disaccharides do not produce the desired reducing ring fragmentation, because the proton cannot bridge the two sugars as well as lithium. Therefore, the protonated dimer falls apart in preference to fragmenting on the reducing ring. By this interpretation, lithium is indirectly inducing the ring fragmentation, by stabilizing the dimeric structure. Although lithium does not appear to be directly involved in the fragmentation mechanism, it is not inconceivable that the observed ring cleavage may be an example of remote site fragmentation.[25,26]

Other possible ways in which lithium can affect the fragmentation of these disaccharides are that it can induce ring opening of the hemiacetal to the hydroxy aldehyde, or it can assist in isomerization of the carbonyl group. Cooks has suggested that lithium may induce ring opening of sugars to the hydroxy aldehyde form,[7] but we currently have no direct evidence to support this hypothesis. It is also not clear if this ring opening takes place upon bombardment of the sample with Cs^+ ions (vide supra), or whether this occurs under CID. We believe that CID is imperative for observing reducing ring fragmentation, particularly those fragmentations that necessitate prior isomerization. However, whether lithium affects the carbonyl isomerization is unknown. We are currently exploring a means for determining the range of internal energies available to the molecular ion in these systems, for comparison to the calculated monolithiated gentiobiose structures. Furthermore, we are investigating the metastable, unimolecular decomposition pathways in these systems.

In summary, the CID product ion spectra of lithiated disaccharides result in useful linkage position information for two primary reasons. First, reducing ring fragmentation is observed, and according to our mechanistic analysis, it appears to be directly dependent on the linkage position. Furthermore, this technique would not be successful without adding lithium to the molecular ion. The lithium ion serves to stabilize the sugar dimer, so that the reducing ring fragmentation can occur. Other more subtle ways in which lithium assists in fragmentation are possible, but are not clear at this time.

Supplementary Material Available: Tables of Cartesian coordinates (10 pages). Ordering information is given on any current masthead page.

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$SiOH^+/HSiO^+$ and $SiOH^\bullet/HSiO^\bullet$: Gas-Phase Generation and Characterization. A Combined Neutralization–Reionization Mass Spectrometry and ab Initio Molecular Orbital Study[†]

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Abstract: Molecular orbital calculations (MP4(fc)6-311G(3df,3pd)//MP2(full)/6-311G(3df,3pd) + ZPE(MP2/full)/6-311G(3df,3pd)) are used to describe the geometries, energies, and vibrational frequencies of the four species $SiOH^+$ (**1⁺**), $HSiO^+$ (**2⁺**), $SiOH^\bullet$ (**1•**), and $HSiO^\bullet$ (**2•**), respectively, and the transition states for the 1,2-hydrogen migrations. In line with previous theoretical findings, all four species reside in potential minima. The most stable form invariably corresponds to the $SiOH^{+/\bullet}$ connectivity. Substantial barriers (35.3 kcal/mol for the cation and 29.5 kcal/mol for the radical) prevent facile isomerization. In line with the theoretical predictions, a combination of several mass spectrometric experiments (collisional activation and neutralization–reionization) provides evidence that all four species, which are believed to play a role in ionospheric chemistry, do indeed exist in the gas phase.

The anomalous distribution of atomic silicon in the ionosphere[1] has triggered numerous experimental and theoretical studies aimed at providing evidence for the pathways by which the depletion of ground-state Si^+ (^2P) occurs. Reactions 1–3 were proposed[2] to be responsible for the formation of protonated silicon monoxide ($SiOH^+$), which upon neutralization (eq 3) is suggested to give rise to silicon monoxide in interstellar gas clouds.[3]

$$Si^{\bullet+} + H_2O \rightarrow SiOH^+\ (\mathbf{1^+}) + H^\bullet \qquad (1)$$

$$SiO^+ + H_2 \rightarrow SiOH^+ + H^\bullet \qquad (2)$$

$$SiOH^+ + e^- \rightarrow SiO + H^\bullet \qquad (3)$$

The rates for processes 1 and 2 were first measured by Fahey et al., using the flowing afterglow technique,[4] and later by Bohme

