Gas phase studies of silacyclobutanes: recent developments employing triple quadrupole detection [1]

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Abstract

Four silacyclobutyl anions have been prepared and studied by gas phase ion–molecule chemistry using newly modified tandem flowing afterglow instrumentation. These silacyclobutyl anions, which include a pentacoordinate adduct of 1,1-dimethylsilacyclobutane and fluoride and an α-silylcarbanion, siloxide, and mercaptide corresponding to 1,1-dimethylsilacyclobutane, have been characterized by their chemical reactivity and collision-induced loss of ethylene under a variety of conditions. The C–H, O–H, and S–H gas phase acidities of 1,1-dimethylsilacyclobutane, 1-hydroxy-1-methylsilacyclobutane, and 1-mercapto-1-methylsilacyclobutane have been measured and show no effect of the silacyclobutyl attachment. The full capabilities of the newly modified instrumentation include the mass selection of ions, their chemical characterization, collision-induced dissociation of both mass selected ions and those prepared by chemical reactions, and triple quadrupole detection.

Keywords: Silicon; Silacyclobutanes; Mass spectrometry; Triple quadrupole spectrometry; Acidities

1. Introduction

Silacyclobutanes have fascinated organosilicon chemists for a long time because of their enhanced reactivity and central role in the preparation of silicon–carbon double bonds (silenes) [1–4]. Reactions in condensed phase have revealed strong tendencies for ring expansion and ring opening [1,4–7]. These reactions are considered to be 'driven' by a combination of high ring strain in the silacyclobutanes and the considerable polarity of the silicon–carbon bond.

Gas phase studies of silacyclobutanes were instrumental in opening the silicon multiple-bond era that has recently dominated organosilicon chemistry [1–4]. This work was initiated by Gusel'nikov and coworkers in the mid-1960s with the discovery that 1,1-dimethylsilacyclobutane (DMCSB) undergoes efficient pyrolysis to dimethylsilene and ethylene [1–4,8–11]. Since then, such 2 + 2 cycloreversion reactions have been studied in detail. Careful examination of the products by both chemical and physical trapping experiments verifies the 2 + 2 cycloreversion mechanism of ethylene loss from 1,1-dimethylsilacyclobutane [2,3].

The ion-molecule chemistry of silacyclobutanes has also been studied in the gas phase [12,13]. We reported in 1981 that DMSCB as well as two spirosilacyclobutanes react with fluoride to form siliconates (pentacoordinate silicon anions) (Eq. (1a)) as well as α-silyl carbanions (Eq. (1b)). Although the formation of siliconates is now known to be characteristic of a wide

$$(1a)$$

$$(1b)$$

variety of silicon compounds [14-17], the formulation of the pentacoordinate siliconate in Eq. (1a) was the first of a simple alkyl-substituted siliconate [12,18]. Later work demonstrated that siliconate 1 formed indirectly in a secondary reaction between an excess of DMSCB and 2 (see Eq. (3)) [13]. The primary reaction path leads to $CH_3CH_2CH_2Si(CH_3)(F)CH_2^-$ (3), an isomer of 1 that is formed by ring opening and subsequent proton transfer [13]. Chemical reactions with N_2O were used to differentiate between products [13]. These studies demonstrated the sensitivity of the product distribution to slight changes in reaction conditions. The other reaction channel (Eq. (1b)) in which ethylene is lost is characteristic of silacyclobutanes and serves as an important probe of structure in the studies reported in this paper.

The ease with which silacyclobutanes and other silanes form siliconates served as a stimulus for other studies of the chemical and computational properties of pentacoordinate silicon [8-13]. Indeed, a recent ab initio computational study by Skancke [19] addresses questions concerning the fluoride affinities of various silaalkanes. The ab initio fluoride affinity of silacyclobutane of 43 kcal mol^{-1} (forming the siliconate 1) is consistent with the experimental value of 40 ± 5 kcal mol^{-1} for 1,1-dimethylsilacyclobutane reported in 1981 [12]. The marked tendency of DMSCB to lose ethylene under a variety of reaction conditions limited any additional study of the ion-molecule chemistry of such anions. As a result the examination of the reaction chemistry of silacyclobutanes, as well as various properties like their acidity, could not be carried out in the flowing afterglow (FA) or in the tandem selected ion flow tube (FA-SIFT) instruments [12,15,20].

