addition. Proton abstraction from this silene yields the silicon analogue of the isobutene anion. Its chemical behavior indicates that it is more highly stabilized than either the isobutene anion or $Me_3SiCH_2^-$. Attempts to measure the acidity of dimethylsilene, while not wholly successful, have established that it is more acidic than isobutene.

Cycloaddition reactions of dimethylsilene with O_2 and butadiene have been attempted. Oxygen appears to react to give dimethylsilanone, which has been detected as its deprotonated anion. Reaction with butadiene may occur, but products have only been detected in a stream of F^-.

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Note Added in Proof. A recent report on $Me(CH_2^-)$-Si=O has been published: Tumas, W.; Saloman, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2541.

Registry No. $Me_2Si{=}CH_2$, 4112-23-6.

Gas-Phase Ion Chemistry of Dimethylsilylene

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A pyrolysis port fitted to the flowing afterglow instrument has been used to prepare dimethylsilylene. Its ion–molecule chemistry has been explored by reaction with fluoride and amide ions. Fluoride ion adds to dimethylsilylene giving an adduct anion which has been characterized by reaction with nitrous oxide. Amide ion abstracts a proton from dimethylsilylene. Characterization of the resulting M − 1 ion has been made by reaction with carbon disulfide and various acids. The gas-phase acidity of this anion has been determined to be near that of methanol (379 kcal/mol). The isomerization of dimethylsilylene and methylsilene has been probed by fluoride ion followed by nitrous oxide reaction. We have also demonstrated at the highest temperatures we can study that methylsilene slightly predominates over dimethylsilylene. Reaction of dimethylsilylene and butadiene has also been studied.

Introduction

Silylene chemistry has been actively pursued since the mid-1960s, undoubtedly the result of the tremendous interest in the chemistry of carbenes.[2] One of the first indications of the preparation of dimethylsilylene was provided by Gilman and co-workers in its reverse Diels–Alder extrusion from several bicyclic precursors.[3] Subsequently, dimethylsilylene has been prepared by a variety of methods with its extrusion from disilanes being one of the most reliable preparative methods for thermal generation.[2-4] Studies of silylenes of recent vintage have examined in detail their reactivity, structure, and theoretical characterization,[2] culminating most recently in the resolution of the conflicting reports on the equilibrium between dimethylsilylene and methylsilene.[5]

Our interest in dimethylsilylene focuses on its chemistry with anionic reagents in the gas phase. Previous work using the flowing afterglow (FA) techniques has provided a wealth of novel chemistry of organosilicon compounds.[6] We have not only examined the reactivity of organosilicon compounds but also utilized them both to prepare unusual gas-phase species and to examine important fundamental questions in gas-phase chemistry. We sought, then, to apply the powerful FA technique to the chemistry of dimethylsilylene and to study its reactions with anions and neutral molecules as well as its acid–base behavior.

Experimental Section

These experiments were performed in a flowing afterglow system at 298 K as previously described[7] with one modification. A port at 90 cm has been added to allow the introduction of neutral pyrolysates. Thus, neutral reactants are passed through a quartz tube wrapped with resistance wire. The resulting pyrolysis mixture is swept into the flow tube by the normal flow of helium bath gas although additional helium flow can be directed through the quartz tube when necessary. The resistance heater is controlled by a variable transformer, and approximate temperatures are measured by using a chromel–alumel thermocouple inserted in a small indentation at the end of the quartz tube. Further details of the pyrolysis system are reported in the companion paper.[6e]

Amide and fluoride ions were produced by electron impact on NH_3 and NF_3, respectively, HO^- was produced by dissociative electron attachment to N_2O followed by hydrogen atom ab-

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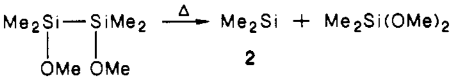
straction from CH_4, and CH_3O^- was produced by reaction of H_2N^- with dimethoxyethane. Typical helium pressures and flow rates were 0.4 torr and 140 STP cm^3/s, respectively. Neutral reactants were obtained from commercial suppliers; their flow rates were measured by monitoring the pressure increase with time into a calibrated volume. Rate constants were measured by following reactant ion counts as a function of reaction distance.

The identity of product ions was determined not only from mass-to-charge ratios but also by reaction with various neutral molecules like N_2O, CO_2, CS_2, and COS (see Results and Discussion and ref 6 for additional details). Since neutral products are not detected in the FA, their identity has been inferred from knowledge of the reactants and the observed anionic products.