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et al.[5] The latter authors also reported detailed studies of reactions of $Si^{•+}$ with numerous other neutral molecules which also produce $SiOH^+$, and by combining their findings with thermochemical data and the results of ab initio studies they concluded that the ionic species formed in reactions 1 and 2 corresponds to $SiOH^+$ and not its isomeric form $HSiO^+$.[3,5,6] The formation of $SiOH^+$, and not $HSiO^+$, from $(CH_3)_3SiOH$ is also supported by the observation of the v_1 (H–O) and v_3 (O–Si) stretches of $SiOH^+$ and $SiOD^+$, using a tunable infrared diode laser spectrometer and a hollow cathode discharge cell.[7] The experimentally observed frequencies of 3662 and 1127 cm^{-1} agree well with the theoretically predicted value (3658 and 1110 cm^{-1} respectively of Botschwina and Rosmus[8]) when the coupled electron pair approximation is used. For the as yet experimentally *not* characterized $HSiO^+$ isomer, DeFrees and McLean[10] performed a detailed vibrational frequency analysis at several levels of MO theory, the highest being MP2/6-31G*. The interest of theoreticians in the $SiOH^+/HSiO^+$ problem is further indicated by several papers[11] published since Wilson's seminal study in 1978.[12] Common to these investigations are the predictions that (i) $SiOH^+/HSiO^+$ are separated by a significant barrier (ca. 30 kcal/mol) and (ii) both ions correspond to minima on the potential energy surface with $SiOH^+$ being the global minimum. Depending on the level of theory used this structure is predicted to be >60 kcal/mol more stable than $HSiO^+$. This order of stability, when compared with the analogous, well-studied system HCO^+/HOC^+, in which HCO^+ is >40 kcal/mol *more* stable than HOC^+,[10,11,13] confirms previous conjectures that "little of the chemistry of silicon can be inferred from that of carbon".[14,15] This also holds true for the corresponding radical pairs $SiOH^•/HSiO^•$ versus $HCO^•/HOC^•$. While $HCO^•$ is more stable than $HOC^•$,[16] according to MO calculations[17] the opposite is predicted for the silicon analogues, with $SiOH^•$ forming the global minimum (>10 kcal/mol more stable than $HSiO^•$). Schaefer's detailed computational studies on the $SiOH^•/HSiO^•$ isomers[17b,d] inter alia predict a barrier of >25 kcal/mol for the isomerization $HSiO^• \rightarrow SiOH^•$, thus suggesting "that both isomers should be makeable". However, on the basis of ESR experiments only the thermochemically less stable $HSiO^•$ isomer has been unambiguously identified as a stable radical at 4 K.[18,19] Arguments in favor of the existence of the $SiOH^•$ form are at best circumstantial.

In this paper, we provide evidence that all four species $SiOH^+/HSiO^+$ and $SiOH^•/HSiO^•$ do indeed exist in the gas phase. The connectivities of the ionic system are established by collisional activation (CA) mass spectrometry.[20] The corresponding neutrals $SiOH^•/HSiO^•$ are generated from the cations and characterized with use of neutralization–reionization mass spectrometry (NRMS).[21] This method has also been used recently to identify other "elusive" silicon molecules in the gas phase, including $SiCH_x$ (x = 1, 2, 3),[22] $HC{\equiv}CSi^•$,[23] and SiC_2H_2.[24] Our experimental findings are supported by state-of-the-art ab initio molecular orbital (MO) calculations, which at their highest level are of the type MP4(fc)/6-311G(3df,3pd)//MP2(full)/6-311G(3df,3pd) + ZPE(MP2/full)/6-311G(3df,3pd).

Experimental and Computational Section

The mass spectrometric experiments were carried out with a modified VG Instruments ZAB mass spectrometer. This is a four-sector instrument of BEBE configuration (B stands for magnetic and E for electric sector) which has been built by AMD Intectra, Harpstedt, Germany, by combining the BE part of a ZAB-HF-3F machine (MS I) with an AMD 604 double-focusing mass spectrometer (MS II).[25] Positive $[H,Si,O]^+$ ions are generated by 70-eV electron impact ionization of $Si(OCH_3)_4$; the anionic analogue $[H,Si,O]^-$ was generated in the negative ion mode by using $PhSiH_3$ as precursor and N_2O as the electron moderation gas,[19] $p \simeq 5 \times 10^{-5}$ Torr. The following ion-source conditions were employed: ion source temperature, 200 °C; ion trap current, 100 μA; acceleration voltage, 8 kV; mass resolution $m/\Delta m$ = 1500 (10% valley definition). For experiments on $[H,Si,O]^-$, slits were fully open to obtain maximum signal intensities. Collision-induced dissociations,[20] used to characterize the ions formed in the source, were brought about by mass selecting an 8-keV beam of $m_1^{+/-}$ by means of B(1)/E(1) and colliding it in the case of $[H,Si,O]^+$ (m/z 45) with helium in a collision chamber located in the third field-free region (Figure 2: 80% transmittance (T)). Ionic products were recorded by scanning B(2). Charge reversal (CR) experiments[20b,c,26] were conducted by colliding the beam of mass-selected anionic $[H,Si,O]^-$ ions (m/z 45) with oxygen (80% T) in the third field-free region of the 4-sector machine and recording the positively charged ion $[H,Si,O]^+$ and the ionic fragments formed thereof by scanning B(2). In the NRMS experiment, a beam of mass-selected $[H,Si,O]^+$ (having 8-keV transla-

