

are the errors in this type of measurement.<sup>12, 15</sup> 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  $\cdot\text{SiH}_2$  radical, 81 kcal/mole, agrees within experimental error with the value of 72 kcal/mole cited by Vedeneyev, *et al.*<sup>16</sup> A comparison of the thermal properties of silylarsine and the  $\cdot\text{AsH}_2$  radical with those reported earlier for silylphosphine and the  $\cdot\text{PH}_2$  radical<sup>11</sup> shows that  $D(\text{H}_2\text{P}-\text{SiH}_3)$  is more positive than  $D(\text{H}_2\text{As}-$

(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.

$\text{SiH}_3$ ), 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  $\cdot\text{PH}_2$  and  $\cdot\text{AsH}_2$  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.<sup>15</sup>

(16) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, 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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Received July 25, 1966

Proton magnetic resonance data for several series of alkylalkoxysilanes,  $\text{R}_{n-4}\text{Si}(\text{OR})_n$ , together with  $\text{Si}^{29}$  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  $\pi$ -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  $\pi$ -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  $\pi$ -bonding effects.

In the course of an investigation of alkoxy-alkoxy exchange<sup>2</sup> in some alkylalkoxyboranes by proton magnetic resonance methods, the chemical shifts of the  $\alpha$  protons of the alkoxy groups were taken as evidence of extensive  $\pi$  bonding between oxygen and boron in alkylalkoxyboranes.

The present study of four series of alkylalkoxysilanes was initiated in order to determine whether evidence for  $\pi$  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 Emel us and Robinson.<sup>3</sup> 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-

(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.

(2) P. A. McCusker and P. L. Pennartz, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 22-N.

(3) H. J. Emel us and S. R. Robinson, *J. Chem. Soc.*, 1592 (1947).

methylsilane and/or carbon tetrachloride ranged from 5 to 50%. The ethoxy protons gave simple  $A_3X_2$ -type signals. The signal for the ethyl protons in the ethylalkoxysilanes was a complex  $A_3B_2$  multiplet, having 18 distinctly observable peaks. The multiplet in every case begins within the region  $-0.253$ – $0.327$  ppm and terminates, for the ethylmethoxysilanes, in the region from  $-0.950$  to  $-0.968$  ppm. For the ethylethoxysilanes the exact termination is obscured by the superposition of the ethoxy triplet. The only observable variation in these series is a slight shift of those peaks which occur at high field.

Calculations<sup>4</sup> of theoretical spectra by an exact solution of the spin Hamiltonian for  $A_3B_2$  systems indicate that there are 39 possible transitions of which 18 are of relatively high intensity and 21 are of very low intensity. These results are in agreement with those of McGarvey and Slomp,<sup>5</sup> who analyzed the ethyl multiplet in tetraethylsilane.

In agreement with the results of McGarvey and Slomp calculations using  $J = 7.9$  cps and  $\delta = -0.425$  ppm ( $\delta = \nu_A - \nu_B$  for the  $A_3B_2$  system) give a theoretical spectrum satisfactorily matching the experimental spectrum for tetraethylsilane. A satisfactory theoretical spectrum for triethylmethoxysilane is obtained using  $J = 7.9$  cps and  $\delta = -0.388$  ppm.

The calculations place  $\nu_B$ , the chemical shift of the  $\alpha$  protons, between two experimental peaks but close (within 0.066 ppm) to the most intense of the  $\alpha$ -proton peaks, which is readily recognized as the third most intense peak of the ethyl multiplet. The value for the chemical shift of the  $\alpha$ -ethyl protons was obtained by adding  $-0.066$  ppm to the chemical shift of the most intense peak of the  $\alpha$  protons. The most intense peak in the ethyl multiplet is  $\nu_A$ , the chemical shift for the  $\beta$  protons. The chemical shifts for the various types of protons in the alkylalkoxysilanes, in ppm from tetramethylsilane, are listed in Table I.

### Discussion

The effect of successive replacement of alkyl groups by alkoxy groups in tetraalkylsilanes on the chemical shifts of  $Si^{29}$ , the alkyl protons, and the alkoxy protons is most clearly shown in the series  $(CH_3)_{4-n}Si(OC_2H_5)_n$ , for which  $Si^{29}$  chemical shifts are available in the literature.<sup>6</sup>

When one methyl group in tetramethylsilane is replaced by an ethoxy group there is a downfield shift of the  $Si^{29}$  resonance from  $-21$  to  $-27$  ppm, suggesting a decreased electron density on silicon. This is accompanied by a downfield shift of the methyl proton resonance from zero to  $-0.055$  ppm. The  $\alpha$ -alkoxy protons are at an expected lowfield position,  $-3.583$  ppm. These results indicate that replacement of one methyl group by ethoxy results in a net withdrawal of electron density from silicon presumably owing to the

(4) Grateful acknowledgment is made to Professor Louis Pierce for helpful discussions on the calculations and to Dr. Clarence H. Thomas for assistance in diagonalizing some matrices using the IBM 1620 computer at the Notre Dame Computing Center.