Results and Discussion

The dimethylsilylene (2) used in these experiments was prepared by pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (1) (eq 1). Because of the configuration

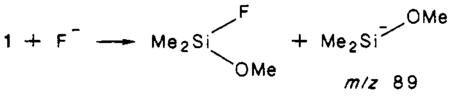


$$\underset{\text{OMe}}{Me_2Si}-\underset{\text{OMe}}{SiMe_2} \xrightarrow{\Delta} Me_2Si + Me_2Si(OMe)_2 \quad (1)$$

1

of the pyrolyzer, it was not possible to determine the exact temperature at which pyrolysis was occurring. We, therefore, separately studied both 1 and $Me_2Si(OMe)_2$ with the pyrolyzer turned off, examining their ambient-temperature ion–molecule reactions. We then raised the temperature until product ions which could be ascribed as arising from dimethylsilylene were observed. Both F^- and H_2N^- were used to probe the extent of this pyrolysis. At present we cannot assess whether the neutrals produced by pyrolysis react in vibrationally excited states or are cooled by reaction with helium buffer gas before reaction.

At room temperature 1 reacts with F^- to cleave the silicon–silicon bond and form an ion of mass 89 (eq 2).

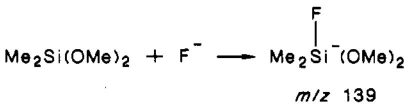


This type of cleavage is expected; we have demonstrated an analogous reaction with hexamethyldisilane to form the trimethylsilyl anion. It is important to understand that we have characterized ions like $Me_2(MeO)Si^-$ by reaction with various neutral reagents as described in detail later and in ref 6e. Thus, the isomeric ion Me_3SiO^- has been ruled out because downstream reaction of the m/z 89 ion with CO_2 and CS_2 yield $Me_2(MeO)SiO^-$ and $Me_2(MeO)SiS^-$, respectively.

As the pyrolysis temperature is increased, the m/z 89 ion decreases in intensity and a new ion at m/z 77 appears. We ascribe this ion to the product of addition of F^- to dimethylsilylene (or to its isomer methylsilene, 3, see below) (eq 3). No ion of this mass appears in the spectra

$$Me_2Si + F^- \rightarrow Me_2\bar{Si}F \quad (3)$$

at room temperature. We also see new ions at mass 139 which corresponds in mass to the product of addition of F^- to dimethyldimethoxysilane (eq 4), the other expected



$$Me_2Si(OMe)_2 + F^- \longrightarrow \underset{m/z\ 139}{Me_2\overset{F}{Si^-}(OMe)_2} \quad (4)$$

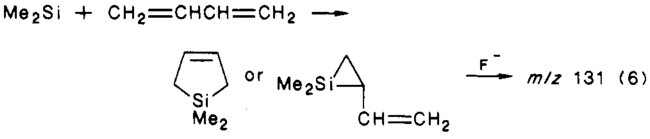
product of pyrolysis of 1 (eq 1), and at m/z 135 (a small signal) which can plausably be assigned to the addition of fluoride ion to one of the accessible isomers which are expected to be formed by dimerization of dimethylsilylene or methylsilene.[5] Although it is difficult to compare the conditions of our experiments with those summarized in ref 5, we believe that it is reasonable to assume that the relative amounts of dimethylsilylene and methylsilene and their dimers are similar to that found previously.[5a,b] Another possibility pointed out by a reviewer involves reaction of $Me_2(F)Si^-$ and dimethylsilylene to form $Me_2(F)SiSiMe_2^-$. We cannot rule out such a possibility but wish to emphasize that the m/z 135 signal is quite small compared to those at m/z 77 and 139.

Although simple addition reactions are rare in gas-phase ion chemistry because the product ions still contain the reaction exothermicity and hence dissociate, F^- reactions with silicon compounds are an exception. For example, F^- reacts with tetramethylsilane on every collision to form the pentacoordinate anion Me_4SiF^-. Apparently the silicon fluorine bond is sufficiently strong so that the adduct lives long enough to collide with helium buffer gas and thus cool itself.