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Table I. Total Energies (au) and Relative Energies (kcal/mol) of $[Si,O,H]^+$ Species and the Transition State (TS)

method	$SiOH^+$ total energies	$HSiO^+$ total energies	$HSiO^+$ rel energies	TS total energies	TS rel energies
HF/6-31G(d,p)	−364.113 31	−363.985 56	80.0	−363.912 30	126.0
HF/6-311G(2d,2p)	−364.160 56	−364.037 90	76.9	−363.964 70	122.8
MP2(fu)/6-311G(2d,2p)	−364.600 13	−364.503 15	60.8	−364.443 57	98.2
MP2(fu)/6-311G(3df,3pd)	−364.670 92	−364.571 08	62.6	−364.511 34	100.1
MP4(fu)/6-311G(3df,3pd)[a]	−364.507 80	−364.415 25	58.0	−364.356 44	94.9

[a] At MP2(fu)/6-311G(3df,3pd) optimized geometry.

Table II. Total Energies (au) and Relative Energies (kcal/mol) of $(Si,O,H)^{\bullet}$ Radicals and the Transition State (TS)

method	$SiOH^{\bullet}$ total energies	$HSiO^{\bullet}$ total energies	$HSiO^{\bullet}$ rel energies	TS total energies	TS rel energies
HF/6-31G(d,p)	−364.339 18	−364.304 10	22.0	−364.254 59	53.0
$\langle S^2 \rangle$	0.764	0.769		0.808	
HF/6-311G(2d,2p)	−364.389 96	−364.359 00	19.4	−364.307 55	51.7
$\langle S^2 \rangle$	0.774	0.769		0.811	
MP2(fu)/6-311G(2d,2p)	−364.833 39	−364.819 84	8.5	−364.763 85	43.6
$\langle S^2 \rangle$	0.774	0.771		0.803	
MP2(fu)/6-311G(3df,3pd)	−364.905 93	−364.891 47	9.1	−364.837 52	42.9
$\langle S^2 \rangle$	0.777	0.770		0.803	
MP4(fc)/6-311G(3df,3pd)[a]	−364.747 05	−364.733 66	8.4	−364.684 02	39.5
$\langle S^2 \rangle$	0.777	0.770		0.803	
CISD/TZ2P[b]	−364.680 30	−364.655 85	15.3	−364.609 24	44.6

[a] At MP2(fu)/6-311G(3df,3pd) optimized geometry. [b] Reference 17d.

tional energy) was neutralized in the first cell of a differentially pumped tandem collision cell (located in the field-free region between E(1) and B(2)) by colliding the beam with xenon (Figure 3: 80% *T*). Unreacted ions were deflected away from the beam of neutral species m_i by applying a voltage of 1000 V on the deflector electrode; subsequent reionization $m_i \rightarrow m_i^+$ occurred in the second collision cell by collision with oxygen (80% *T*). The resulting mass spectra were recorded by scanning B(2). If the anionic $[H,Si,O]^-$ species were subjected to a CR/NRMS experiment (Figure 7) the combination O_2/O_2 as collision gas turned out to be the most efficient one (80%/80% *T*). The minimal lifetime *t* (identical with the transit time from cell I to cell II) is of the order of a microsecond. The availability of a multisector machine[27] and the fact that collision cells are located in field-free regions between B(1)/E(1) and E(1)/B(2) as well as B(2)/E(2) enabled us to perform two further experiments for the $[H,Si,O]^+$ system which, on sensitivity grounds, could not be conducted for $[H,Si,O]^-$: (1) $[H,Si,O]^+$ ions are mass selected by B(1), and they are neutralized with xenon (80% *T*) and subsequently reionized with oxygen (80% *T*) with use of the tandem collision cell located between B(1) and E(1). The reionized $[H,Si,O]^+$ species are subjected to a kinetic energy analysis by means of E(1). The interference-free beam of $[H,Si,O]^+$ was then collisionally activated with helium (80% *T*), and the CA mass spectrum, which basically contains no contribution for reionized neutrals, was recorded by scanning B(2) (Figure 4). (2) A related experiment was conducted with the difference that $[H,Si,O]^+$ was mass selected under "high-resolution" conditions, by means of B(1)/E(1). Neutralization and reionization were brought about in the collision cell located between E(1) and B(2), momentum analysis of the reionized *m/z* 45 was carried out by B(2), and this was followed by collision with helium in the field-free region between B(2) and E(2). The resulting ions were recorded by scanning of E(2). This sequence corresponds to an interference-free CA/NRMS experiment under "high-resolution" conditions (Figure 5). In all experiments signal-averaging techniques were used to improve the S/N ratio. The data were accumulated by on-line processes with the AMD-Intectra computer system DP 10.

