electron density on oxygen in a series $R_{n-4}Si(OR)_n$, 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 α-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 π-bonding contribution, one would expect that the differences in electron density on oxygen, as reflected in the differences in positions of the α protons of the alkoxy groups, would steadily decrease from $R_3Si(OR)$ to $Si(OR)_4$. These differences do decrease in all four series. In the case of the methylmethoxy series the decrease is from 0.076 to 0.023 ppm. The differences in the last two members of the ethylmethoxy and ethylethoxy series become undetectable.

The importance of π bonding in alkylalkoxysilanes is further indicated by a comparison of the pmr spectra for trimethylmethoxysilane and its carbon analog, *t*-butyl methyl ether.[8] 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 π 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 π-bonding contribution from chlorine to silicon is insufficient to overcome the inductive effect.

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(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.[1,2]

$$KH + Si_2H_6 \longrightarrow SiH_4 + KSiH_3 \quad (1)$$

$$xSi_2H_6 \xrightarrow{LiX} xSiH_4 + (1/x)(\text{-}SiH_2\text{-})_x \quad (2)$$

For the reaction presented by eq 2 X = Cl, Br, or I. This latter reaction appears to be a base-catalyzed condensation similar to that reported for trisilylamine,[3] disilyl sulfide,[4] disiloxane,[5] and hexachlorodisilane.[6]

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_2H_6 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_4. However, the products (and unreacted disilane) from the longer runs did contain slight amounts of silicon–deuterium bonds as evidenced by weak infrared absorbances in the silicon–deuterium stretching region.

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

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TABLE I

$LiD-Si_2H_6$

mmoles							Time,
Si_2H_6 +	LiD $\longrightarrow$	SiH_4 +	Si_2H_6 +	$LiSiH_3$ +	$LiSi_2H_5$ +	$LiSi_3H_7$	hr
0.567	Excess	0.035	0.554	0	0	0	1.5
1.56	3.9	1.62	0.046	0.069	0.056	0.056	13
1.12	1.3	1.16	0.092	0.092	0.046	0.035	23

ligands.[1] Therefore the deuterium present in the products probably is the result of this exchange. Thus the reaction between disilane and lithium hydride can be represented by

$$xSi_2H_6 \xrightarrow{LiH} xSiH_4 + (1/x)(\text{-}SiH_2\text{-})_x \qquad (3)$$

$$LiH + (1/x)(\text{-}SiH_2\text{-})_x \longrightarrow LiSiH_3 \qquad (4)$$

$$LiH + (y/x)(\text{-}SiH_2\text{-})_x \longrightarrow LiSi_yH_{2y+1} \qquad (5)$$

For reactions 3 through 5 the relative rate of reaction 3 is much greater than that of reactions 4 and 5.

2. $KH-Si_2H_6$ Reaction.—The reaction between disilane and potassium hydride (in excess) in 1,2-dimethoxyethane was examined in a semikinetic fashion. Figure 1 shows the ratio of the quantity of each product (potassium silyl, silane, and dimethylsilane) to the quantity of disilane initially present plotted as a function of time. The silicon not accounted for as either potassium silyl or silane was assumed present as the solvent-insoluble polymer.

These results show that most of the potassium silyl was formed after all of the disilane had reacted. Thus the formation of potassium silyl from disilane must take place in at least two steps.

$$xSi_2H_6 \xrightarrow{KH} xSiH_4 + (1/x)(\text{-}SiH_2\text{-})_x \qquad (6)$$

$$KH + (1/x)(\text{-}SiH_2\text{-})_x \longrightarrow KSiH_3 \qquad (7)$$

The reaction represented by eq 6 is analogous to the condensation of disilane by lithium chloride and lithium deuteride.

The decrease in yield of silane with time is probably due to reaction between silane and products formed from the action of potassium hydride on the solvent. It is obvious that methyl groups in the dimethylsilane must come from the solvent. It has been reported that ethers react with hydridic bases to yield alcohols[7] which in turn can react with silane.[8]

3. $LiCl-Si_2H_6$ Reaction.—In an attempt to learn more about the salt-catalyzed condensation of disilane, we have examined the reaction between lithium chloride and an equimolar mixture of disilane and disilane-d_6 in 1,2-dimethoxyethane. The results obtained from this study are listed below. The first three experiments listed were required as control reactions.

(1) Disilane and disilane-d_6 do not exchange hydrogen atoms in this solvent.

(2) Silane and silane-d_4 do not exchange hydrogen atoms in the presence of lithium chloride dissolved in 1,2-dimethoxyethane.

(3) When disilane-d_6 reacts with lithium chloride in this solvent, the silane produced and the unreacted disilane remain completely deuterated.