When H_2N^- is used as the reactant ion at high pyrolysis temperatures, we observe an ion at mass 57. This corresponds in mass to the M − 1 ion of dimethylsilylene (eq 5). As a further probe of the presence of dimethylsilylene,

$$Me_2Si + H_2N^- \rightarrow \underset{m/z\ 57}{MeSiCH_2^-} + NH_3 \quad (5)$$

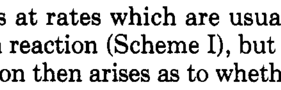
we carried out the copyrolysis of 1 and butadiene. Dimethylsilylene is known to add to butadiene. When this copyrolysis was carried out and added to a F^- stream, an ion of mass 131, corresponding in mass to the F^- adduct of 4, was observed (eq 6). Taken together these results



4

certainly suggest that we have succeeded in pyrolyzing 1 to form, at least initially, dimethylsilylene (2). In turn we have been able to generate an anion which corresponds in mass to its M − 1 ion by proton abstraction and to its fluoride adduct by reaction with F^-. We, therefore, set out to investigate the structure of these ions in greater detail.

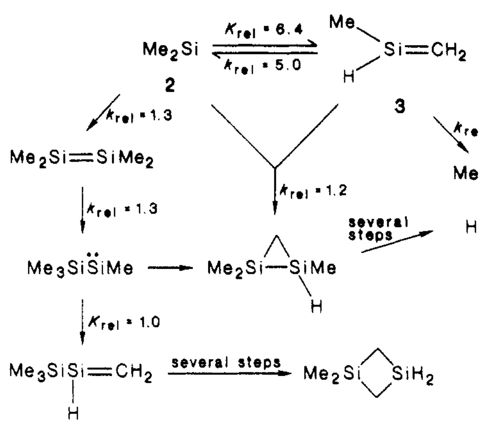
The Isomerization of Dimethylsilylene (2). The isomerization of dimethylsilyene (2) to methylsilene (3) (eq 7) has been a controversial matter in the chemistry of



3

organosilicon reaction intermediates until its recent resolution.[5] It now seems certain that 2 and 3 can interconvert readily at high temperatures, that their interconversion is nearly thermoneutral, though slightly favoring 3, and that each isomer can be "funnelled off" to a variety of dimeric products at rates which are usually slower than the isomerization reaction (Scheme I), but still reasonably high. The question then arises as to whether the products we observe come from dimethylsilylene (2), from methylsilene (3), or from a mixture of these two isomers (remember, we do see minor amounts of dimeric F^- adducts). If we could establish that the ions we observe do, indeed, arise from dimethylsilylene (2), we might then raise the pyrolysis temperature and, perhaps, observe the onset of the interconversion of the two isomers, thus using our FA as a chemical ionization probe of this rearrangement. Ion–molecule reactions would be particularly suited for this type of analysis since they occur rapidly with rate constants

Scheme I



at 850 K starting from Me₂Si

typically an order of magnitude greater than even diffusion-controlled neutral reactions. Indeed, when this equilibrium is probed with neutral reagents, it is common for the equilibrium to be disturbed by the reagent and one or the other of the isomers to be "funnelled off".[5]

We have shown that a variety of anions could be distinguished in the FA by reaction with either N_2O, CO_2, COS, or CS_2. Thus, trimethylsilyl anion reacts with N_2O and CO_2 in an oxygen transfer reaction giving a net m/z increase of 16 (eq 8) and with COS and CS_2 by sulfur transfer (eq 9). In contrast, its isomer, $\mathrm{Me_2(H)SiCH_2^-}$,

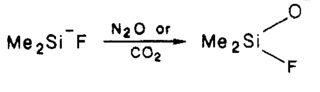
$$\mathrm{Me_3Si^-} \xrightarrow[\mathrm{CO_2}]{\mathrm{N_2O\ or}} \mathrm{Me_3SiO^-} \qquad (8)$$

$$\mathrm{Me_3Si^-} \xrightarrow[\mathrm{CS_2}]{\mathrm{COS\ or}} \mathrm{Me_3SiS^-} \qquad (9)$$

reacts with N_2O by oxygen transfer with simultaneous loss of neutral diazomethane giving a net m/z increase of 2 (eq 10).