A very recent modification of our FA-SIFT instrument to include a triple quadrupole (TQ) detector gives an instrument of enormous flexibility and power for

studying ion-molecule reactions [21]. Now, ions can not only be mass selected and converted, by chemical reactions with neutrals into new ions, but can be further manipulated in the TQ to provide critical information concerning their structure. We have returned to studies of DMSCB to further examine the characteristic ion-molecule chemistry of silacyclobutanes using these new instrumental capabilities. It is the results of these studies that we report here.

2. Experimental

The tandem flowing afterglow selected ion flow tube triple quadrupole (FA-SIFT-TQ) instrument consists of four sections: a source flow tube for ion preparation (A), an ion selection and purification region (B), a reaction flow tube for studying the chemical reactions of selected ions (C), and an ion detection region (D). A schematic diagram of the FA-SIFT-TQ is shown in Fig. 1. In the source flow tube (A) (often called the first flow tube), ions like F^-, HO^-, or H_2N^- are prepared and entrained in a rapidly flowing helium stream (0.2 Torr). These anions either flow directly to the end of the first flow tube or undergo reaction with neutral reagents in this region to produce new ions. All ions are sampled there through a 2 mm sampling orifice into the ion selection region (B). The helium and other neutrals are removed by pumping while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole can be tuned to a particular m/z so that the appropriate ions are injected into the reaction flow tube (C) (often called the second flow tube), where they are entrained in helium (0.5 Torr). These ions are thermalized by multiple collisions with the helium buffer gas. To inject ions from the low pressure (10^{-6} Torr) region of the SIFT quadrupole into the higher pressure region of the second flow tube, they must be extracted
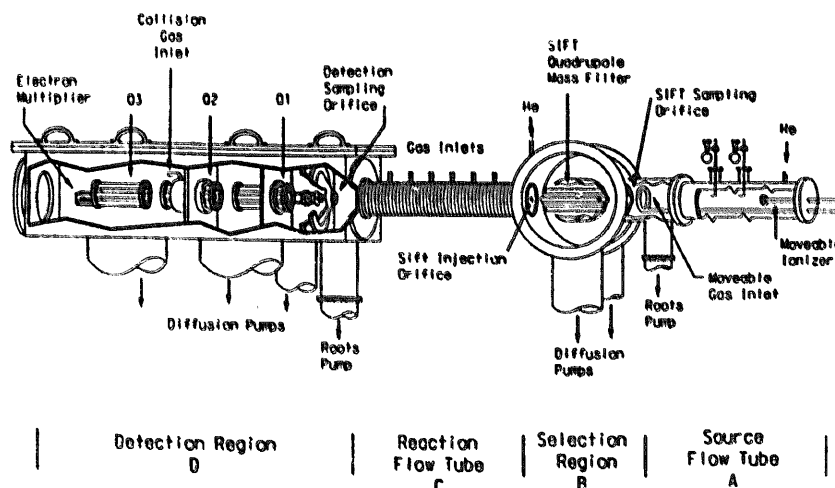

Fig. 1. Schematic diagram of FA-SIFT-TQ instrument.

by an electrical potential. When this potential is made sufficiently high, some ions undergo collisionally-induced dissociation (CID) to form new (daughter) ions, which can be further characterized by their chemical reactivity.

The newest modification of our FA-SIFT is the addition of a TQ detector in ion detection region D, which combines the versatility of the FA-SIFT part of the instrument described above with the analytical capabilities of the TQ mass filter. Our FA-SIFT-TQ is very similar to that described recently by Squires and coworkers [21].