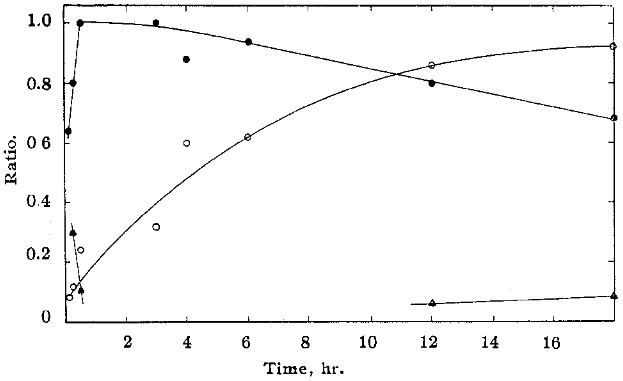

Figure 1.—Kinetic data for the reaction between disilane and potassium hydride. The ratio of the quantity of each product to the quantity of disilane initially present is plotted against time: ●, SiH_4; ○, $KSiH_3$; △, $(CH_3)_2SiH_2$; and ▲, Si_2H_6.

(4) When an equimolar mixture of disilane and disilane-d_6 reacted with lithium chloride, the silane fraction contained all five silanes, SiH_xD_{4-x} (x = 0–4), in about equal amounts. The disilane fraction contained deuterated disilanes in addition to disilane-d_6.

(5) When disilane reacted with lithium chloride in the presence of silane-d_4 the silane fraction now contained small amounts of silane-d_2 and silane-d_1. The disilane fraction also contained deuterated disilanes other than disilane-d_6.

Discussion

In 1,2-dimethoxyethane, disilane undergoes a condensation or redistribution reaction catalyzed by the bases lithium deuteride, potassium hydride, and lithium chloride.

$$xSi_2H_6 \xrightarrow{salt} xSiH_4 + (1/x)(\text{-}SiH_2\text{-})_x \qquad (8)$$

The relative rates are KH > LiD > LiCl. A second step occurs with the hydride salts (MH).

$$(1/x)(\text{-}SiH_2\text{-})_x + MH \longrightarrow MSiH_3 \qquad (9)$$

The relative rates are KH > LiD.

The results of the reaction between an equimolar mixture of disilane and disilane-d_6 with lithium chloride shed some light on possible mechanisms from the salt (base)-catalyzed condensations of disilane. Since the monosilane fraction produced in this reaction contained all of the possible species SiH_xD_{4-x} (x = 0–4), the condensation reaction must be intermolecular.

A possible mechanism for the condensation reaction would be one similar to that suggested by Urry[6] for amine-catalyzed reactions of hexachlorodisilane. This mechanism consists of the formation of a Lewis base polysilane complex followed by the exchange of a hydrogen atom from the complex with a silyl group from another polysilane. This mechanism predicts that silane, silane-d_1, silane-d_3, and silane-d_4 would be obtained in about equal amounts and that silane-d_2 would not be obtained in the reaction of a mixture of disilane and disilane-d_6 with lithium chloride. Our results suggest that this route cannot be the main mechanism.

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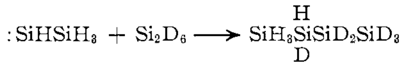
Another possible mechanism would involve silene moieties solvated or coordinated in some manner. Skell and Goldstein[9] have observed the insertion of dimethylsilene into the Si–H bond in trimethylsilane. Thus, a silene obtained from disilane could insert into an Si–H bond of a polysilane producing a larger polysilane which would undergo cleavage to other silanes and silenes. Such a mechanism would predict that the products from the lithium chloride catalyzed reaction of disilane and disilane-d_6 would be all five monosilanes, which is exactly what we observed. Thus a mechanism involving silenes will explain our results. The following series of equations is representative of the reactions involved in this general type of mechanism.

$$Si_2H_6 \xrightarrow{LiCl} :SiH_2 + SiH_4 \tag{10}$$

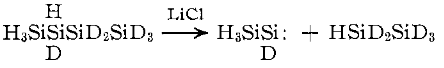
$$Si_2D_6 \xrightarrow{LiCl} :SiD_2 + SiD_4 \tag{11}$$

$$:SiD_2 + Si_2H_6 \longrightarrow HSiD_2SiH_2SiH_3 \tag{12}$$

$$HSiD_2SiH_2SiH_3 \xrightarrow{LiCl} H_2SiD_2 + :SiHSiH_3 \tag{13}$$



$$:SiHSiH_3 + Si_2D_6 \longrightarrow SiH_3\overset{H}{\underset{D}{Si}}SiD_2SiD_3 \tag{14}$$



$$H_3Si\overset{H}{\underset{D}{Si}}SiD_2SiD_3 \xrightarrow{LiCl} H_3Si\underset{D}{Si}: + HSiD_2SiD_3 \tag{15}$$

$$HSiD_2SiD_3 \xrightarrow{LiCl} :SiD_2 + HSiD_3 \tag{16}$$

etc.

This mechanism would also account for the formation of disilane molecules other than Si_2H_6 or Si_2D_6.

The mechanism involving a silene intermediate which we propose is analogous to one proposed for the thermal redistribution (condensation) reaction of 1,2-dimethoxytetramethyldisilane which produced dimethyldimethoxysilane and a polymer. In this reaction dimethylsilene was trapped by diphenylacetylene.[10] The lithium chloride–disilane reaction is the catalyzed thermal redistribution reaction of disilane.