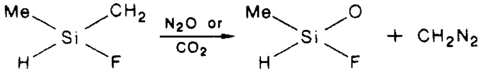
$$\mathrm{Me_2(H)SiCH_2^-} \xrightarrow{\mathrm{N_2O}} \mathrm{Me_2(H)SiO^-} + \mathrm{CH_2N_2} \qquad (10)$$

We have used these reagents to probe the dimethylsilylene–methylsilene equilibrium. At low pyrolysis temperatures (between approximately 320 and 370 °C) the ion of mass 77, obtained when the pyrolyzed dimethylsilylene precursor 1 enters the flow tube and reacts with F^- (eq 3), is converted to a new ion at m/z 93 when either N_2O or CO_2 is added. As the pyrolysis temperature increases, reaction with F^- produces another signal (m/z 79). At the highest pyrolysis temperatures we can reach (approximately 470 °C), somewhat greater quantities of the m/z 79 ion result. These data indicate that at low pyrolysis temperature, where $\mathrm{Me_2Si}$ predominates, its F^- adduct reacts with CO_2 or N_2O (eq 11) to give $\mathrm{Me_2Si(F)O^-}$ (m/z 93). As the pyrolysis temperature increases, the rate of isomerization increases and methylsilene becomes a significant component of the reaction mixture. Its reaction with F^- and subsequently with CO_2 or N_2O gives rise to the ion of mass 79 (eq 12). The relative rates of the "funneling off" reactions leading to the dimers of dimethylsilylene and methylsilene (Scheme I) show that they are fairly slow relative to the isomerization of dimethylsilylene and methylsilene (eq 7).[5] We thus have observed the dimethylsilylene–methylsilene products without significant interference from the dimeric products. We attribute this not only to the fact that there are only small amounts of dimeric species present but also to the possibility that reaction with them may give only very small product signals. That is what we have observed with a closely related compound. Reactions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and both F^- and H_2N^- at ambient temperature lead to very small product signals under a variety of conditions. Thus, though we have a clear view of the dimethylsilylene–methylsilene isomerization, we are unable to refine the other complexities of this system.



$$\mathrm{Me_2Si^-F} \xrightarrow[\mathrm{CO_2}]{\mathrm{N_2O\ or}} \mathrm{Me_2Si(O^-)F} \qquad (11)$$

m/z 93



$$\mathrm{Me(H)Si(F)\bar{C}H_2} \xrightarrow[\mathrm{CO_2}]{\mathrm{N_2O\ or}} \mathrm{Me(H)Si(F)O^-} + \mathrm{CH_2N_2\ or\ CH_2CO} \qquad (12)$$

m/z 79

Acidity Studies on the Dimethylsilylene–Methylsilene Equilibrium. We have studied the M – 1 ion (m/z 57) which is formed when the approximately 400 °C pyrolysate reacts with H_2N^- in the flow tube. At this temperature dimethylsilylene (**2**) predominates over methylsilene (**3**) by about tenfold. The M – 1 ion (**5**) is expected to be mainly a resonance hybrid formed from dimethylsilylene (eq 13). This ion is unreactive with CO_2 and COS

$$\mathrm{Me_2Si + H_2N^- \rightarrow MeSiCH_2^-} \underset{\mathbf{5}}{\leftrightarrow} \mathrm{Me\bar{S}i{=}CH_2} \qquad (13)$$

but gives a product ion at m/z 75 with CS_2 (eq 14). It

$$\mathbf{5} \xrightarrow{\mathrm{CS_2}} \mathrm{MeSiS^-} \qquad (14)$$

seems remarkable that the anionic species produced in reaction with H_2N^- is so unreactive. As a result we have asked Professor M. S. Gordon to perform ab initio calculations on this anion. Some preliminary results suggest that the negative charge in **5** is highly delocalized with significant negative charge buildup on silicon relative to the neutral parent. The actual Mulliken charge on silicon is also slightly negative. This would, of course, explain its attenuated reactivity. Full details of these calculations will be published at a later date.

Acidity measurements on the pyrolysate at approximately 400 °C were carried out. It can be clearly demonstrated that the m/z 57 ion does not abstract a deuteron from D_2O, thus putting an upper limit of 391 kcal/mol on the acidity of the mixture. Other experiments were somewhat ambiguous, since reaction with MeOD ($\Delta H°_{\mathrm{acid}}$ = 379 kcal/mol) gave some signal diminution while the reverse reaction between the silylene–silene mixture and $\mathrm{MeO^-}$ also occurred. These experiments are fraught with the same difficulties we experienced from the anion of dimethylsilene.[6e] Thus, the small signal intensities coupled with the other anionic and neutral species present in the flow tube suggest that accurate acidity measurements must await the completion of the SIFT apparatus currently under construction.[6e] Nevertheless, we believe that the acidity of this mixture is close to that of MeOH.