Table III. Geometrical Parameters (Å) for $SiOH^+$ Isomers and the Transition State (TS)

$SiOH^+$

method	*r*(SiO)	*r*(HO)
HF/6-31G(d,p)	1.532	0.947
HF/6-311G(2d,2p)	1.520	0.944
MP2/6-311G(2d,2p)	1.544	0.962
MP2/6-311G(3df,3pd)	1.540	0.963

$HSiO^+$

method	*r*(SiO)	*r*(HSi)
HF/6-31G(d,p)	1.462	1.457
HF/6-311G(2d,2p)	1.451	1.458
MP2/6-311G(2d,2p)	1.509	1.469
MP2/6-311G(3df,3pd)	1.505	1.470

TS: $SiOH^+ \rightarrow HSiO^+$

method	*r*(SiO)	*r*(HSi)	*r*(HO)
HF/6-31G(d,p)	1.511	1.535	1.962
HF/6-311G(2d,2p)	1.497	1.539	1.962
MP2/6-311G(2d,2p)	1.518	1.565	1.873
MP2/6-311G(3df,3pd)	1.513	1.558	1.869

Standard, but high-level ab initio molecular orbital calculations have been carried out with the Gaussian 86 program package as installed on an IBM 3090 equipped with Vector Facility. Initial geometry optimizations were performed at the Hartree–Fock level of theory (unrestricted Hartree–Fock (UHF) for open-shell systems) employing the 6-31G(d,p) and 6-311G(2d,2p) basis sets. These geometries were refined at the correlated MP2 level (second-order Møller–Plesset perturbation theory, all electrons correlated) with use of the 6-311G(2d,2p) and the larger 6-311G(3df,3pd) basis sets. On the latter level, i.e. MP2(fu)/6-311G(3df,3pd), the force constant matrix of all structures considered has been computed by numerical differentiation of the analytically obtained gradients. The number of negative eigenvalues of the force constant matrix has been used to determine the nature of each stationary point as a minimum or a transition state. In addition, the harmonic frequencies have been obtained to allow for zero-point energy (ZPE) corrections and to predict the IR spectra of the various species. The harmonic frequencies have been scaled by a uniform factor of 0.93[28] to correct for the known overestimation of frequencies at this level of theory. With use of the MP2(fu)/6-311G(3df,3pd) optimized geometries, single-point energy calculations employing the same 6-311G(3df,3pd) basis set and Møller–Plesset perturbation theory up to full fourth order (keeping the core electrons frozen) have been carried out. Thus in standard notation our final level can be described as follows: MP4(SDTQ)6-311G-(3df,3pd)//MP2(fu)/6-311G(3df,3pd) + ZPE. For a detailed description of the basis sets and Møller–Plesset perturbation theory, see ref 28.

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Table IV. Geometrical Parameters (Å) for $SiOH^•$ Isomers and the Transition State (TS)

SiOH

method	r(SiO)	r(HO)	angle
HF/6-31G(d,p)	1.646	0.944	119.6
HF/6-311G(2d,2p)	1.632	0.940	119.2
MP2/6-311G(2d,2p)	1.658	0.959	115.7
MP2/6-311G(3df,3pd)	1.654	0.959	118.6
TZ2P/CISD[a]	1.652	0.953	118.8

HSiO

method	r(SiO)	r(HSi)	angle
HF/6-31G(d,p)	1.501	1.506	122.9
HF/6-311G(2d,2p)	1.489	1.504	122.6
MP2/6-311G(2d,2p)	1.534	1.511	121.9
MP2/6-311G(3df,3pd)	1.529	1.505	121.7
TZ2P/CISD[a]	1.516	1.503	121.8

TS: $SiOH^• \rightarrow HSiO^•$

method	r(SiO)	r(HSi)	r(HO)
HF/6-31G(d,p)	1.607	1.603	1.329
HF/6-311G(2d,2p)	1.587	1.603	1.325
MP2/6-311G(2d,2p)	1.583	1.612	1.378
MP2/6-311G(3df,3pd)	1.574	1.610	1.391
TZ2P/CISD[a]	1.598	1.608	1.354

[a] Reference 17d.

