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SOME GAS PHASE REACTIONS OF SILICENIUM IONS DERIVED FROM *sym*-TETRAMETHYLDISILOXANE

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Summary

Ion cyclotron resonance spectroscopy has been used to study reactions of the silicenium ions, $Me_2HSiOSiMeR$ (R = H and Me), generated from *sym*-tetramethyldisiloxane in the gas phase. These silicenium ions react with neutral *sym*-tetramethyldisiloxane by an addition—elimination process, to form the homologous silicenium ions, $H(Me_2SiO)_nSiMeR$ (n = 2 and 3). Analogous addition—elimination products, $MeO(Me_2SiO)_nSiMeR$, are derived from their reaction with methanol. Bimolecular adducts are observed in the presence of benzene and anisole, while oxygen abstraction occurs in the presence of anisole and acetone.

Many attempts to establish the existence of the silicon analog of the familiar carbenium ion have been made [1, 2]. Yet, after numerous mechanistic and spectroscopic studies, there is still no concrete evidence to suggest that the silicenium ion* has even a transient existence in solution. This reluctance of silicon to form silicenium ion has been attributed [8, 9] to diminished stabilization derived from π—π and σ—π conjugation between the vacant silicon orbital and substituents (e.g., aryl, alkyl, oxygen), to the availability of energetically more favorable kinetic processes for silicon [1, 2], and, in "magic acid" studies, to the very high affinity of silicenium ions for oxygen and fluorine ligands [10, 11]. In contrast, appearance potential measurements [12] have

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* The nomenclature recommended by Olah [3] is adopted in this paper and usefully serves to distinguish between the trivalent silicenium ion and the pentacovalent siliconium ion [4-7].

shown that silicenium and carbenium ions are formed with comparable facility in the gas phase, and recent mass spectroscopic studies have revealed a number of interesting rearrangements and fragmentations involving R_3Si^+ species [13-21]. Most of the observed gas phase reaction have been intramolecular processes and little is known about the ability of the silicenium ion to participate in bimolecular processes [22-24]. As others have recognized [25], ion cyclotron resonance (ICR) spectroscopy is a useful technique for studying the gas phase chemistry of ionic silicon compounds. We report here on some ion—molecule reactions of R_3Si^+ derived from *sym*-tetramethyldisiloxane using this technique.

Experimental

A Varian V-5900 ICR Spectrometer equipped with a standard 3-section flat cell, grid modulation, split drift voltages, and a 20 l/s Noble Ion pump, was employed. All compounds were degassed at least three times by a freeze-pump-thaw cycle. The ionizing voltage was varied between 11 and 15 eV. Double resonance experiments were carried out by the standard technique [26, 27] when the intensity and resolution of the ions permitted.

sym-Tetramethyldisiloxane and hexamethyldisiloxane were prepared by hydrolysis of the corresponding chlorosilanes. Other compounds were obtained from commercial sources. All compounds were purified by distillation and their purity verified by GLC.

Results and discussion

sym-Tetramethyldisiloxane

The ICR cation spectra of this compound at 8 and 100 μtorr, obtained using an ionizing voltage of 11 eV, are summarized in Table 1. Double resonance experiments established the relationships:

$$119^+ \rightarrow 193^+;\ 133^+ \rightarrow 267^+ \rightarrow 207^+$$

The ions with *m/e* 119 and 133 can be assigned unambiguously to the silicenium ions $Me_2HSiOSiMeH$ (I) and $Me_2HSiOSiMe_2$ (II), formed from the parent molecular ion by loss of Me· and H·, respectively [13-21]. The remaining four ions, whose relative intensities increase with pressure, arise from the reaction of