Conclusion

We have been able to generate both dimethylsilylene at low temperatures and mixtures of varying composition of dimethylsilylene and methylsilene at higher temperatures. As we approach the temperature limit of the pyrolyzer, the pyrolysate contains a predominance of methylsilene. This isomerization has been studied by reaction with F^-. Characterization of the F^- products has been achieved with either N_2O or CO_2.

Deprotonation of the isomeric mixture has been accomplished by using H_2N^- followed by characterization of the resulting mixture with CS_2. The lack of reactivity of the anion corresponding to proton loss from dimethylsilylene has been attributed to significant negative charge delocalization to silicon. Attempts to measure the acidity of dimethylsilylene have met with marginal success and suggest that its acidity is close to that of MeOH.

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Registry No. 1, 10124-62-6; 2, 6376-86-9; N_2O, 10024-97-2; CO_2, 124-38-9; CS_2, 75-15-0; COS, 463-58-1; NH_2^-, 17655-31-1; F^-, 16984-48-8.

π-Bond Strengths in Main-Group Olefin Analogues

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π-Bond strengths in main-group olefin analogues $H_2X{=}CH_2$ (X = C, Si, Ge, Sn) have been obtained theoretically from direct energy differences between planar (π-bonded) and perpendicular (biradical) structures and, according to a procedure proposed by Benson, from the energies of disproportionation of the products of hydrogen atom addition. Both methods yield nearly the same π-bond strengths: C═C, 64–68 kcal mol^{-1}; C═Si, 35–36 kcal mol^{-1}; C═Ge, 31 kcal mol^{-1}; C═Sn, 19 kcal mol^{-1}. The similarity of π-bond energies for silaethylene and germaethylene is rationalized in terms of d-block contraction.

Introduction

Very few compounds exist which incorporate multiple bonds between carbon and its heavier main-group analogues. In fact, only for silicon have stable, isolable compounds with double bonds to carbon been prepared. Among the simplest of these are 1,1-dimethylsilaethylene and parent silaethylene, both of which have now been detected in the gas phase.[1-3] An electron diffraction study of the former[3] has suggested a silicon–carbon double-bond length of 1.83 Å, not markedly shorter than typical single linkages, e.g., 1.875 Å in tetramethylsilane.[4] Significantly shorter bond distances have, however, been reported from X-ray crystal structures of $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl) (Si═C = 1.764 Å)[5] and both a tetrahydrofuran adduct of $Me_2Si{=}C(SiMe_3)[Si(Me)(t\text{-}Bu)_2]$ (Si═C = 1.747 Å)[6a] as well as the corresponding tetrahydrofuran-free complex (Si═C = 1.702 Å).[6b] These data, together with the results of high-level quantum chemical calculations[7,8b,c] which suggest Si═C bond lengths in the vicinity of 1.70 Å in simple silaolefins, cast doubt on the validity of the bond distance obtained in the electron diffraction work.

A number of experimental and theoretical estimates of π-bond energies for compounds incorporating double bonds between carbon and silicon have appeared in the literature.[7e,8] These estimates, for the most part based on comparisons with hypothetical singlet biradicals, i.e., incorporating twisted double bonds, are in the range of 34–46 kcal mol^{-1} and are to be compared with an experimentally determined π-bond strength of 65 kcal mol^{-1} in ethylene (obtained from the rate of cis–trans isomerization in 1,2-dideuterioethylene[9]). The highest level theoretical work[7e] is in accord and suggests an energy difference of 37 kcal mol^{-1} between planar silaethylene and a twisted singlet biradical. Very little experimental data exist for compounds incorporating double bonds between carbon and its main-group analogues beyond silicon. Pietro and Hehre[8d] have estimated π-bond strengths of 43, 45, and 30 kcal mol^{-1} in 1,1-dimethylgermaethylene, 1,1-dimethylstannaethylene, and 1,1-dimethylplumbaethylene, respectively, on the basis of gas-phase deprotonation thresholds for trimethylgermyl, trimethylstannyl, and trimethylplumbyl cations. These authors have noted, however, that the values for the germanium and tin systems appear to be out of line with the π-bond strengths in silicon compounds and have cautioned about their dependence on ancillary experimental thermochemical data of uncertain quality. The only previous theoretical estimate for the π-bond strength in germaethylene, 29 kcal mol^{-1} from a pseudopotential SCF method,[10] is, as might

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