The TQ unit is housed in a customized vacuum chamber that was designed to optimize ion transmission by differentially pumping four different regions of the detector chamber (D) (Fig. 1). The TQ is aligned coaxially with the second (reaction) flow tube. The bulk of the buffer gas flowing through the second (reaction) flow tube is pumped in the first region by a roots blower. Ions are sampled through a 0.5 mm orifice into the second region, where any escaping buffer gas is removed by diffusion pumping. The entrance to the TQ protrudes into this second region and ions are focused into it by five electrostatic lenses and a conical extractor mounted on the front of the TQ. Pressure in this region is 1×10^{-5} Torr during operation. The third region of the TQ vacuum chamber is independently diffusion pumped and contains the major part of Q1 (quadrupole 1) and the front section of Q2. A solid stainless steel casing encloses Q2, thus isolating it as a collision cell for CID experiments. The fourth region of the TQ chamber encases the back section of Q2, Q3, and an electron multiplier. It is independently pumped. A gas inlet for introduction of collision gases into Q2 and a pressure port to directly read the collision cell gas pressure are attached here as well. The Q3 operating pressure is 5×10^{-8} Torr.

Despite the long ion transmission pathway in the TQ, we observe no loss in ion count efficiency compared with our previously used single quadrupole instrument. The collision energy for our CID experiments is the difference between the potential of the ions as they exit the reaction flow tube (ground) and the offset voltage applied to the rods of Q2 (typically 5–20 V in the lab frame). The range of collision gas pressures used was 5×10^{-5} to 1×10^{-4} Torr as measured in the Q2 collision cell [21]. When the collision gas pressure and the collision voltage are incrementally increased, we observe increasing CID product signals up to a critical point, after which increases in these parameters decrease the CID signals.

All reactions were studied at 300 K at a helium buffer gas pressure of 0.5 Torr and a flow of ca. 225 STP cm^3 s^{-1}. Gases were obtained from commercial sources with the following purities: NH_3 (99.99%), N_2O (99.99%), CH_4 (99.99%), CO_2 (99.5%), and COS

(97.7%). Other reagents also were obtained from commercial sources and used without further purification. The helium buffer gas was passed through a liquid-nitrogen cooled molecular sieve trap before entering the flow tubes.

## 3. Results and discussion

3.1. Reactions of dimethylsilacyclobutane and fluoride

Our earlier studies of the chemistry of DMSCB were carried out with an FA instrument that lacked mass selection capabilities (see Eq. (1) and earlier discussion) [12,13]. Re-examination of the reaction of fluoride and DMSCB using FA-SIFT and TQ capabilities has now been carried out. When fluoride is mass selected from the source flow tube and DMSCB is added in the reaction flow tube, $m/z = 91$ (2) and 119 anions can be detected, depending on the amount of DMSCB added in the reaction flow tube. At high flows rates of DMSCB, the $m/z = 119$ anion is almost exclusively 1, although the ring-opened species 3 can also be shown to be present in small amounts when the amount of DMSCB added is decreased. Although these results are identical to those obtained in early experiments in the simple FA instrument, our added instrumental capabilities allow a fuller characterization of the silacyclobutyl-containing anions as we will show [12]. To do so, we have prepared 1 cleanly in two unambiguous ways: (1) by soft fluoride transfer from $[(CH_3)_4SiF]^-$ (mass selected in the source region) to DMSCB (added in the reaction flow tube) (Eq. (2)); (2) by soft fluoride transfer of 2 (mass selected in the source region) to DMSCB (added in the reaction flow tube) (Eq. (3)) [12].

$$(2)$$

$$(3)$$
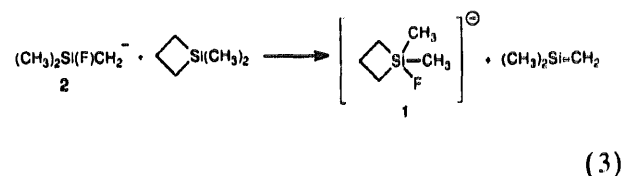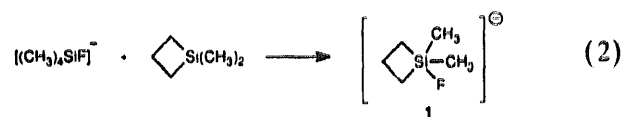
The $m/z = 119$ products have been characterized by a combination of chemical reactions [13,17] and CID in the new TQ detector. Thus, the anion obtained by soft transfer (Eqs. (2) and (3)) does not react with COS, which is consistent with siliconate reactivity but not that of 3, which would be expected to give a product with