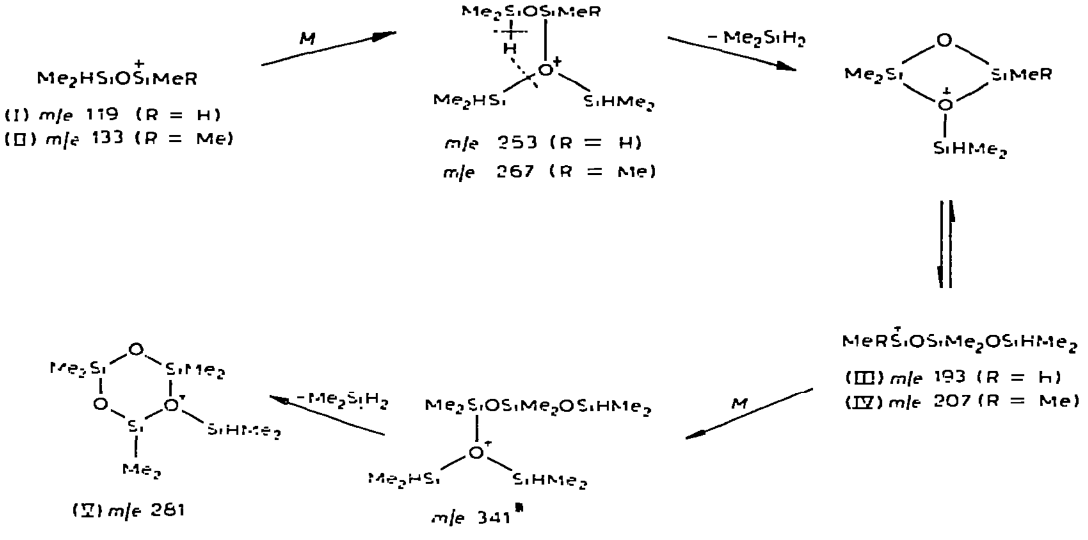
TABLE 1

ICR SPECTRUM OF *sym*-TETRAMETHYLDISILOXANE

m/e	Relative intensity (%)	
	8 μtorr	100 μtorr
119	13	1
133	41	3
193	6	8
207	40	78
267	0	7
281	0	2

SCHEME 1

ION MOLECULE REACTIONS OF *sym*-TETRAMETHYLDISILOXANE



* Postulated but unobserved intermediates

I and II with neutral $(Me_2HSi)_2O$. The proposed structures of these ions are shown in Scheme 1 and are based on the double resonance experiments, the nucleophilicity of oxygen and the high heat of formation of the Si—O bond [28] and the fact that all of the products may be explained in terms of a single thermodynamically reasonable mechanism*. This mechanism involves the Lewis acid—base reaction of I or II with $(Me_2HSi)_2O$ to form an oxonium ion, which then eliminates the elements of dimethylsilane to generate a new silicenium ion (III or IV). Much of the driving force for this process may be associated with the formation of a silicenium ion which, in its cyclic oxonium form, is effectively stabilized by 1,4-$O \rightarrow Si^+$ interaction. This interaction may well be energetically more favorable than the 1,2 interaction (i.e. $R_3SiO{=}SiR_2$) present in I and II, because the latter involves $2p_\pi$—$3p_\pi$ conjugation [9].

Although the sequence $207^+ \rightarrow [341^+] \rightarrow 281^+$ could not be confirmed by double resonance experiments, because of low ion intensities and the mass limit of the spectrometer, it is analogous to the process $133^+ \rightarrow 267^+ \rightarrow 207^+$.

Further evidence in support of the structures of these ions was provided by the ICR spectra of mixtures of $(Me_2HSi)_2O$ with methanol, benzene, anisole, and acetone.

sym-Tetramethyldisiloxane—methanol

The ICR spectra of a mixture of these two compounds (30 μtorr each),

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* It must be emphasized that the proposed structures are based primarily on the molecular weights of the reactant and product ions and chemical plausibility. In common with all mass spectroscopic studies, concrete proof of structure similar to proof of neutral molecule structure is not obtainable.

using an ionizing voltage of 12 eV showed ions with *m/e* 119 (1%), 133 (2%), 135 (1%), 149 (5%), 163 (33%), 179 (3%), 191 (1%), 193 (7%), 207 (10%), 223 (4%), 237 (30%) and 267 (2%). Only small changes in intensity occurred when the ionizing voltage was increased to 40 eV.