Table V. Harmonic Frequencies (cm^{-1}) and IR Intensities (km/mol) for $[Si,O,H]^+$ Isomers and the Transition State (TS)

$SiOH^{+a}$

mode	π	σ	σ	ZPE, kcal/mol
unscaled	414	1130	3863	8.3
scaled (0.93)	385	1051	3593	7.7
intensity	230	128	595	

$HSiO^+$

mode	π	σ	σ	ZPE, kcal/mol
unscaled	440	1247	2303	6.3
scaled (0.93)	409	1160	2142	5.9
intensity	6	0	86	

TS^+

method	a′	a′	a′	ZPE, kcal/mol
unscaled	1096i	1351	1859	4.6
scaled (0.93)	1019i	1256	1729	4.3

[a] The *harmonic* frequencies for $SiOH^+$ computed by Botschwina and Rosmus (ref 8) at the CEPA level of theory are in good agreement with our results: π 242, σ 1136, σ 3894 cm^{-1}.

The organization of the paper is such that we will first describe the results of the MO studies followed by a discussion of the experimental findings.

Results and Discussion

Table VI. Harmonic Frequencies (cm^{-1}) and IR Intensities (km/mol) of $[Si,O,H]^•$ and the Transition State (TS)

$SiOH^•$

mode	a′	a′	a′	ZPE, kcal/mol
unscaled	746	874	3903	7.9
scaled (0.93)	694	813	3630	7.3
intensity	159	76	140	
Xie and Schaefer[17d]	823	888	3966	
intensity	143	75	133	

$HSiO^•$

mode	a′	a′	a′	ZPE, kcal/mol
unscaled	721	1229	2056	5.7
scaled (0.93)	671	1143	1912	5.3
intensity	49	55	82	
Xie and Schaefer[17d]	715	1245	2067	
intensity	101	45	151	

TS

mode	a′	a′	a′	ZPE, kcal/mol
unscaled	1369i	1152	1655	4.0
scaled (0.93)	1273i	1071	1539	3.7
Xie and Schaefer[17d]	1819i	1032	1811	

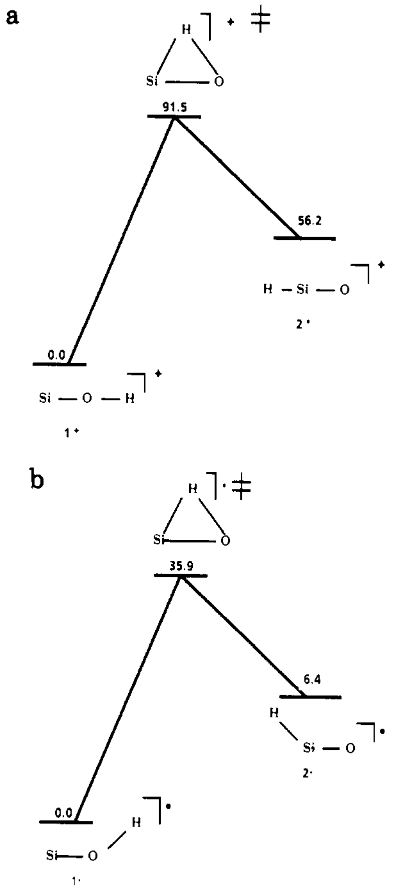

Figure 1. (a) $[Si,O,H]^+$ and (b) $[Si,O,H]^•$ potential energy surfaces. Relative energies in kcal/mol.