Experimental Section

The reactions were carried out in Pyrex glass vessels of about 100-ml volume which were fitted with a Teflon needle valve and a ground joint to allow for transfer of reactants and volatile products to and from a standard vacuum system. All of the reactions were carried out at room temperature. Separations were made by trap-to-trap distillation through standard low-temperature slush baths.

The disilane and disilane-d_6 were prepared by the reduction of hexachlorodisilane with lithium aluminum hydride and lithium aluminum deuteride.[11] The 1,2-dimethoxyethane was dried by treatment of the solvent with potassium sand at −78°. It must be emphasized that the dryness of the solvent is very important. Even drying the solvent with molten potassium was not sufficient for this investigation. The starting materials and volatile products were identified by the use of infrared spectra and vapor pressure measurements. The infrared spectra of the deuterated silanes have been previously reported.[1,12] The infrared spectra were obtained in 10-cm gas cells on a Perkin-Elmer spectrophotometer, Model 137 or 337.

Lithium Deuteride–Disilane Reactions.—The reactions between lithium deuteride and disilane were carried out as follows. Lithium deuteride (obtained from Metal Hydrides, Inc.) was transferred to the reaction vessel in an inert-atmosphere glove bag. The reactor was evacuated on the vacuum system and about 7 ml of 1,2-dimethoxyethane and disilane (see Table I) were condensed into the reaction vessel at −196°. The reactor was then allowed to warm to room temperature. After a given time (Table I) the volatile products and the solvent were distilled off and separated. The analysis for lithium silyl and the lithium polysilanyls was made by treating the dry solid products with excess hydrogen chloride. The calculations were based on the assumption that lithium silyl and lithium polysilanyls react quantitatively to yield silane or the corresponding polysilane.

Potassium Hydride–Disilane Reaction.—The reactions between potassium hydride and disilane were carried out in the same manner as those with lithium deuteride. The potassium hydride was obtained as a 50% slurry in Bayol-85 from Metal Hydrides, Inc. This slurry was added to the reaction vessel which was then evacuated. About 5 ml of 1,2-dimethoxyethane was condensed into the slurry and this mixture was decanted into a side arm. The solvent was distilled back onto the potassium hydride slurry and the new mixture was decanted. The oil in the side arm was now sealed from the reaction vessel. The oil was removed to prevent it from coating the potassium silyl. Hydrogen chloride will not react with potassium silyl which is coated with oil. Fresh 1,2-dimethoxyethane and disilane were then condensed into the reaction vessel at −196°. Again the reaction was carried out at room temperature.

The analysis for potassium silyl was made by treating the solid product with hydrogen chloride and measuring the silane obtained. It is known that potassium silyl reacts quantitatively with hydrogen chloride to produce silane.[1]

Lithium Chloride–Disilane Reactions.—(1) Disilane (0.298 mmole) and disilane-d_6 (0.298 mmole) were treated with 7 ml of 1,2-dimethoxyethane for 168 hr. The disilane recovered (0.508 mmole) contained only infrared bands which could be assigned to disilane and disilane-d_6.

(2) Silane (0.311 mmole) and silane-d_4 (0.311 mmole) were also treated with 5 ml of 1,2-dimethoxyethane containing excess lithium chloride. The recovered silane (0.624 mmole) was a mixture of only silane and silane-d_4.

(3) Disilane-d_6 (0.576 mmole) was condensed into 7 ml of 1,2-dimethoxyethane containing excess lithium chloride. After 9.5 hr the volatile silicon compounds found were silane-d_4 (0.092 mmole) and disilane-d_6 (0.508 mmole).

(4) The above experiment was repeated using disilane (0.576 mmole) and disilane-d_6 (0.576 mmole). After 7.5 hr a silane fraction (0.346 mmole) was obtained. The relative concentrations in this mixture were $SiH_2D_2 > SiH_3D \cong SiHD_3 \cong SiD_4 \cong SiH_4$. This analysis was based on an infrared spectrum of the silane mixture. The disilane fraction did contain molecules other than disilane and disilane-d_6. Detection of deuterated disilanes other than disilane-d_6 was based on observing the 850-cm^{-1} triplet of disilane at 808 and 896 cm^{-1} in the infrared spectrum of the disilane fraction. However, since infrared spectra are not reported for the other deuterated disilanes, an analysis of the disilane fraction could not be made.

(5) Disilane (0.657 mmole) and silane-d_4 (0.426 mmole) were condensed into 5 ml of a 1,2-dimethoxyethane solution of excess lithium chloride. After 17 hr, a silane fraction (0.657 mmole) and a disilane fraction (0.426 mmole) were obtained. The silane fraction contained mostly silane and silane-d_4, but silane-d_1 and silane-d_2 were present. The disilane fraction did contain some deuterated disilanes.

Acknowledgment.—The authors are indebted to the U. S. Army Research Office (Durham) for financial support.

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