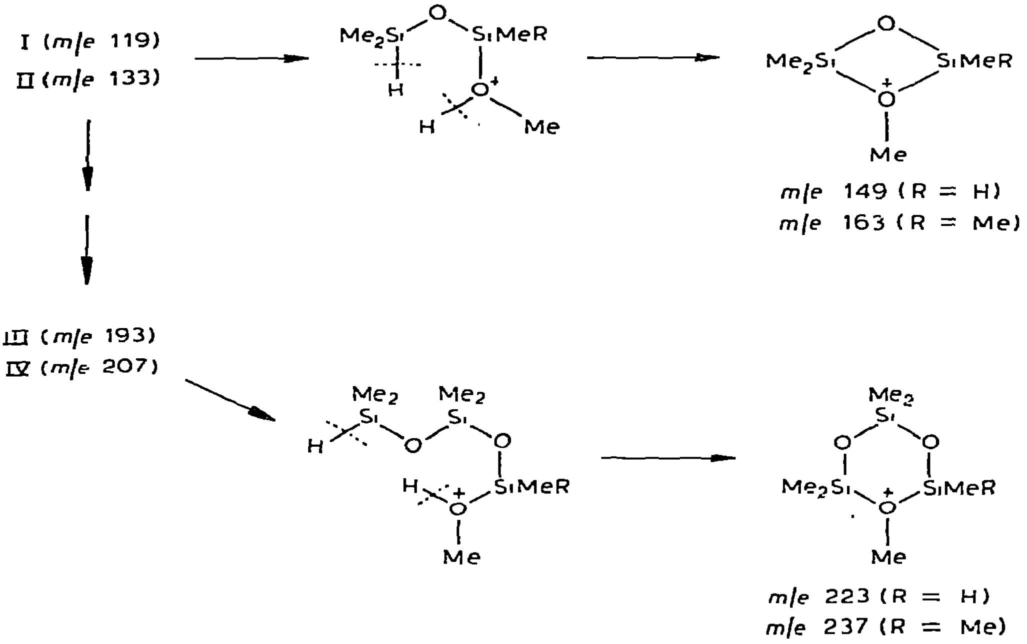
The silicenium ions with *m/e* 119, 133, 193 and 207, which were observed in the spectrum of $(Me_2HSi)_2O$ alone, were again observed although with reduced intensities. Double resonance experiments established the relationships:

$133^+ \rightarrow 163^+$; $133^+ \rightarrow 267^+ \rightarrow 207^+ \rightarrow 237^+$

When methanol-d_4 was substituted for methanol the ions with *m/e* 149, 163, 223 and 237 were shifted by +3 mass units while the ions with *m/e* 119, 133, 193 and 207 were unchanged. This establishes that the former set of ions arise from the reaction of the silicenium ions *m/e* 119, 133, 193, 207 with methanol, resulting in the incorporation of a OCH_3 group. This is understandable in terms of the mechanistic process already invoked, the only difference being the loss of H_2 rather than Me_2SiH_2 from the initial oxonium adduct (Scheme 2).

SCHEME 2

ION—MOLECULE REACTIONS OF *sym*-TETRAMETHYLDISILOXANE—METHANOL

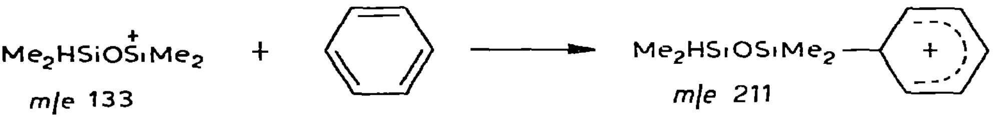


The fact that the ions with *m/e* 193 and 207 behave so similarly to the parent silicenium ions (*m/e* 119) and II (*m/e* 133) is strong evidence that they are homologously related.

sym-Tetramethyldisiloxane—benzene and —anisole

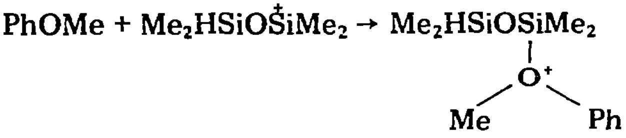
The ICR spectrum of a benzene—$(Me_2HSi)_2O$ mixture was measured in order to determine whether the silicenium ions derived from the disiloxane are capable of reacting with the benzene π system to form a σ-aryl complex corresponding to the intermediate in electrophilic aromatic substitution.