Table I contains the computed total and relative energies of the $[H,Si,O]^+$ cations $SiOH^+$ and $HSiO^+$ on the various levels of theory; for the corresponding radicals $SiOH^•$ and $HSiO^•$ the data are given in Table II. Tables III and IV show the geometrical parameters, and Tables V and VI summarize the theoretically predicted harmonic frequencies and IR intensities. Parts a and b of Figure 1 give a schematic representation of the potential energy surfaces of the $[H,Si,O]^+$ isomers and the $[H,Si,O]^•$ radicals, respectively, as computed at MP4(SDTQ)/6-311G-(3df,3pd)//MP2(fu)/6-311G(3df,3pd) + ZPE. In the case of the radical, the recent results obtained by Xie and Schaefer[17d] using configuration interaction (CI) and a TZ2P basis set have been included for comparison. It can be seen that the overall agreement between the two studies is excellent, which is not unexpected since the spin contamination of our UHF wave functions is in all cases small ($\langle S^2 \rangle \leq 0.8$, while the exact value is 0.75) and the calculational approaches are of similar quality. The major difference is the relative stability of $HSiO^•$ which we compute as 6.4 kcal/mol with respect to $SiOH^•$, while Xie and Schaefer obtain an energy difference of 11.6 kcal/mol. This most probably reflects the importance of triple excitations for the correlation energy. At MP4(SDQ), neglecting the triple excitations, an energy difference of 12.5 kcal/mol is computed, as compared to 8.4 at MP4(SDTQ). Thus the effect of the triple excitations amounts to 4.1 kcal/mol! It should be noted that at the HF level the $HSiO^•$ vs $SiOH^•$ energy difference is virtually the same at our 6-311G(2d,2p) and Xie and Schaefer's TZ2P level, 19.4 and 19.5 kcal/mol, respectively. Schaefer et al.[17b,d] located a second $HSiO^•$ isomer on the HF surface, characterized by a small H–Si–O angle (93.2°) and a long Si–O bond (1.626 Å),

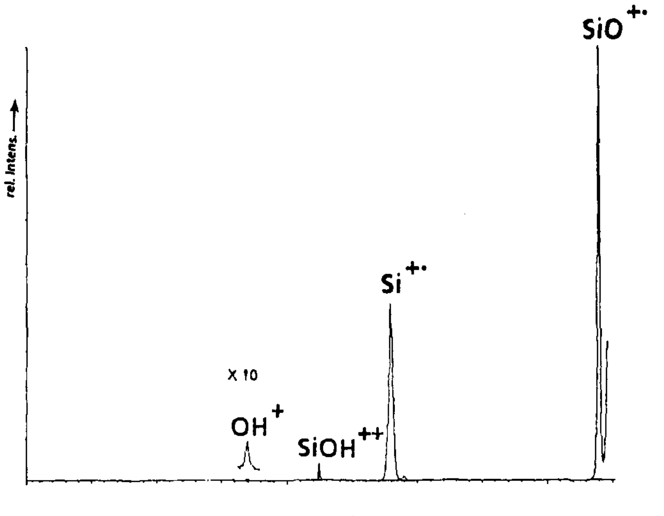

Figure 2. CA mass spectrum of $SiOH^+$, m/z 45, generated from $Si(OCH_3)_4$.

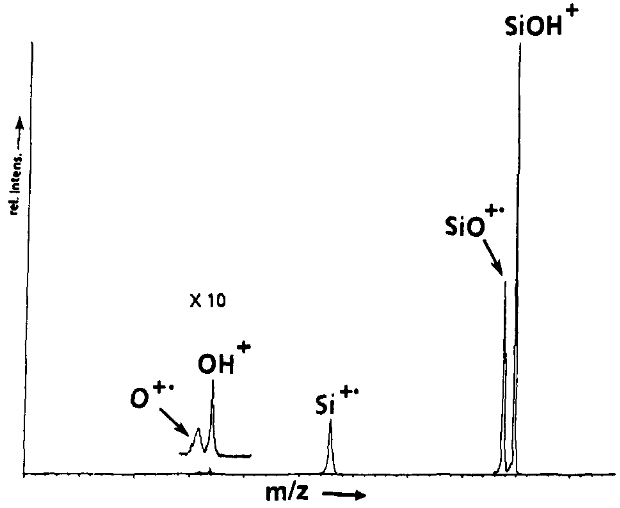

Figure 3. NR mass spectrum of $SiOH^+$.

25 kcal/mol above the global minimum. However, this isomer was no longer found as a stationary point when electron correlation was taken into account.[17d] Since this structure is clearly an artifact of the HF approach we did not include it in our investigation.

In accord with all previous studies, the connectivity SiOH is found to be the more stable isomer for the cation and the radical. However, while in the case of the radical the energy difference is rather modest (6.4 kcal/mol), ionization leads to a significant destabilization of $HSiO^+$ which is predicted to be 56.2 kcal/mol above $SiOH^+$. However, a sizable barrier of 29.5 (radical) and 35.3 kcal/mol (cation) prevents facile rearrangements of the HSiO into the more stable SiOH isomers. Hence, all four species ($SiOH^•$, HSiO, $SiOH^+$, $HSiO^+$) are theoretically predicted as being experimentally observable. In addition, for the cation as for the radical an unambiguous distinction between the two isomers should be possible by means of IR spectroscopy. The computed harmonic IR spectra of $SiOH^+$ and $SiOH^•$ are both dominated by a very strong band around 3600 cm^{-1} (3593 and 3630 cm^{-1}, respectively) while for $HSiO^+$ and $HSiO^•$ no absorbtion above 2150 cm^{-1} is predicted.