$m/z = 137$ (CH_2 loss and S gain) (vide infra) [13]. This $m/z = 119$ anion was isolated in Q1 of the TQ and submitted to increasingly energetic collisions with argon collision gas (CID) in Q2. The only anion obtained, $(CH_3)_2Si(F)CH_2^-$ (2) ($m/z = 91$), corresponds to the loss of ethylene, thus confirming the intact nature of the silacyclobutane ring (Eq. (4)). The ready loss of ethylene is a consequence of the relief of the considerable
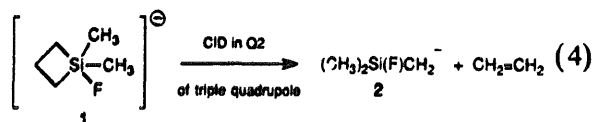
strain in silacyclobutanes [19]. In contrast, when lower flow rates of DMSCB were introduced into the reaction flow tube, small amounts of $CH_3CH_2CH_2Si(CH_3)$-$(F)CH_2^-$ (3) were observed. Its structure was verified by reaction with COS and consequent formation of $CH_3CH_2CH_2Si(CH_3)(F)S^-$ (vide infra) [13].

We also have briefly studied the anions directly produced in the source flow tube by reaction of F^- and DMSCB ($m/z = 91$, 95, 99, 115, 119, and 123). These are formed by highly energetic processes and are believed to be $(CH_3)_2Si(F)CH_2^-$(2), $CH_3Si(F)_2CH_2^-$, $F_3SiCH_2^-$, $[(CH_3)_2SiF_3]^-$, $[CH_3SiF_4]^-$, and $[SiF_5]^-$ respectively.

3.2. Reactions of dimethylsilacyclobutane and strong bases

DMSCB reacts with strong bases like HO^- and H_2N^- giving an $m/z = 99$ anion that can be mass selected from the source region and subsequently characterized (Eq. 5). By a combination of chemical reactions and CID studies, it is clear that the $m/z = 99$

anion is 4. Since the silacyclobutane ring of this anion can be shown to be intact, it represents the first tetraco-

ordinate silacyclobutane anion observed and gives us an entrée to chemical studies that were impossible earlier.
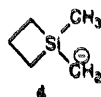
That it is an α-silyl carbanion is established by its

reaction chemistry with COS, CS_2, CO_2, and N_2O (Eqs. (6)-(9)). With the exception of the N_2O reaction, these
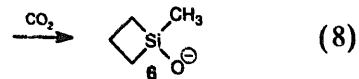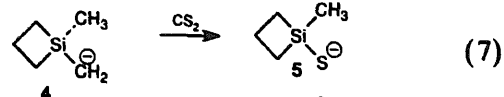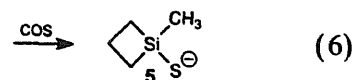
are the results typical of α-silyl carbanions [13,17]. Although earlier studies suggest that N_2O also might react to give 6, it is generally the least reactive of the neutral reagents we have used for chemical characterization and is seldom used now [22,23].

Proof of the intact silacyclobutane ring of the $m/z = 99$ anion was obtained when the $m/z = 99$ anion was isolated in Q1 of the TQ and submitted to increasingly energetic collisions with argon collision gas in Q2. Under relatively mild collision conditions, it undergoes characteristic loss of ethylene to an anion with $m/z = 71$. This is the M-1 anion of dimethylsilene, which was synthesized and studied in earlier FA work [22]. The same results are obtained when anion 4 is mass selected from the source flow tube and dissociated by energetic inection into the reaction flow tube. The products shown as 5 and 6 have both been characterized as silacyclobutanes by ethylene loss when submitted to CID in the TQ. Anion 6 is also one of the products of reaction between DMSCB and HO^-. Prepared in this way, it has been mass selected from the source flow tube and characterized by its CID behavior as well as its reactions with both COS and CS_2 (Eqs. (10) and (11)). Anion 5 prepared in this way undergoes CID in Q2 to
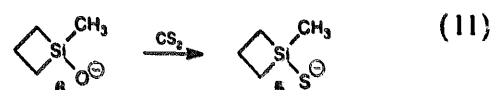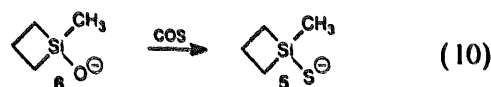

lose ethylene. Anion 5 also has been prepared in the source region by the reaction of 4 with CS_2 [17]. After mass selection, it too undergoes CID in Q2 to lose ethylene.