With 30 μtorr of each compound and an ionizing voltage of 14 eV, the ICR spectrum was essentially the same as that of $(Me_2HSi)_2O$ alone. When the benzene pressure was raised to 52 μtorr, a weak ion with m/e 211 was observed as a shoulder (<5%) on the silicenium ion with m/e 207. This ion corresponds to an adduct, which may be a σ-adduct:



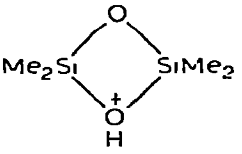
However, its low intensity indicates that the silicenium ions initially formed from the disiloxane react preferentially with the oxygen lone pair electrons of the neutral disiloxane, rather than the benzene π-system.

The ICR spectrum of an anisole—$(Me_2HSi)_2O$ mixture (30 μtorr each), using an ionizing voltage of 14 eV, showed ions with m/e 109 (46%), 119 (2%), 133 (3%), 135 (2%), 149 (9%), 207 (14%), 223 (10%), 241 (12%), 267 (2%). The ion with m/e 109 corresponds to protonated anisole. Of the remainder, only the ions with m/e 149, 223, and 241 are not present in the spectrum of $(Me_2HSi)_2O$ alone and so may be attributed to reaction of silicenium ions with anisole. Double resonance experiments established that the ion with m/e 241 is derived from the reaction of $Me_2HSiOSiMe_2$ (m/e 133) with anisole. Although this product might be formulated as a σ-aryl complex, the formation of which would be enhanced by the methoxy substituent, it is more probably the oxonium adduct:

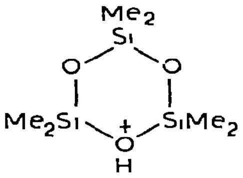


$$PhOMe + Me_2HSiO\overset{+}{S}iMe_2 \rightarrow \underset{\overset{|}{O^+(Me)(Ph)}}{Me_2HSiOSiMe_2}$$

Double resonance showed that the remaining two products, m/e 149 and 223, are derived from the silicenium ions m/e 133 and 207, respectively, by addition of 16 mass units (O or H_4C). Considering the already demonstrated affinities of these silicenium ions for oxygen, the most probable structures of these protons are VI and VII. However, the mechanism by which they are formed is obscure.



(VI) m/e 149



(VII) m/e 223

sym-Tetramethyldisiloxane—acetone

The ICR spectrum of a mixture of these two compounds (35 μtorr each), using an ionizing voltage of 12.5 eV, showed ions at m/e 119 (6%), 133 (1%), 149 (15%), 207 (49%), 223 (12%), 267 (6%) and 281 (10%).

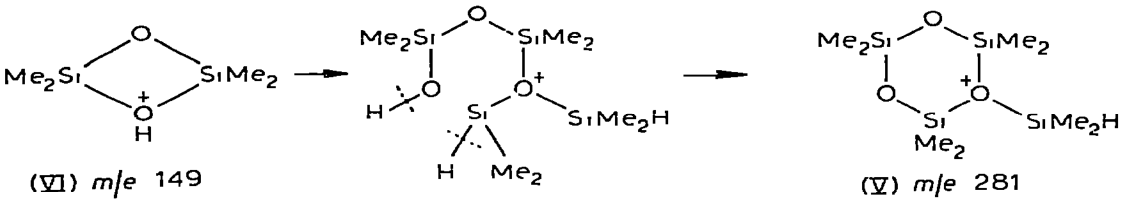
This spectrum has only two ions, m/e 149^+ and 223^+, which are not observed in the spectrum of pure $(Me_2HSi)_2O$. These ions are also common to mixtures of the disiloxane and anisole and are therefore assigned the same structures, VI and VII.