In the following, we will demonstrate that the combination of the powerful methods of collisional activation and neutralization–reionization mass spectrometry provides evidence that the four species $SiOH^+$, $HSiO^+$, $SiOH^•$, and $HSiO^•$ are indeed viable, clearly distinguishable molecules in the gas phase.

The interpretation of the CA mass spectrum of $SiOH^+$ (Figure 2) is relatively straightforward. The base peak corresponds to

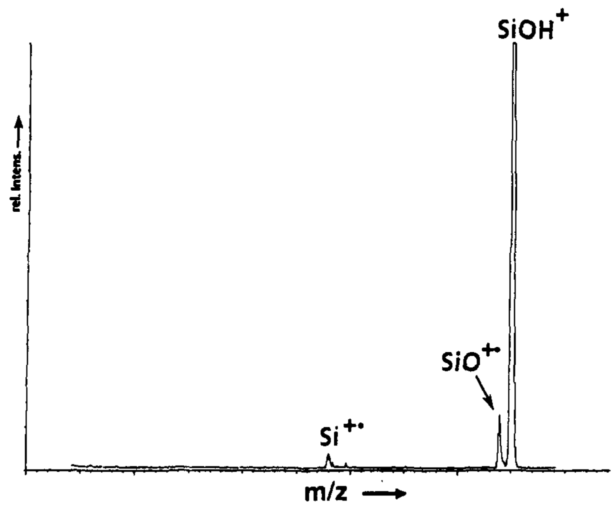

Figure 4. CA mass spectrum of reionized $SiOH^+$: mass selection of m/z 45 by means of B(1); neutralization reionization with Xe/O_2; energy analysis of reionized $SiOH^+$ with E(1); collisional activation with He. See text for further details.

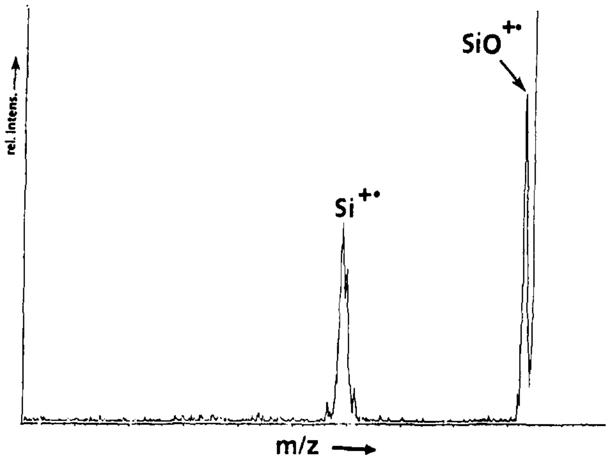

Figure 5. CA mass spectrum of reionized $SiOH^+$: mass selection of m/z 45 by means of B(1)E(1); neutralization reionization with Xe/O_2; selection of the reionized m/z 45 with B(2); collisional activation with He. See text for further details.

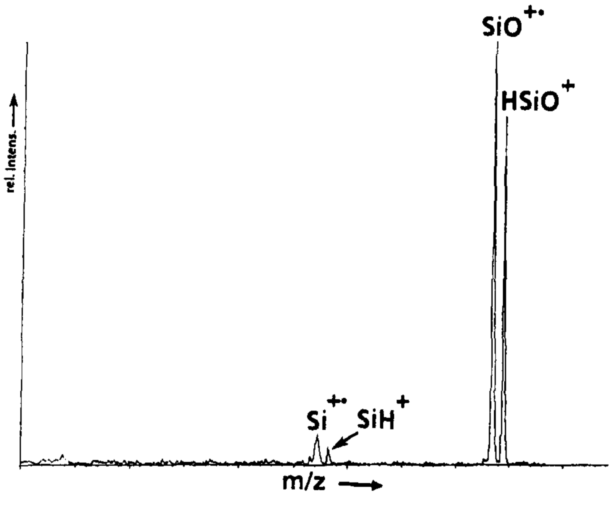

Figure 6. CR spectrum of $[Si,O,H]^-$ generated from $PhSiCH_3$ in the presence of N_2O (negative ion mode). See Experimental Section or further details.