(5) B. R. McGarvey and G. Slomp, Jr., *J. Chem. Phys.*, **30**, 1586 (1959).

(6) See footnote b of Table I.

TABLE I

NMR CHEMICAL SHIFTS FOR ALKYLALKOXY-SILANES<sup>a</sup>

Compound	$Si^{29}$ <sup>b</sup>	$\alpha$ -Alkyl protons	$\beta$ -Alkyl protons	$\alpha$ -Alkoxy protons	$\beta$ -Alkoxy protons
$(CH_3)_4Si$	-21	0.000	...	...	...
$(CH_3)_3SiOC_2H_5$	-27	-0.055	...	-3.583	-1.122
$(CH_3)_2Si(OC_2H_5)_2$	-16	-0.025	...	-3.667	-1.153
$CH_3Si(OC_2H_5)_3$	+19	0.000	...	-3.725	-1.167
$Si(OC_2H_5)_4$	+59	...	...	-3.750	-1.193
$(CH_3)_3SiOCH_3$	...	-0.053	...	-3.317	...
$(CH_3)_2Si(OCH_3)_2$	...	-0.022	...	-3.393	...
$CH_3Si(OCH_3)_3$	...	0.000	...	-3.445	...
$Si(OCH_3)_4$	...	...	...	-3.468	...
$(C_2H_5)_4Si$	...	-0.658	-0.957	...	...
$(C_2H_5)_3SiOC_2H_5$	...	-0.706	-0.965	-3.620	-1.143
$(C_2H_5)_2Si(OC_2H_5)_2$	...	-0.679	-0.963	-3.697	-1.163
$(C_2H_5)Si(OC_2H_5)_3$	...	-0.653	-0.963	-3.750	-1.193
$(C_2H_5)_3SiOCH_3$	...	-0.704	-0.960	-3.372	...
$(C_2H_5)_2Si(OCH_3)_2$	...	-0.684	-0.962	-3.433	...
$C_2H_5Si(OCH_3)_3$	...	-0.659	-0.962	-3.468	...

<sup>a</sup> Values for the proton chemical shifts are in parts per million from tetramethylsilane. <sup>b</sup> Data from G. K. Holzman, P. C. Lauterber, J. H. Anderson, and W. Koth, *J. Chem. Phys.*, **25**, 127 (1956).

fact that inductive electron withdrawal exceeds any  $\pi$ -bonding contribution.

Replacement of a second methyl group by an ethoxy group, however, results in an upfield shift of  $Si^{29}$  resonance from  $-27$  to  $-16$  ppm and of the methyl proton resonance from  $-0.053$  to  $-0.022$  ppm suggesting that electron density on silicon has been increased by the action of the second ethoxy group to a value even higher than that in tetramethylsilane. This is interpreted to mean that the increased  $\pi$  bonding due to the second ethoxy group is much greater than the increased inductive effect. This viewpoint is supported by a downfield shift in the  $\alpha$ -proton resonance in the alkoxy group from  $-3.583$  to  $-3.667$  ppm. Presumably the inductive gain of electron density by oxygen is reduced when two alkoxy groups are present but the  $\pi$ -bonding loss is reduced little if at all. This results in a decreased electron density on oxygen and a resultant decreased electron density on the  $\alpha$  protons as indicated by a shift to lower field.

These effects appear to continue when a third methyl group is replaced by an ethoxy group. The  $Si^{29}$  resonance moves to still higher field,  $+19$  ppm, the methyl proton resonance also to higher field, 0.000, and the  $\alpha$ -ethoxy proton resonance to still lower field,  $-3.725$  ppm. That electron density on silicon increases still further on the replacement of the fourth methyl group by ethoxy is shown by the further upfield shift of the silicon resonance to  $+59$  ppm. A further decrease in electron density on oxygen is indicated by the downfield shift of the  $\alpha$ -proton resonance to  $-3.750$  ppm. These results are what would be expected if  $\pi$  bonding loss of electron density by oxygen continues with little or no decrease as successive replacement of methyl by alkoxy occurs, but that inductive electron withdrawal *per alkoxy group* is greatly diminished.