While the ion with *m/e* 281 is present in the spectrum of $(Me_2HSi)_2O$ alone, it is enhanced when acetone is present. The reason for this was revealed by the double resonance experiments, which showed that this ion is derived by two different processes:

207^+ (IV) $\xrightarrow{M}$ $281^+ + Me_2SiH_2$

133^+ (II) $\rightarrow$ 149^+ (VI) $\xrightarrow{M}$ $281^+ + H_2$

The first of these processes has already been depicted in Scheme 1. The second probably occurs by a related mechanism, i.e.



(VI) *m/e* 149

(V) *m/e* 281

There was no evidence for the formation of bimolecular acetone—silicenium adducts of the type $R_3SiO\overset{+}{C}Me_2$.

Hexamethyldisiloxane

The ICR spectra of this compound, obtained using an ionizing voltage of 15 eV and pressures of 40 and 120 μtorr, are summarized in Table 2. The spectrum is simpler than that of the tetramethyl analog because only one precursor silicenium ion, $Me_3SiO\overset{+}{Si}Me_2$, is formed and the mass limit of the instrument prevented detection of homologs $Me(Me_2SiO)_n\overset{+}{Si}Me_2$ greater than $n = 2$. However, the observed spectra and double resonance experiments indicate that the same basic addition—elimination sequence is occurring (Scheme 3). A minor difference is much greater stability of the initial oxonium adduct, *m/e* 309; apparently the Si—C cleavage required in the elimination Me_4Si is less favorable than Si—H cleavage.

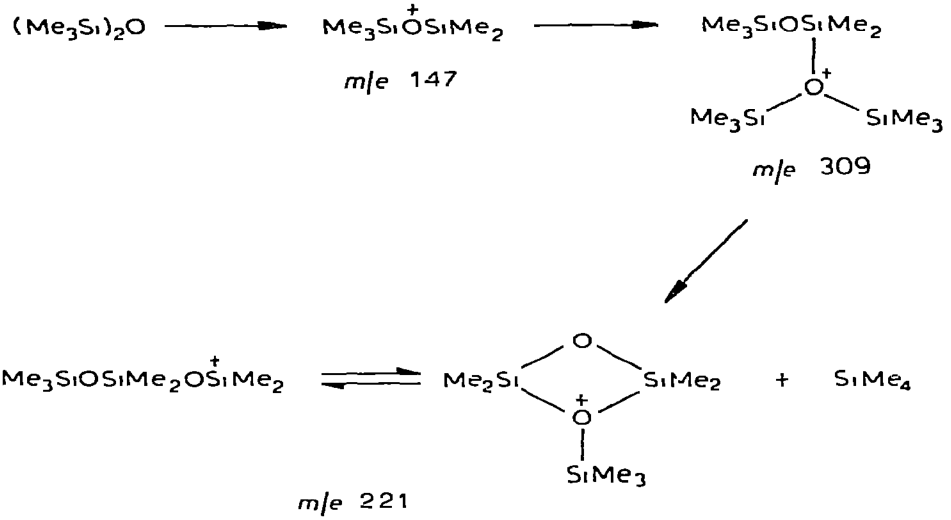
TABLE 2

ICR SPECTRUM OF HEXAMETHYLDISILOXANE

m/e	Relative intensity (%)	
	40 μtorr	120 μtorr
147	33	7
163	1	1
221	23	23
309	43	69

SCHEME 3

ION—MOLECULE REACTIONS OF HEXAMETHYLDISILOXANE



Diisopropyl ether

Having examined the gas phase chemistry of the silicenium ions derived from *sym*-tetramethyldisiloxane, it was of interest to compare the behavior of the isostructural carbenium ions. The ICR spectra of diisopropyl ether obtained at 14 eV and various pressures are summarized in Table 3.

