were unchanged when concentrations in tetra-

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[1] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC document COO-38-492.

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