There is independent evidence in the literature from the work of West, *et al.*,<sup>7</sup> that there is a decrease in

(7) R. West, L. S. Whatley, and K. L. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).

electron density on oxygen in a series  $R_{n-4}\text{Si}(\text{OR})_n$ , as  $n$  increases. This evidence is based on the phenol O-H and pyrrole N-H stretching frequency shifts due to hydrogen-bond formation with members of the methylethoxysilane series.

The same trends in chemical shifts for alkyl and alkoxy protons are shown in the three other series for which data is given in Table I. An additional feature consistent with the interpretation given above becomes evident when one compares the extent of the downfield shift in the  $\alpha$ -proton resonance of the alkoxy group as successive replacement of alkyl by alkoxy occurs. If there is a considerable decrease in inductive withdrawal *per alkoxy group* as replacement proceeds, with little or no decrease in  $\pi$ -bonding contribution, one would expect that the differences in electron density on oxygen, as reflected in the differences in positions of the  $\alpha$  protons of the alkoxy groups, would steadily decrease from  $R_3\text{Si}(\text{OR})$  to  $\text{Si}(\text{OR})_4$ . These differences do decrease in all four series. In the case of the methyl-methoxy series the decrease is from 0.076 to 0.023 ppm. The differences in the last two members of the ethyl-

methoxy and ethylethoxy series become undetectable.

The importance of  $\pi$  bonding in alkylalkoxysilanes is further indicated by a comparison of the pmr spectra for trimethylmethoxysilane and its carbon analog, *t*-butyl methyl ether.<sup>8</sup> The methoxy proton singlet for trimethylmethoxysilane is at 0.200 ppm lower field than the methoxy proton singlet for *t*-butyl methyl ether in which no  $\pi$  bonding can occur. From inductive considerations alone one would expect that the methoxy protons in trimethylmethoxysilane would absorb at higher field than those in *t*-butyl methyl ether.

Replacement of a methyl group in tetramethylsilane by a chlorine, to give trimethylchlorosilane, causes the proton signal to move downfield by 0.363 ppm. Replacement of a second methyl group, to give dimethyldichlorosilane, causes a further downfield shift to -0.727 ppm. It thus appears that any  $\pi$ -bonding contribution from chlorine to silicon is insufficient to overcome the inductive effect.

(8) The authors thank Dr. John F. Deters for the pmr data on *t*-butyl methyl ether.

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## An Examination of Alkali Metal Salt Cleavage Reactions of Disilane

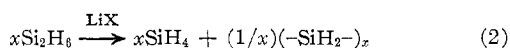
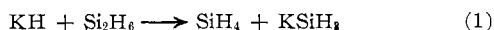
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Received August 1, 1966

Results are reported which demonstrate that the initial products from the reaction between potassium hydride or lithium deuteride and disilane are silane and a polymer, while the final products are silane and a metal silyl. Results from the reaction between lithium chloride and an equimolar mixture of disilane and disilane- $d_6$  suggest that this reaction involves a silene intermediate.

### Introduction

Reactions between disilane and several alkali metal salts in 1,2-dimethoxyethane have been reported.<sup>1,2</sup>



For the reaction presented by eq 2  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ . This latter reaction appears to be a base-catalyzed condensation similar to that reported for trisilylamine,<sup>3</sup> disilyl sulfide,<sup>4</sup> disiloxane,<sup>5</sup> and hexachlorodisilane.<sup>6</sup>

In this paper we report the results of an investigation of some aspects of the reactions between lithium deuteride, potassium hydride, and lithium chloride with

disilane in 1,2-dimethoxyethane. We have shown that the metal hydride reactions involve at least two steps. Reactions between lithium chloride and a mixture of disilane and disilane- $d_6$  have allowed us to eliminate some possible mechanisms for the salt-catalyzed condensations of disilane. In addition, we have proposed a mechanism which does fit our experimental data.

**1. LiD-Si<sub>2</sub>H<sub>6</sub> Reaction.**—The results from the reaction between disilane and lithium deuteride in 1,2-dimethoxyethane are listed in Table I. The silane and hydrogen not accounted for in Table I were assumed to be present as the solvent-insoluble polymer. The infrared spectrum of the silane obtained from the 1.5-hr run did not have an observable Si-D stretching frequency and was thus relatively pure SiH<sub>4</sub>. However, the products (and unreacted disilane) from the longer runs did contain slight amounts of silicon-deuterium bonds as evidenced by weak infrared absorptions in the silicon-deuterium stretching region.

It is known that silane- $d_4$  and the silyl anion exchange

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