The ions with *m/e* 87 and 101 may be assigned to be carbenium ions $Me_2HCO\overset{+}{C}HMe$ and $Me_2HCO\overset{+}{C}Me_2$, respectively, and are the isostructural analogs of the silicenium ions I and II. These ions, together with the molecular ion (*m/e* 102), and the $M + 1$ ion, are the dominant species and bimolecular adducts are much less evident. Double resonance experiments established that $Me_2HCO\overset{+}{C}HMe$ is the precursor in the sequence of reactions:

$$87^+ \rightarrow 101^+ \rightarrow 203^+ \rightarrow 161^+$$

Based on the results of studies with other aliphatic alcohols [29-31] and ethers

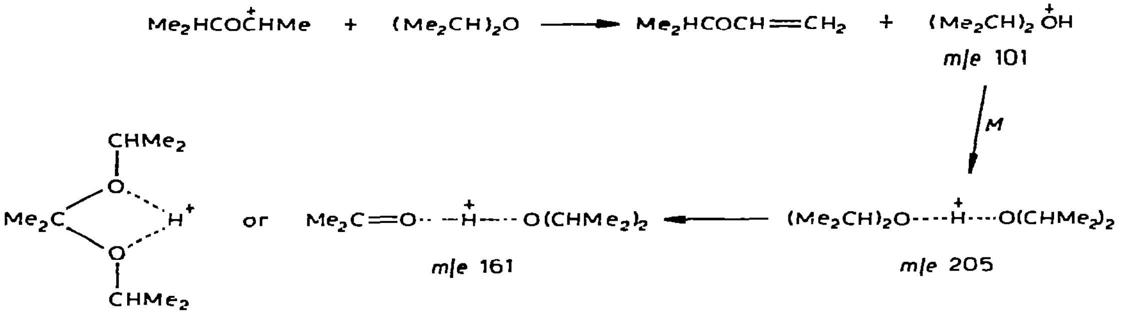
TABLE 3

ICR SPECTRUM OF DIISOPROPYL ETHER

m/e	Relative intensity (%)		
	7 µtorr	50 µtorr	100 µtorr
87	42	17	22
101	13	0	0
102	8	0	0
103	37	70	56
117	0	1	1
161	0	3	4
205	0	9	17

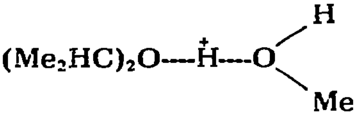
SCHEME 4

ION—MOLECULE REACTIONS OF DIISOPROPYL ETHER



[32], the mechanism shown in Scheme 4 is most probable. No products comparable to the homologous silicenium ions III and IV could be detected, although the possibility that the weak ion with *m/e* 117 is formed by oxygen abstraction cannot be discounted.

The ICR spectrum of a mixture of diisopropyl ether (30 μtorr) and methanol (40 μtorr) at 14 eV was comparable to that of the ether alone, with the exception of a minor (3%) ion with *m/e* 135. This corresponds to the adduct



$$(Me_2HC)_2O{-}\overset{+}{H}{-}O(H)Me$$

Similar products have been observed in spectra of other aliphatic alcohols [29-31].

The ICR spectrum of a mixture of diisopropyl ether and anisole failed to show any ions not present in the spectra of the pure components.

Conclusions

The ion—molecule reactions which silicenium ions of the structural type $R_3SiO\overset{+}{Si}R_2$ undergo in the gas phase appear to be dictated by a high affinity for oxygen. This is understandable in terms of the high Si—O bond strength. Another factor may be the poor internal charge delocalization by the resonance structure $R_3Si\overset{+}{O}{=}SiR_2$, which involves p_π—p_π conjugation between 1st and 2nd row elements. As a result, some of the driving force for the observed transformations may be derived from the more favorable intramolecular charge delocalization possible in the larger homologs.

In the case of isostructural carbenium ions, charge is much more effectively delocalized by the resonance structure $R_3C\overset{+}{O}{=}CR_2$. Consequently, the electrophilicity of the carbenium ion, as well as the driving force for homologation, should be diminished.

Acknowledgements

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