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REACTIONS OF ATOMIC SILICON II:
OBSERVATIONS ON THE REACTIVITY OF SILENE INTERMEDIATES

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In the course of examining reactions of silicon atoms with a wide variety of substrates, we have found that monatomic silicon reacts, in the majority of cases studied, to form intermediate silenes. We report here the observation of intermediates of two different types of reactivity.

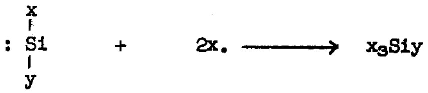
The apparatus used was basically the same as that described previously for the study of carbon atom chemistry.[1] Reactions were carried out by simultaneously depositing silicon vapor and a large excess (100 to 500 fold) of a substrate on the liquid nitrogen cooled walls of an evacuated reaction flask. Silicon vapor was produced by electron bombardment heating or by resistive heating of a silicon electrode. Co-depositions were carried out under pressures low enough ($< 1 \times 10^{-4}$ Torr) to essentially preclude vapor phase collisions of silicon atoms and substrate molecules. Thus, reactions occurred in the cold, condensed phase at the walls of the system.

We have previously reported that the reaction of silicon atoms with trimethylsilane produced 1,1,1,3,3,3-hexamethyltrisilane in $\sim$30% yield.[2] Formation of this product was rationalized by an initial silicon atom insertion into a substrate Si-H bond to form trimethylsilylsilene, followed by insertion of the silene into the Si-H bond of another substrate molecule to form the trisilane. Similarly, Kirk and Timms[3] have postulated the formation of bis(difluoroboro)silene as an intermediate in the reaction of silicon atoms with B_2F_4.

We have found that relatively good yields of di-substituted silanes and large quantities of substituted polysilanes are obtained from silicon atom reactions with a number of substrates. In all of these reactions, the product distributions were best explained by the formation of an intermediate silene which then reacts by two competing processes to form stable products: insertion into another substrate molecule or polymerization to a polysilane.

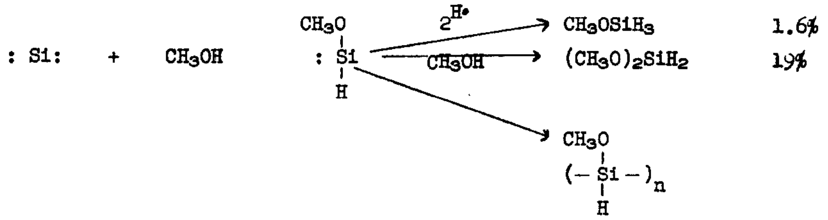
$$(-\mathrm{SiXY-})_n \longleftarrow\!\!\!-\!\!\!-\!\!\!- \ :\mathrm{SiXY} \xrightarrow{xy} \mathrm{SiX_2Y_2}$$

In some cases, radical abstraction was available, to a minor extent, as another route to stable products.



$$:\underset{y}{\overset{x}{Si}} \quad + \quad 2x\cdot \longrightarrow x_3Siy$$

From the reaction of silicon atoms with methanol, mono- and dimethoxysilane were recovered along with a methoxy-substituted polysilane.



Similarly, di-substituted monosilanes and substituted polysilanes were obtained from reactions with hydrogen chloride, hydrogen bromide, disilane, methylsilane, and dimethylsilane.

One of the striking features of these reactions was that only monosilanes and non-volatile polysilanes was produced, with little or no product which corresponded to intermediate chain length polymeric species; i.e., disilanes and trisilanes from the coupling of only two or three silene units. Normally, one would expect the polymerization of a reactive intermediate to result in a continuous distribution of polymer chain lengths in the product mixture. Thus, a high yield of monomeric product would lead one to expect relatively large amounts of dimer and trimer. The observation of only monomeric product and non-volatile polymer with the almost complete absence of intermediates of two different types of reactivity must have been present in silicon atom reactions.

It is reasonable to assume that polymerization of silene intermediates in our system occurs as is described by Margrave for the polymerization of singlet SiF_2 to give triplet diradicals.[4] The fact that intermediate chain length species were not formed in our system

$$\uparrow\downarrow SiF_2 \xrightarrow{SiF_2} \uparrow\dot{S}iF_2\dot{S}iF_2\uparrow \xrightarrow{SiF_2} \uparrow\dot{S}iF_2SiF_2\dot{S}iF_2\uparrow \xrightarrow{SiF_2} \text{etc.}$$

indicates that radical abstraction was not a facile chain terminating process. The intermediate silene responsible for the formation of monosilane products must, then, have been considerably more reactive than the triplet diradicals formed by silene polymerization, suggesting that it was in the singlet state.

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