loss of $H^•$ (m/z 44), and the next intense signal is due to the structure-indicative elimination of $OH^•$ to generate $Si^{•+}$ (m/z 28). This signal, together with the one for OH^+, is best compatible with a connectivity $SiOH^+$. For the alternative structure $HSiO^+$

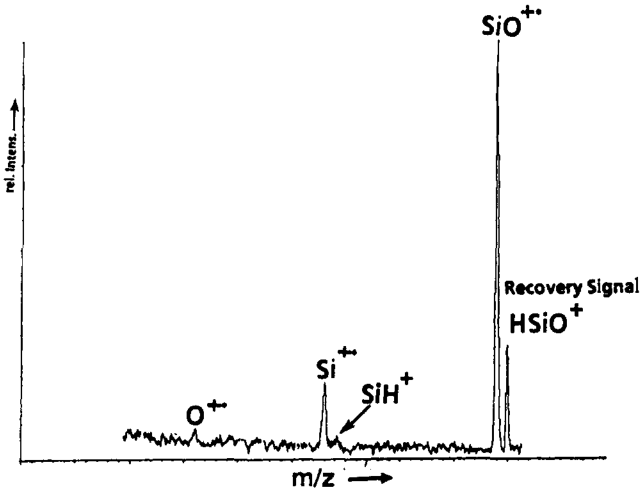

Figure 7. NR mass spectrum of [Si,O,H]$^-$. See Experimental Section for details.

we would expect the presence of a signal at *m/z* 29. The very weak signal at *m/z* 29 (Figure 2) most likely corresponds to ^{29}Si$^{\bullet+}$, formed from ^{29}SiO$^{\bullet+}$.

Reduction of SiOH$^+$ in a NRMS experiment (Figure 3) yields an intense recovery signal at *m/z* 45 (100%).[29] In view of the vertical nature[30] of the electron transfer processes SiOH$^+$ → SiOH$^\bullet$ → SiOH$^+$ we conclude that the neutral SiOH$^\bullet$ molecule retains the connectivity of its cationic precursor SiOH$^+$, i.e. the species formed corresponds to SiOH$^\bullet$ and not HSiO$^\bullet$. This conclusion is supported by the abundant fragment *m/z* 28 (Si$^{\bullet+}$) in Figure 3; we note the absence of a signal at *m/z* 29 (SiH$^+$).

Further evidence supporting this assignment is provided by two multistep collision experiments, which give rise to the interference-free CA mass spectra of reionized SiOH species (Figures 4 and 5, for details see the Experimental Section). We note in both cases the formation of Si$^{\bullet+}$ and the absence of SiH$^+$, together with signals for SiO$^+$ and the reionized SiOH$^+$ species.

In the CR spectrum of [Si,O,H]$^-$, generated by 70-eV ionization of PhSiH$_3$ in the presence of N$_2$O (Figure 6), we observe a new signal at *m/z* 29 (SiH$^+$, 40% of *m/z* 28) in addition to a "recovery" signal at *m/z* 45 for [Si,O,H]$^+$ and those at *m/z* 44 (SiO$^{\bullet+}$) and *m/z* 28 (Si$^{\bullet+}$). We suggest that the signal at *m/z* 29 (SiH$^+$) points to the fact that a major portion of the [Si,O,H]$^-$ population has been formed with the connectivity HSiO$^-$ which upon double charge reversal is converted to HSiO$^+$. We also note the absence of a charge-stripping signal[31] for the doubly charged ion HSiO^{2+}; in contrast, the latter is clearly detectable in Figure 2 for SiOH^{2+}.

Neutralization of [Si,O,H]$^-$ followed by reionization (Figure 7) gives rise to the spectrum shown in Figure 7. Again a "recovery" signal was observed. A comparison of the relative intensity contribution of the relevant signals at *m/z* 45, 44, 29, and 28 of Figures 3 and 7 suggests that two different ionic and neutral [Si,O,H]$^{+/\bullet}$ systems are generated. One corresponds to SiOH$^{+/\bullet}$ and the other to the thermochemically less stable HSiO$^{+/\bullet}$ connectivity.

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(29) The contribution of ^{29}SiO$^{\bullet+}$ to the "recovery" signal of ^{28}SiOH$^+$ is 4.6%.

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(31) (a) Reference 20. (b) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321 and references therein. (c) Cooks, R. G.; Ast, T.; Mabud, Md. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209.