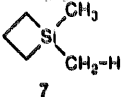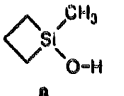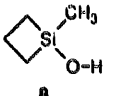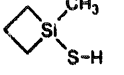### 3.3. Acidity of silacyclobutane species

The acid-base behavior of each of the silacyclobutane anions, 4, 5, and 6, has been probed using bracket-

ing [17,24,25] techniques (Table 1). Such experiments, which yield the gas phase acidity of the corresponding conjugate acids, 7, 8, and 9, are typically carried out by reacting a series of reference acids [25] with bases like
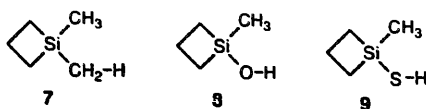
4, 5, and 6. Since the acidities of a large number of methylsilanes and silanols are known, it is of some interest to compare these with the silacyclobutane acids 7, 8, and 9. Whether the ring strain of the silacyclobutanes [19] and the consequent s-character increase of its exocyclic bonds is reflected in their C–H, O–H, and S–H acidity is an important question. Reference to Table 1, in which their acidities as well as those of several related compounds are collected, suggests that the ring strain has essentially no effect on acidity. Thus, typical acyclic methylsilanes have C–H acidities of

Table 1
Acidities of various methylsilanes, silanols, and silanethiols

Compound	ΔH^0_{acid} (kcal mol^{-1})	Ref.
SiH₃CH₂-H	388	[26]
CH₃SiH₂CH₂-H	391	[26]
(CH₃)₂SiHCH₂-H	391	[26]
(CH₃)₃SiCH₂-H	391	[27]
7	389 [a,b]	
SiH₃O-H	359	[28]
CH₃SiH₂O-H	360	[28]
(CH₃)₂SiHO-H	360	[28]
(CH₃)₃SiO-H	360	[28]
	362	[29]
8	360 [a,c]	
9	338 [a,d]	

a This work. We estimate a ±4 kcal mol⁻¹ absolute error for the methylsilane 7 and silanol 8 based on the methodology and the reference acids [25] used by us. The error for the silanethiol 9 is estimated to be ±8 kcal mol⁻¹.

b The acidity of 7 was bracketed between pentafluorophenol (ΔH_{acid} = 390 kcal mol⁻¹) with which it reacted to give the corresponding phenoxide and 2,2,6,6-tetramethylpiperidine (ΔH_{acid} = 388 kcal mol⁻¹) with which it was unreactive.

c The acidity of 8 was bracketed between between pyrrole (ΔH_{acid} = 359 kcal mol⁻¹) with which it reacted to give the corresponding pyrrolide and N-methylformamide (ΔH_{acid} = 360 kcal mol⁻¹) with which it was unreactive.

d The acidity of 9 was bracketed between between HCl (ΔH_{acid} = 333 kcal mol⁻¹) with which it reacted to give chloride and methoxyacetic acid (ΔH_{acid} = 342 kcal mol⁻¹) with which it was unreactive.

about 390 kcal mol⁻¹, which is essentially the same acidity obtained for 7. Similarly, the O–H acidity of typical silanols is close to 360 kcal mol⁻¹, as is that of 8. No experimental studies of the acidity S–H in typical silanethiols have been published, but ab initio computations indicate that acidities near 340 kcal mol⁻¹ are likely [17,30]. Interestingly, the acidity of the low-valent silathioformaldehyde has been reported to be 340 kcal mol, [31]. Although we have been unable to obtain a narrow bracket for the acidity of 9, we estimate its acidity as 338 kcal mol⁻¹.

4. Summary

A TQ detector newly added to the FA-SIFT instrument has been evaluated in a study of DMSCB. The added capability of carrying out CID in the TQ has been used to characterize the silacyclobutane ring, since anions containing this moiety undergo CID with the characteristic loss of ethylene. Thus, various silacylobutyl anions that could not be studied previously are now accessible using the mass selection capabilities of the FA-SIFT combined with the versatile TQ detection unit.

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